Mobility of organic matter, iron oxide and lead in a model sand and disturbed natural soil as affected by surface properties under flow conditions

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Abstract

During the past two decades, the transport of dissolved and colloidal lead (Pb) along with organic and inorganic colloids received attention. Dissolved organic matter (DOM) is the most mobile fraction of soil organic matter (SOM) and controls the mobility of metals and colloids in soil. In order to evaluate the mechanisms controlling the mobility of Pb^{2+}, colloids and colloidal Pb, it is necessary to consider certain properties, such as, physical and chemical heterogeneities on the solid matrix, the interaction of organic matter (OM) with colloids and colloidal Pb, and flow conditions. The aim of the dissertation was to systematically evaluate (1) the effect of surface roughness and charge heterogeneity of complex model sand on the transport of organic matter-coated goethite (OMCG) colloids under flow conditions, classic DLVO (Derjaguin-Verwey-Landau-Overbeek) theory served as a tool to predict the general trend on OMCG colloids, (2) the impact of cycles drying and rewetting on OM retention in a disturbed natural soil material, and (3) the effect of OMCG colloids and DOM on Pb^{2+} transport under a heterogeneous structure of the solid matrix.

For the first aim, the experiments conducted by assessing solid the surface properties of solid matrix with different complexity, from simple model sand, quartz sand (QS), to a complex matrix with varying percentages of goethite coated quartz sand (GCQS). The results showed that physical and chemical heterogeneities of the solid matrix significantly reduced colloid mobility under flow interruption phases. The results indicated that colloid retention on the solid matrix was strongly related to microscale surface roughness under continuous flow conditions. The additional colloid retention with increasing complexity on GCQS was caused by charge heterogeneity. Flow interruption increased retention due to physical heterogeneity. Mobility at different nanoscale roughness properties of colloid reduced colloid retention with lower nanoscale roughness height. Applying predictive model DLVO theory showed the shallower depth of secondary minimum in colloid with higher nanoscale roughness height led to release colloid into the effluent.

For the second aim, OM retention on subsoil Cambisol was tested with extracted OM from an Oi-horizon. The cycle of drying and rewetting modified the magnitude of OM retention on the solid matrix. The results showed that drying increased soil water repellency and led to preferential retention of more hydrophobic components on the surface. Re-wetting increased mobility of hydrophilic components into the outflow. However, OM retention on the surface depended on the prior OM surface loading. The positive relation between hydrophilic components retention with higher OM surface loading during the second cycle of drying-rewetting decreased the release of hydrophilic components into the effluent. It was due to the formation of a multi-layer structure of OM coating on the surface in the second cycle of drying-rewetting.

For the third aim, mobilization studies of dissolved $Pb^{2+}$and colloidal Pb were conducted in the columns filled with model sands (QS, GCQS) and disturbed natural soil material (Cambisol). There was a particular focus on preconditioning the surface of GCQS and Cambisol with DOM from different origins (extracted from Oa-horizon and Oi-horizon samples). Based on these studies, the mobility of dissolved Pb^{2+} and colloidal Pb in the columns was highly controlled by OMCG colloids and OM of the solid matrix. The results showed that mobile colloids did not act as a co-transport for Pb in the column, and Pb mostly co-retained on the OM.

In summary, the results suggest that mobility of colloidal Pb, OMCG colloid, and OM components cannot easily be assessed without considering the surface properties of the solid matrix and flow conditions. To obtain more insights into the mechanisms of mobility and retention of OMCG colloids, colloidal Pb and OM, upcoming results should be transferred to natural conditions.

Keywords: Surface heterogeneities, drying-rewetting, Pb immobility, OMCG colloid

Zusammenfassung

In den letzten zwei Jahrzehnten wurde dem Transport von gelöstem und kolloidalem Blei (Pb) zusammen mit organischen und anorganischen Kolloiden Aufmerksamkeit geschenkt. Die gelöste organische Substanz (DOM) ist die mobilste Fraktion der organischen Bodensubstanz (SOM) und steuert die Mobilität von Metallen und Kolloiden im Boden. Um den Mechanismus zu bewerten, der die Mobilität von Pb^{2+}, kolloidalem und kolloidalem Pb steuert, müssen bestimmte Eigenschaften berücksichtigt werden, wie z. B. physikalische und chemische Heterogenitäten der festen Matrix, die Wechselwirkung der organischen Substanz (OM) mit Pb^{2+}, kolloidalem, kolloidalem Pb und die Fließbedingungen. Ziel der Dissertation war die systematische Bewertung (1) der Auswirkungen der Oberflächenrauigkeit und der Ladungsheterogenität eines komplexen Modellsandes auf den Transport von mit organischen Stoffen beschichteten Goethit-Kolloiden (OMCG) unter Fließbedingungen (die klassische DLVO-Theorie (Derjaguin-Verwey-Landau-Overbeek) diente als Werkzeug zur Vorhersage des allgemeinen Trends bei OMCG-Kolloiden), (2) die Auswirkungen des zyklischen Trocknens und Wiederbefeuchtens auf die OM-Retention in einem gestörten natürlichen Bodenmaterial und (3) die Auswirkungen von OMCG-Kolloiden und DOM auf den Pb2+Transport unter einer heterogenen Struktur der festen Matrix.

Für das erste Ziel wurden Experimente durchgeführt, bei denen die Oberflächeneigenschaften einer festen Matrix mit unterschiedlicher Komplexität bewertet wurden, von einfachem Modellsand, Quarzsand (QS), bis hin zu einer komplexen Matrix mit unterschiedlichen Anteilen von goethitbeschichtetem Quarzsand (GCQS). Die Ergebnisse zeigten, dass die physikalischen und chemischen Heterogenitäten der festen Matrix die Kolloidmobilität in den Phasen der Strömungsunterbrechung stark reduzieren. Die Ergebnisse wiesen darauf hin, dass die Kolloidretention auf der festen Matrix unter kontinuierlichen Fließbedingungen stark mit der mikroskaligen Oberflächenrauhigkeit zusammenhängt. Die zusätzliche Kolloidretention mit zunehmender Komplexität auf GCQS wurde durch Ladungsheterogenität verursacht. Eine Unterbrechung des Flusses erhöhte die Retention aufgrund physikalischer Heterogenität. Die Mobilität bei verschiedenen nanoskaligen Rauhigkeitseigenschaften des Kolloids verringerte die Kolloidretention mit geringerer nanoskaliger Rauhigeitshöhe. Die Anwendung des Vorhersagemodells der DLVO-Theorie zeigte, dass eine geringere Tiefe des sekundären Minimums im Kolloid mit einer höheren nanoskaligen Rauhigkeitshöhe zur Freisetzung des Kolloids in die ausfliessende Loesung fuehrte.

Für das zweite Ziel wurde die OM-Retention an Unterbodenmaterial eines Cambisol mit extrahiertem OM aus einem Boden-Oi-Horizont getestet. Der Zyklus von Trocknung und Wiederbefeuchtung veränderte das Ausmaß der OM-Retention im Effluent. Die Ergebnisse zeigten, dass das Trocknen die wasserabweisende Wirkung des Bodens erhöhte und zu einer bevorzugten Retention hydrophoberer Komponenten an der Oberfläche führte. Die Wiederbefeuchtung erhöhte die Mobilität der hydrophilen Komponenten im Effluent. Die OM-Retention an der Oberfläche hing jedoch von der vorherigen OM-Beladung der Oberfläche ab. Die positive Beziehung zwischen der Retention hydrophiler Komponenten und einer höheren Oberflächenbeladung mit OM während des zweiten Zyklus der Trocknung und Wiederbefeuchtung verringerte die Freisetzung hydrophiler Komponenten die ausfliessende Loesung. Dies war auf die Bildung einer mehrschichtigen Struktur der OM-Beladung auf der Oberfläche im zweiten Zyklus der Trocknung und Befeuchtung zurückzuführen.

Für das dritte Ziel wurden Mobilisierungsstudien von gelöstem Pb^{2+} und kolloidalem Pb in den mit Modellsanden (QS, GCQS) und gestörtem natürlichen Bodenmaterial (Cambisol) gefüllten Saeulen durchgeführt. Ein besonderer Schwerpunkt lag auf der Vorkonditionierung der Oberfläche von GCQS und Cambisol mit DOM unterschiedlicher Herkunft (extrahiert aus Proben des Oa-Horizonts und des Oi-Horizonts). Auf der Grundlage dieser Studien konnte gezeigt werden, dass die Mobilität von gelöstem Pb^{2+} und kolloidalem Pb in den Säulen in hohem Maße durch OMCG-Kolloide und OM der festen Matrix kontrolliert wurde. Das Ergebnis zeigte, dass die mobilen Kolloide nicht als Co-Transportmittel für Pb in der Säule fungierten und Pb hauptsächlich an der OM gebunden war.

Zusammenfassend deuten die Ergebnisse darauf hin, dass die Mobilität von kolloidalem Pb, OMCG-Kolloid und OM-Komponenten nicht ohne Berücksichtigung der Oberflächeneigenschaften der festen Matrix und der Fließbedingungen beurteilt werden kann. Um einen besseren Einblick in den Mechanismus der Mobilität und Retention von Substanzen (OMCG-Kolloide, kolloidales Pb und OM) zu erhalten, sollten die kommenden Ansaetze auf natürliche Bedingungen übertragen werden.

Stichwörter: Oberflächenheterogenitäten, Trocknung-Wiederbefeuchtung, Pb-Immobilität, OMCG-Kolloid

Table of Contents

List of Tables

Study I

Study II

Study III

Table 1 Overview of the experimental series in the matrices quartz sand (QS) and goethite coated quartz sand (GCQS) with three different variants, Pb, OMCG colloids and Pb+OMCG colloids. Dissolved organic matter (DOM) extracted from Oa horizon under spruce (Oa DOM) and Oi horizon under beech (Oi DOM). The breakthrough percentage is shown in two replicates with mean and the range of two replicates. Pulse 1 shows the injection of an initial suspensions and pulse 2 shows the second injection of suspensions after DOM preconditioning on the GCQS surface.

Table 2 Calculated charge of lead (Pb) and measured surface charge (SC) of dissolved organic matter (DOM) extracted from Oa horizon under spruce (Oa DOM) and Oi horizon under beech (Oi DOM). The samples quantified at target pH 4.5 for Oa DOM and pH 5.5 for Oi DOM suspensions at pH 5.0 for Pb^{2+}.

Table 3 Zeta potential and sessile drop method contact angles (θ) and inferred van der Waals free energy (Y_s^{LW}) for quartz sand (QS), goethite, and organic matter coated goethite (OMCG) colloids.

Study IV

Table 1 Chemical and physical properties in disturbed natural soil material (n = 3 with standard deviation).

Table 2 Sessile drop method contact angles θ for six replicate given as mean and standard deviations and inferred surface free energies of the Cambisol subsoil. θ = contact angle for the fluids indicated, γ^{LW}= van der Waals free energy, γ^{+}=Lewis acid free energy, γ^{-}= Lewis base free energy.

List of Figures

Study I

Study II

percolation pulses. This led to a total of four experimental variants, each conducted in two replicates.

Fig. 2. Breakthrough of DOC and SUVA ratios for the high OM loading experiments, given as mean of two replicates and the range. “no d.” refers to the continuously water saturated variants, “drying” to the variants with drying and subsequent rewetting. Vertical red lines indicate the time points of the drying. The bar diagrams above show the quantity of leached DOC, either at full water saturation or during rewetting after drying. (SUVA results shown for DOC $C/C_0 > 0.05$; values below that scatter considerably due to proximity to the detection limits).

Fig. 3. Breakthrough of DOC and C/N ratios for the high OM loading experiments, given as mean of two replicates and the range. “no d.” refers to the continuously water saturated variants, “drying” to the variants with drying and subsequent rewetting. Vertical red lines indicate the time points of the drying. The bar diagrams above show the quantity of leached DOC, either at full water saturation or during rewetting after drying. (C/N ratio results shown for DOC $C/C_0 > 0.05$; values below that scatter considerably due to proximity to the detection limits).

Fig. 4. Percent of potential SUVA for the effluent DOM of the high OM loading and low OM loading variants, given as mean of two replicates and the range. “no drying” refers to the experiments at continuously full water saturation, “drying” to the experiments with drying and rewetting cycles. “L1” and “L2” refer to the first and second leaching phases, respectively.

Fig. 5. Effluent DOM C/N ratios for the high OM loading and low OM loading variants, given as mean of two replicates and the range. “no drying” refers to the experiments at continuously full water saturation, “drying” to the experiments with drying and rewetting cycles. “L1” and “L2” refer to the first and second leaching phases, respectively.

Fig. 6. Breakthrough of DOC and SUVA ratios for the low OM loading experiments, given as mean of two replicates and the range. “no d.” refers to the continuously water saturated variants, “drying” to the variants with drying and subsequent rewetting. Vertical red lines indicate the time points of the drying. The bar diagrams above show the quantity of leached DOC, either at full water saturation or during rewetting after drying. (SUVA ratio results shown for DOC $C/C_0 > 0.05$; values below that scatter considerably due to proximity to the detection limits).

Fig. 7. Breakthrough of DOC and C/N ratios for the low OM loading experiments, given as mean of two replicates and the range. “no d.” refers to the continuously water saturated variants, “drying” to the variants with drying and subsequent rewetting. Vertical red lines indicate the time points of the drying. The bar diagrams above show the quantity of leached DOC, either at full water saturation or during rewetting after drying. (C/N ratio results shown for DOC $C/C_0 > 0.05$; values below that scatter considerably due to proximity to the detection limits).

Study III

Fig. 1 a.d. Modification of zeta potential and particle size of goethite colloids by DOM (dissolved organic matter). a) Changes of zeta potential in the presence Oa DOM (DOM derived from Oa horizon under spruce), and b) in the presence of Oi DOM (DOM derived from Oi horizon under beech) ; c) changes of particle size in the presence of Oa DOM, and d) in the presence of Oi DOM.

Fig. 2 a.d. Influence of Pb on changes of zeta potential and particle size of OMCG (organic matter coated goethite) colloids. a) Changes of zeta potential in the presence of Oa-OMCG colloid (goethite coated with DOM extracted from Oa horizon under spruce), b) Oi-OMCG colloid (goethite coated with DOM extracted from Oi horizon under beech); c) changes of particle size in the presence of Oa-OMCG colloid, d) Oi-OMCG colloid.

Fig. 3 a.c. Breakthrough curves of a) Pb, b) OMCG colloids (Oa OMCG and Oi OMCG colloids) and c) Pb+OMCG (Pb+ Oa OMCG and Pb+ Oi OMCG colloids) released in quartz sand (QS) solid matrix in a single pulse experiment. Results are depicted in two replicates. The samples of dissolved organic matter (DOM) extracted from Oa horizon under spruce (Oa DOM) and Oi horizon under beech (Oi DOM), OMCG colloids represent goethite coated with DOM extracted from Oa and Oi horizons. The experiments conducted at pH 4.5.

Fig. 4 a.c. Breakthrough curves of a) Pb, b) OMCG colloids (Oa OMCG and Oi OMCG colloids) and c) Pb+OMCG (Pb+ Oa OMCG and Pb+ Oi OMCG colloids) released in goethite coated quartz sand (GCQS) solid matrix in triple pulse experiments. Results are depicted in two replicates. The samples of dissolved organic matter (DOM) extracted from Oa horizon under spruce (Oa DOM) and Oi horizon under beech (Oi DOM), OMCG colloids represent goethite coated with DOM extracted from Oa and Oi horizons. The experiments conducted at pH 4.5.

Fig. 5 a.b. Total interaction energy between Oa OMCG and Oi OMCG (organic matter coated goethite) colloids and the solid surfaces; quartz sand (QS) stands for the uncoated sand, goethite for goethite coated on QS (GCQS), and OMCG coated stands for dissolved organic matter (DOM) preconditioning on GCQS surface. a) Oa DOM (DOM derived from Oa horizon under spruce) and b) Oi DOM (DOM derived from Oi horizon under beech. KT is the product of Boltzmann constant (K) and temperature (T). The data are depicted in the presence of energy barrier.

Fig. 6 a.b. Total interaction energy in the presence of secondary minimum between Oa OMCG and Oi OMCG (organic matter coated goethite) colloids and the solid surfaces; quartz sand (QS) stands for the uncoated sand, goethite for goethite coated on QS (GCQS), and OMCG coated stands for dissolved organic matter (DOM) preconditioning on GCQS surface. a) Oa DOM (DOM derived from Oa horizon under spruce) and b) Oi DOM (DOM derived from Oi horizon under beech. KT is the product of Boltzmann constant (K) and temperature (T).). Dash lines stand for DLVO interactions in the absence of Pb. The data are depicted in the presence of secondary minimum.

Study IV

Abbreviations

CLSM	Confocal Laser Scanning Microscopy
DLVO	Derjaguin-Verwey-Landau-Overbeek
DOC	Dissolved organic carbon
$\mathrm{DOC}_{\mathrm{eff}}$	DOC concentration of the effluent
DOM	Dissolved organic matter
GCQS	Goethite coated quartz sand
Oa horizon	Humified organic layer layer under Norway spruce (*Picea abies* L. Karst)
Oi horizon	Litter layer under European beech (*Fagus sylvatica*)
OM	Organic matter
OMCG	Organic matter coated goethite
Pb	Lead
PCD	Particle charge detector
PZC	Potential zeta charge
QS	Quartz sand
SC	Surface charge
SDM	Sessile drop method
SUVA	Specific UV absorption at 280 nm
$\mathrm{SUVA}_{\mathrm{eff}}$	SUVA of the effluent
$\mathrm{SUVA}_{\mathrm{added}}$	SUVA of the added
XPS	X-ray photoelectron spectroscopy
ζ	Zeta potential

1. General introduction

1.1 Problem of soil pollution

Worldwide interest and concern regarding the impacts of environmental pollution on human health have been increasing over the past several decades. In many cities, one of the main causes of environmental pollution and degradation has been improperly managed solid waste (Klein and Wiren, 1993).

Of the different environmental pollutants, heavy metals used for multiple industrial purposes are of particular concern, since they do not undergo biological degradation but accumulate in living organisms, thus causing various diseases and disorders even in relatively low concentrations. One of the most relevant heavy metal with respect to public health is Pb.

The release of heavy metals such as Pb by anthropogenic activities has been responsible for increasing concentrations of these contaminants in soil environments (Fonseca et al., 2011). The toxicity of Pb in humans is related to the impairment of calcium-dependent intracellular processes (Schanne et al., 1989). In addition, it stimulates the formation of inclusion bodies that may translocate the metal into cell nuclei and alter gene expression (Klein and Wiren, 1993). Due to these adverse health effects, the contaminant sorption and migration as well as the development of remediation techniques are areas of intense research.

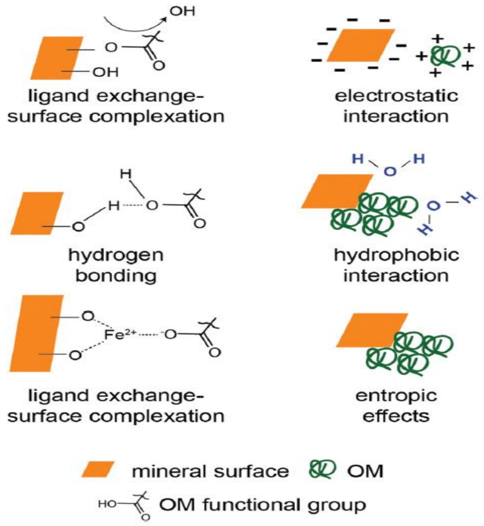
Pb is released into the environment from different sources, and soils are considered as sinks for Pb retention as Pb are not degraded and persist in terrestrial ecosystems for many decades and longer (Bolan et al., 2014). Generally, retention of heavy metals in soil reduces the risk of groundwater pollution or uptake by plants. However, studies have shown that mobile colloids in pore water can facilitate heavy metal mobility in soils. Such a co-transport of heavy metals imposes a significant risk of ground water contamination. (Jonge at al., 2004).

1.1.2. Mobilization and immobilization of Pb^{2+} into groundwater

The term colloid generally applies to suspended particles in the size range of 1 nm to 10 μm, which includes many soil fractions such as clay minerals, metal oxides, and organic matter (OM). Mobile colloids through association with Pb^{2+}has been recognized a key role for transport of Pb^{2+} into groundwater (Yin, 2010). In soils, heavy metals such as Pb can either be immobilized on iron oxides associated with the solid matrix, or can become highly mobile and travel over remarkable distances in case they are bound to mobile colloidal iron oxides (Namiesnik and Rabajczyk, 2010). So far, the mechanisms governing the co-transport of heavy metals with colloidal mineral particles in soils have been investigated based on binary systems in batch experiments and column leaching experiments – i.e. in systems involving mineral colloids and heavy metals (He at al., 2006; Christl, 2001; Ostergren, 2000). However, the interactions are more complex in natural systems, where not only heavy metals and mineral colloids, but furthermore soil OM is present. These are referred to as “ternary systems”. In fact, the heavy metal ion binding behavior in ternary systems is more complicated than binary systems. Therefore, in order to estimate heavy metal mobility under environmental conditions, the application of the ternary system is required, which only a few studies have evaluated systematically so far (Xiong et al., 2015). In order to determine the mobility of colloidal particles and adsorbed heavy metals under flow conditions, column experiments are widely applied (Weng et al., 2002). One specific example is a study by Papelis et al. (2002), who showed that mobile mineral colloids facilitated the transport of Pb through flow columns filled with sediments; in the absence of a mobile colloid phase, Pb was immobilized in the columns. Several studies have been performed in order to establish the influence of different parameters on heavy metal sorption/desorption in soils (Lee et al., 2001; Liu et al., 2006; Hanna et al., 2009). In particular, studies have shown that oxides of metals, such as Fe, Al, and Mn (Kumpiene, 2011), clays (Puls, 1988) and organic matter (Stevenson, 1976) play an important role in heavy metal geochemistry in soils. Pb has an affinity for adsorption onto iron oxide colloid surfaces; thus, mobile iron oxide colloids can facilitate transport of lead (Pb) in the environment. Due to their high point of zero charge above pH 7, iron oxides are electrostatically attracted to negatively charged minerals forming the soil matrix at pH values common for humid climate soils. Thereby, iron oxide colloids are subjected to immobilization (Kretzschmar and Sticher, 1997; Förstner et al., 2001; Bosch et al., 2010b). However, the surface charge of iron oxides can be turned to negative via the adsorption of soil organic matter. For instance, this was shown in batch experiments by Herrera Ramos and McBride (1996). The adsorption of organic matter on oxides commonly proceeds by ligand exchange, as reported by numerous studies (Kaiser and Guggenberger, 2000: Kaiser et al., 2007; Mikutta et al., 2007). Negatively charged, OM-coated iron oxide colloids were observed to be highly mobile in negatively charged sand matrices (Förstner et al., 2001; Li et al., 2013) and disturbed soil samples (Kretzschmar and Sticher, 1997). However, in case organic matter concentration is only sufficient to partially coat the iron oxides, thus causing surface charge heterogeneity, aggregation of the colloids can occur (Herrera Ramos and McBride, 1996). The larger the size of colloid aggregates, the more they can be subjected to mechanical filtering in the solid matrix, a term referred to as “straining” in colloid sciences (Bradford et al., 2002). Thus, when regarding the ternary system Pb – iron oxides – organic matter, the specific concentration of organic matter is of significant importance. However, the extent of changing surface charge of iron oxide through association with OM depends on the composition of DOM adsorbed on the surface. DOM is a complex composition and including a variety of hydrophobic and hydrophilic components (Guggenberger et al., 1994). There are several studies concerning OM coating on goethite colloid to modify the mobility of goethite colloid (Kretzschmar and Sticher, 1997; Jansen et al., 2005; Li et al., 2013). While there are still unknown questions regarding OM coting on the solid matrix on Pb^{2+} mobility in the ternary system. The well-known mechanism concerning the influence of OM on the heavy metal is adsorption of heavy metal through forming complexation on the active sorption sites of OM. Guggenberger et al. (1994) stated the favor of hydrophilic acid components for bonding with metals (Cr, Cu and Cd) on the topsoil decreased the leaching of metals in the B horizon. In order to address effect of OM coating on the mobility of colloidal Pb in a ternary system, a detailed mechanism concerning interactions of (i) solid phase with Fe oxy (hydroxides) and (ii) iron oxide colloids with OM need to be considered, these interaction is given in section (1.2). But, it is not adequately evaluated OM coating on the surface of solid matrix can increase mobility of colloidal Pb in a ternary system (Pb-colloid-OM) in the column experiments.

1.2. Interaction of iron oxide colloids with solid phase and OM

Oxy (hydroxides) of aluminum and iron play an important role in the stability of soil structure through changing properties of clay minerals. The interaction of oxides with solid matrices depends on the net surface charge. Subsequently with addition of oxides the positive charge of the surface increases (Goldberg, 2008). Sumner (1963) determined that the presence of positive charge of iron oxide on the negative charge of kaolinite neutralized the kaolinite’s charge via bonding on the surface. Bayer (1972) observed that the physical properties of soils change with coating by iron oxide. This reaction is through dehydration of the surface with an irreversible bonding with the surface (Coston et al., 1995). Organic matter (OM) has an affinity to be adsorbed on the surface of inorganic surfaces such as oxides and clays. Because of the complexity of OM, the prominent mechanism for adsorption is still unclear. The studies by Gu et al. (1994) and Specht et al. (2000) showed that ligand exchange (Fig. 1) is the dominant mechanism in covering OM on the surface and this covering makes changes on the edge of surfaces.



(Gu et al., 1994)

Fig. 1. Schematic of probable mechanism of the covering iron oxide by organic matter (OM).

Addition of OM to the clay and oxides reverses the positive charge to the negative charge and can change the physicochemical properties of the coated substance, i.e. stability and mobility of colloids (Tarchitzky et al., 1993; Kretzschmar et al., 1998). Typically, goethite does not appear as pure mineral in soils, but sorption of OM and co-precipitation of dissolved Fe with OM lead to the formation of OM-goethite complexes (Gu et al., 1994; Chen et al., 2014). This formation of OM coated Fe oxides asserts a key influence on the mobility of Fe oxide colloids in soils, as the associated charge reversal can decrease the colloid-colloid collision (Kretschmar et al., 1997). Hence, colloids with negative charge are highly mobile in negatively charged matrixes (Förstner et al., 2001; Huynh and Chen, 2011; Li et al., 2013). An important parameter for colloid mobility is ionic strength. The solution ionic strength is an important parameter because it directly controls how far the double layers extend from the surface into the bulk solution. At high ionic strength, the surface charge can be balanced by a small double layer because the ion concentration near the surface is high. Conversely, low ionic strength will produce large double layers. Thus, at high ionic strength, the double layers of approaching surfaces will overlap only at small separation distances and the double layer repulsion between the surfaces is reduced. In contrast, the double layer repulsion is increased at low ionic strength Ryan and Elimelech. (1996). Mobility of iron oxide colloids was reported to decrease with increasing ionic strength by several researches (Kretzschmar and Sticher, 1997; Kuhnen et al., 2000; Tosco et al., 2012).

1.2.1. Association of contaminants with iron oxide colloids

Complexation of colloids with contaminants can increase or decrease the mobility of contaminants (Mills et al., 1991). Mobile colloids can provide a pathway for transport of contaminants in ground water. There are a number of investigations about the relation between transport of mobile iron oxide colloids with contaminants such as heavy metals, radionuclides and pesticides (Novikov et al., 2006; Qi et al., 2014). The studies Weng et al. (2002) and Papelis et al. (2002) determined the role of mobile colloid on mobility of Pb^{2+} under flow conditions in column experiments. They showed that mobile iron oxide colloids facilitated the transport of lead through flow columns filled with sediments; in the absence of a mobile colloid phase, Pb was immobilized in the columns. However, in contrast there are certain researches on the immobility of heavy metals with goethite colloids. The report by Mohammadian et al. (2020) stated that Goethite (α-FeOOH) coated with humic acid is the most common nanoparticle useful to immobilize heavy metals and contaminants. Their studies assessed coating humic acid on goethite colloid in high concentration immobilized Pb^{2+} on the surface of goethite colloids. However, goethite colloid were highly mobile in a negatively charged solid matrix. The same mechanism of immobility of Pb^{2+} on goethite colloid observed in the study (Montalvo and Smolders, 2019). Both studies observed the process of immobility of Pb^{2+} with synthesized humic acid under experimental conditions. However, there are still a gap of knowledge concerning the effect of natural OM form Oa horizon and Oi horizon on the process of transport. Based on the studies Montalvo and Smolders, (2019) and Mohammadian et al. (2020) the mechanism of transport is pH-dependent. The former study stated immobility happened in the neutral to slightly alkaline ranges due to the surface of OM is deprotonated and ions are dissolved an soluble in the range of neutral to slightly alkaline that can be adsorbed on the surface. While the later study even observed that the range of pH 4-6 was also effective on adsorption of heavy metal on the surface to be immobilized in the solid matrix. However, the retention of heavy metals on the OM surface depend on the ionic strength of solution. Bradl (2004) in his studies determined the influencing role of ionic strength on the competitive sorption on the surface of OM with heavy metal. The competitive ions are either monovalent cation or divalent cation. The competition of between monovalent ions with heavy metal on the sorption sites are little, while divalent ions has a decreasingly effect on the retention of heavy metal with sorption sites OM. However, in the order to define the role of OM on heavy metals and colloids an extensive knowledge regarding the effect of environmental factors on OM need to be considered. The effect of environmental factor on OM specifically on dissolved organic matter (DOM) are listed in section (1.3.1). DOM is one of the most mobile fractions of soil organic matter (SOM), with high mobility and reactive surfaces related to inorganic colloids and pollutants (Hassett, 2006; Xiao et al., 2014). DOM plays an important role in the mobility/immobility of pollutants and inorganic colloids as well as the cycling of C (carbon), N (nitrogen) and P (phosphorous) (Wang et al., 2018). DOM is composed of a great range of different organic components, such as proteins, amino acids, monosaccharides, polysaccharides, lipids, and polyphenols (Nebbioso and Piccolo, 2013). Based on size and molecular weight, DOM is divided into two groups, hydrophobic and hydrophilic components, which include more aromatic and aliphatic components, respectively (Leenheer, 2003). Specific UV absorbance (SUVA) at 254nm and SUVA 280 nm, divided by total DOC can determine the amount of hydrophobic or hydrophilic components. The high amounts of components detected by SUVA show enrichment in hydrophobic components (Croue et al., 1999; Leinemann et al., 2016). There are inconclusive reports on the origin of DOM either from decomposition of fresh litter or organic horizons (Huang and Schoenau, 1998; Currie et al. 1996). (Qualls et al., 1991) showed that in deciduous forest ecosystems a higher amount of DOM was observed in the upper part of the organic horizon (Oi horizon) and seasonal changes showed a higher amount of hydrophilic components directly after litterfall. Michalzik and Matzner (1999) also observed a similar behavior in pine forests with a higher amount of DOC and DON in the Oi horizon.

1.2.2. Effect of drying and re-wetting on OM

Natural phenomena such as seasonal changes and increasing frequency of droughts followed by heavy rainfall affect microbial communities, soil organic matter (SOM) and also change the amount of CO2 in the atmosphere (Schmitt et al., 2010; Xu and Luo, 2011). During periodic droughts, the activity of soil microorganisms is limited which leads to accumulation of organic matter in the upper horizons. Re-wetting creates a stress on the soil profile which increases re-mobilization of OM into soil profile (Tipping et al., 1999; Zsolnay et al., 1999). Muhr and Borken. (2009) and Lee (2011) stated that the amount of dissolved organic carbon (DOC) released depends on the intensity of water flux after dry periods. Still, there is not information regarding prolonging the cycle of drying under experimental conditions on mobility. In general, the wetting properties alter physic-chemical properties of SOM especially hydrophobicity

(Doerr et al., 2000). There are a few studies by Wang et al. (2002) and Hurrass and Schaumann (2006) concerning the solubility and mobility of heavy metal and inorganic colloid, respectively were highly affected by the period of drying-rewetting. It is likely that in the future due to changes on global warming the importance of prolonging drying periods and then sudden precipitation will modify the retention of hydrophobic and hydrophilic components on the soil horizons. The unknown question is that whether prolonging drying periods can increase preferentially retention of hydrophobic components on the solid matrix. Hence, more research is needed for the evaluation of the influence of prolonging the cycle of drying-rewetting on retention of OM on the soil profile.

1.2.3. Temperature

Warm and humid periods in the climate cycle will modify DOM decomposition patterns via changes in the activity of the microbial community (Deng et al., 2020). Mobilization and immobilization of DOM in the solid matrix are controlled by the activity of microbes (Kalbitz and Knappe, 1997; Marschner and Bredow, 2002). In tropical and humid regions the decomposition of DOM is higher due to increased activity of decomposers and the high input of plants (Zhou et al., 2015). Karhu et al., (2014) found a positive correlation between the decomposition of DOM and humid climate. Kalbitz et al. (2009) also showed that rainfall after dry periods increased the decomposition of DOM. These changes happened because of increased activity of decomposers in the humid period.

1.2.4. pH

DOM solubility is pH-dependent and can be changed with acidification and lime application in the soil (Tipping and Woof, 1990; Guggenberger, 1994). Studies by Murphy et al. (1994) and Wallstedt et al. (2008) showed that solubility decreases at low pH due to (i) high concentrations of protons and (ii) increases in the concentration of Fe and Al which causes a flocculation of DOM. While DOM solubility increases at high pH, the changes in solubility are more pronounced with NaOH addition than $Ca(OH)_2$ addition (Curtin et al., 2016).

1.2.5. Cations and Anions

As it was mentioned in the previous section DOC, can form stable complex stable complexes through interactions with monovalent and polyvalent cations. However, the degree of DOM degradation depends on the type and the concentration of the cation (Skyllberg and Magnusson, 1995). Polyvalent cations inhibit the decomposition of DOM through creating cation bridges (Tipping and Woof, 1991), while monovalent cations (Na^+) have lower affinity to form complexes with DOM (Kalbitz et al., 2000). Guggenberger and Zech (1994) showed that cations can protect organic molecules against decomposition through linkages and bonds on the negative surfaces of organic components. Schwesig et al. (2003) suggested the main mechanism for controlling the mobility and stability of DOM against decomposition in the soil is the ratio between DOC and the metal. Increased amount of DOC through complex with metal decreased the solubility of metal in suspension. Furthermore, the information based on the reports of Adusei-Gyamfi et al., 2020 described that enhanced amounts of Ca^{2+} and Mg^{2+} can remove natural organic matter (NOM) from seawater via coagulation with cations. However, there are some heavy metals (Cu, Pb, and Hg) can form a strong complex with DOM. These metals, via complexation with DOC, can decrease their toxicity characteristics via reducing their solubility (Alberts et al., 1992).Furthermore, anions like PO_4^{3-} and SO_4^{2-} can control distribution and leaching of DOC in the soil profile through displacing DOC from the sorption sites (Kalbitz et al., 2000). In general, anions usually increase the leaching and decomposition of DOC components in the soil horizons.

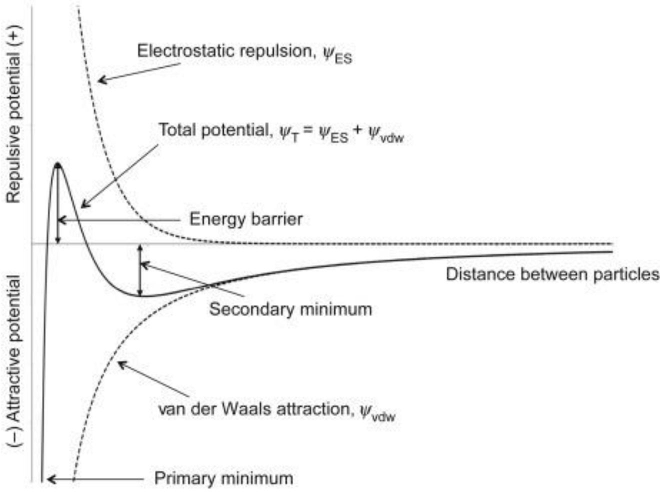
1.3. Stability of iron oxide colloids

Colloidal stability is determined by interaction of forces such as electrostatic repulsion and van der Waals attraction in the soil solution. Colloids are stable in the soil solution if the repulsive interaction is higher than the attractive force between particles. The magnitude of repulsive interactions depends on the concentration and charge of particles. As the concentration of ions increases, the electrical double layers shrink and results in flocculation of particles. This flocculation happens due to attractive van der Waals and Lewis acid/base interactions (Fig. 2) shows a schematic of electrostatic and van der Waals attractions. So, under flocculation, the colloidal suspension is unstable and undergoes settlement in the presence of gravitational force (Sposito, 1989). Ouyang et al. (1996) showed that divalent ions are more likely to coagulate colloids at lower concentrations than monovalent ions.

Classic Derjaguin-Verwey-Landau-Overbeek (DLVO) theory provides a better explanation for predicting the stability and deposition of colloids (Swanton, 1995). The DLVO theory combines van der Waals attraction and diffuse double layer repulsion which determine colloidal stability. In the presence of the same charge the forces between colloids are repulsive and colloids are stable in the suspension when the net charge does not reach zero. Attraction happens in the presence of oppositely charged ions. A factor such as change in the solution chemistry has an effect on the interaction energy and subsequently on the stability of colloids (Elimelech and O' Melia, 1990).

1.3.1. Theoretical modeling for behavior of colloids in porous media

In order to describe colloid interaction and stability, the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory is used. In classic DLVO theory, the total interaction energy between colloidal particles is the sum of electrostatic and Van der Waals interactions (Verwey and Overbeek, 1948). To complete the classic theory, the short-range Lewis acid-base interaction was included in the DLVO approach with the term X-DLVO (X for extended). The XDLVO approach is able to predict surface wettability originating from the presence of hydrophobic components of DOM (Van Oss et al., 1990). Total interaction energies can predict either favorable or unfavorable attachment conditions. Favorable attachment occurs between two particles with opposite surface charge and adsorption is via electrostatic attraction. Particles under favorable attachment accumulate in the primary minimum. Nevertheless, short range repulsive force such as Lewis acid base interactions also exist under favorable attachment due to the presence of hydrophobic surfaces (Bradford et al., 2011). Under unfavorable attachment conditions, electrostatic interactions are repulsive due to the presence of the same charge on the both surfaces and particles cannot be deposited on the surface because of the presence of an energy barrier. Figure 2 illustrates a secondary minima that exists outwards of the energy barrier (Bradford et al., 2006a). However, under unfavorable attachment conditions colloid attachment can happen even on (i) secondary minima and (ii) local gaps due to the presence of physical and chemical heterogeneities.



(Gelardi and Flatt, 2016)

Fig.2. Example of total Derjaguin-Landau-Verwey-Overbeek (DLVO) and extended DLVO (XDLVO) energies for colloid on the surface of solid matrix.

(i) Secondary minima

Weakly adhesive interaction of colloids by secondary energy minimum interaction is reported by (Shen et al., 2012d; Tosco et al., 2012) and colloids that associate with secondary minimum are considered reversibly attached.

(ii) Effect of physical and chemical heterogeneities on the retention of iron oxide colloids

Physical and chemical anomalies are two of the most important heterogeneities that lead to colloid deposition during transport. Heterogeneities induce local gaps in the energy barrier where the barrier is reduced or eliminated. Physical and chemical heterogeneities are patches common on the surface of porous media or even colloids which can lead to less repulsive or even attractive interactions on the irregular solid matrix surfaces. Physical heterogeneity leads to surface roughness with nanoscale and microscale roughness properties. In general, physical and chemical heterogeneities have an effect on DLVO energy profiles via local reduction or absence of the energy barrier (Bradford and Torkzaban, 2012; Shen et al., 2012). There are some studies examining colloid mobility under (i) physical and chemical heterogeneities of solid matrices and (ii) changes of surface charge with OM coatings. But there is still a gap in understanding how mobility of colloids with nanoscale surface roughness properties changes in response to microscale surface roughness and surface charge heterogeneity of the solid matrix. The intensity of colloid mobility under these conditions is also related to flow conditions. The flow conditions are affected by flow velocity with different flow interruption phases that can change the mobility of colloids in the solid matrix. There are still no studies to answer the question of whether flow interruption phases can increase colloid retention on the microscale surface roughness. DLVO theory is un-related to flow conditions in the solid matrix, but changes of physical and chemical heterogeneities on the surface of solid matrix can change predication of mobility by DLVO theory.

1.4 Aim and Hypotheses

The overarching goal of this thesis was therefore to assess the process of transport of OM, Pb^{2+}, OMCG colloids and colloidal Pb in the column experiments under experimental conditions on the solid matrix. Further emphasis was on the (i) properties of solid matrix with respect to heterogeneities, (ii) changes on the conditions of transport and retention of OM, Pb^{2+}, goethite colloids and colloidal Pb into soil profile with respect to changes on the flow interruption phase and the cycle of drying-rewetting.

H1 OMCG colloids mobility in the solid matrix is predominantly controlled by physical and chemical heterogeneities of the solid matrix, enhanced by the charge heterogeneity on the surface of solid matrix.

H2 Preconditioning the surface of solid matrix with DOM increases mobility of OMCG colloids, while decreases mobility of Pb^{2+} despite the presence of mobile colloids in the solid matrix

H3 Flow interruption enhances retention of OMCG colloids on the surface roughness and surface charge heterogeneity.

H4 The affinity of hydrophilic and hydrophobic components for retention on the solid matrix is predominantly controlled by prior OM loading on the surface of solid matrix, and the cycle of drying-rewetting increases retention of hydrophilic components on the outer-layer of hydrophobic components in the solid matrix with higher prior OM loading.

H5 DLVO theory is able to predict control mobility of OMCG colloids in the solid matrix.

H6 The capability of soil to retain OMCG colloids on the surface is higher for the colloids with lower nanoscale roughness height.

In order to verify these hypotheses four studies were conducted to test them in the following way:

I. The influence of physical heterogeneity, chemical heterogeneity, and flow interruption on the mobility of organic matter- coated iron hydroxide in a model sand

Study I aims to systematically assess the relative importance of colloid retention caused by either roughness or charge heterogeneities. Breakthrough experiments were conducted in columns filled with different mixtures of quartz sand (QS) and goethite coated quartz sand (GCQS). Furthermore, the nanoscale surface roughness of the colloids was varied by percolation of 0.25 and 1.0 mg L^{-1} DOM solution on the colloid surface, with the higher OM coating amount leading to a higher nanoscale surface roughness. Experiments were conducted at continuous flow conditions and with phases of flow interruption.

II. Drying and Rewetting Cycles Amplify the Preferential Retention of Hydrophobic DOM in Soils

Study II aims to systematically compare DOM retention in disturbed subsoil material via column breakthrough experiments that were conducted either at full water saturation or with two consecutive cycles of drying and rewetting. Column effluent DOC and DON as well as the specific UV absorption at 280 nm (SUVA) were determined.

III. Interactive control of organic matter loading of colloidal and solid iron oxide on lead mobility in a model sand

Study III aims at assessing the magnitude of Pb transport affected by DOM and organic matter coated goethite (OMCG) colloids in pure quartz sand (QS) and goethite coated quartz sand (GCQS), and depending on GCQS surface loading by organic matter (OM). Double-pulse experiments with goethite colloids and DOM extracted from soil Oa and Oi horizons were conducted in saturated QS and GCQS columns with Pb^{2+}, OMCG colloids, and Pb + OMCG colloids.

IV. Additional experimental data will be shown and discussed. It is directly connected to the experiments of Study III.

Study IV aims to assess the mobility of Pb^{2+} and OMCG colloids in a disturbed natural soil material and also depending by loading OM on soil surface to assess the of transport in Pb^{2+} and OMCG colloids.

2. Study I

The Influence of Physical - Chemical Heterogeneities and Flow Interruption on the Mobility of Organic Matter-Coated Iron hydroxide in a Model Sand

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Contribution: I contributed to the conceptualization of the study. Designed the experiments, conducted the laboratory analysis. I evaluated the data and compiled the tables and figures. I wrote the manuscript. Prepared for the journal: Colloids and Surfaces A.

Abstract

The mobility of organic matter coated goethite (OMCG) colloids in quartz sand can be reduced by phases of flow interruption due to retention at hetero-domains on the sand matrix surfaces, i.e. local gaps in the energy barriers caused by microscale surface roughness and surface charge heterogeneities of the solid matrix. The aim of the present study was to systematically assess the relative importance of colloid retention caused by either roughness or charge heterogeneities. Breakthrough experiments were conducted in columns filled with different mixtures of quartz sand (QS) and goethite coated quartz sand (GCQS). Furthermore, the nanoscale surface roughness of the colloids was varied by percolation of 0.25 and 1.0 mg L^{-1} DOM solution on the colloid surface, with the higher OM coating amount leading to a higher nanoscale surface roughness. Experiments were conducted at continuous flow conditions and with phases of flow interruption. Under continuous flow conditions, total colloid retention amounted to ~25 % at 0.25 mg L^{-1} DOM percolation and 10% at 1.0 mg L^{-1} DOM percolation, even in the almost total absence of goethite coatings on the sand matrix. The higher retention in the low amount of DOM likely was related to lower nanoscale roughness height that led to higher retention. OMCG colloids retention increase in a linear way with the amount of goethite coatings on the solid matrix. Phases of flow interruption lead to an increase of total colloid retention even in the almost absence of goethite coatings on the sand matrix. Classic DLVO theory at two different concentrations of DOM showed basically different graph on the QS matrix. We conclude that colloid retention related to surface charge heterogeneities is mostly a fast deposition process occurring under continuous flow conditions, while flow interruption strongly increases colloid retention related to microscale surface roughness. These trends are even more pronounced at lower nanoscale surface roughness of the colloids, which causes colloid retention at surface charge heterogeneities to be virtually complete under continuous flow conditions, with additional colloid retention during flow stagnation only related to microscale surface roughness.

Keywords: Microscale surface roughness, charge heterogeneity, nanoscale roughness, OMCG colloid

1. Introduction

Colloid transport and the factors that influence the retention and mobility of colloids in porous media are of great importance in the natural and engineered systems (Torkzaban and Bradford, 2015; Bradford et al., 2017; Shen et al., 2019). There are studies reporting that colloid mobility is related to the flow rate and flow conditions. A decrease in the flow rate increased the amount of colloid retention in the Oak Ridge surface soils (Zhu et al., 2014) and Carstens et al. (2017) showed the attachment of iron oxide colloid on QS at flow interruption phases. The amount of colloid retention on the solid matrix had an increasingly trend with increasing duration of flow interruption (Carstens et al., 2017). Also Sasidharan et al. (2014) demonstrated that the sorptive interaction of nanoparticle colloids with the collector surface increased with enhancing contact time.

Carstens et al. (2017) described retention on the surface with attractive locations, i.e. hetero-domains with surface roughness and chemical heterogeneities and secondary minima as major processes of reducing the mobility of OMCG colloids. However, this study did not investigate into the mechanisms of retention and releasing of OMCG colloids under different varieties of physical and chemical heterogeneities of the colloids. So far, the relative importance of charge heterogeneity and surface roughness for colloid retention under flow interruption have not been considered. Nevertheless, it is known that the surface of natural collector grains always exhibit some degree of surface roughness and chemical heterogeneity (Shen et al., 2012). Hence, in this work we presented an approach to determine the amount of retention and release of colloids in the solid matrix as controlled by microscale roughness and chemical heterogeneities.

The definition of surface roughness by Kreder et al. (2016) is an actual deviation from an ideal smooth surface. A smooth surface has a deeper primary minima which leads to irreversible interaction of colloids for a longer time (Shen et al., 2012; Bradford and Torkzaban, 2013; Zhang et al., 2016; Bradford et al., 2017), while a surface with roughness heterogeneities has shallower secondary minima which tend to release particles into suspension after re-establishment of flow. The interaction energy curve based on DLVO calculations on the unfavorable sites with surface roughness characteristics showed that roughness tends to decrease or eliminate the energy barrier height on the unfavorable sites via decreasing the depth of secondary minima (Hoek et al., 2003; Bendersky et al., 2015; Bradford et al., 2017). The changes on the depth of primary and secondary minima depend on the size, height of roughness, and ionic strength's characteristic. Martines et al. (2008) and Bendersky et al. (2015) showed that the presence of patchy collectors with roughness characteristics on negatively charged solid matrixes result in the attachment of negatively charged colloids on the surface. Surface roughness are divided to nanoscale roughness and microscale roughness properties. The presence of nanoscale roughness on the surface of porous media can attach colloids onto matrixes under unfavorable conditions due to the presence of localized primary minimum (Pasmino et al., 2014). In contrast, microscale roughness has a dominant role in conditions with low ionic strength and high hydrodynamic that increase colloid retention on the surface (Bradford and Torkzaban, 2015).

Coating and patches of positive charge on the negatively charged solid matrix not only lead to surface roughness but also tend to create chemical heterogeneity, another factor to predict the mobility of colloid in the solid matrix (Knapp et al., 1998; Ryan et al., 1999; Fischer et al., 2014). Chemical heterogeneity is referred to the coatings of iron, aluminum, manganese oxides and also of organic matter on the surface of silicate minerals. These patches have a strong influence on the retention and mobility of colloids (Stumm and Morgan 1995; Knapp et al., 1998; Fischer et al., 2014). Stevenson (1994) described that humic and fulvic acid through creating a coating on the soils upon changes of charge have a tendency to control mobility of particles. Bradford and Kim (2012), Shen et al. (2013) and Bendersky et al. (2015) elucidated that the presence of chemical heterogeneity on the unfavorable sites has an increasingly effect on the attachment of particles on the surface via decreasing the height of energy barrier. However, changes in the interaction energy curve are more considerable in the presence of both heterogeneities Bradford and Torkzaban (2013), and higher modifications in the interaction energy for controlling inorganic colloids mobility are taking place at presence of surface roughness (Shen et al., 2012; Bradford et al., 2017).

To date no systematic experimental studies have been conducted to investigate the simultaneous role of surface roughness and chemical heterogeneity under flow interruption on the mobility and retention of OMCG colloids in the column experiments. The overall objective of this study was to systematically investigate and predict the interaction energy between OMCG colloid with QS and goethite coated quartz sand (GCQS) in presence of heterogeneities under flow interruption. For that, we increased the amount of goethite loading at the QS in order to increase the charge heterogeneity, and we used high purity QS to assess the effects of surface roughness at almost absence of charge heterogeneity. These considerations led us to the following hypotheses: (i) OMCG colloids mobility decrease under flow interruption phases, (ii) the importance of microscale roughness of the solid matrix on colloid retention, (iii) fast colloid retention on the solid matrix in the presence of charge heterogeneity (iv) the relative importance of nanoscale roughness height on OMCG colloids retention via decreasing the height of roughness.

2. Materials and Methods

2.1 Experimental layout

Experiments with goethite colloids and organic matter (OM) from fulvic acid were conducted under water-saturated conditions with semicircular Plexiglas columns filled with quartz sand (QS) and goethite coated quartz sand (GCQS). The porosity of the quartz sand under saturated condition was 39% and the size of semicircular Plexiglas's columns were 12 cm height and 1 cm radius. At the QS treatment, the full 10 cm of the column was filled with QS, while the GCQS column was first filled by 1 cm QS, followed by 8 cm GCQS and again 1 cm QS. The breakthrough experiments were divided into two series: (i) iron oxide coated by 0.25 mg L^{-1} dissolved organic matter (DOM) and (ii) iron oxide coated by 1.0 mg L^{-1} DOM, each under continuous and interrupted flow conditions. The experiments were designed with the following flow pattern: (1) rinsing the system with 1 pore volume (PV) of $CaCl_2$ solution; (2) injection of 7.5 PV organic matter coated goethite (OMCG) colloids from series (i) and (ii) in separated columns with a flow interruption of 0,2,18 and 112 h; (4) rinsing the column with 8.0 PV of $CaCl_2$ suspension until the outflow was clear. The concentration of background suspension (0.30 3mM hydrated $CaCl_2$ and 37 mg L^{-1} goethite) for the whole experiments were kept constant, and 3ml of the fluid was removed for UV-vis measurement. Derjaguin-Landau-Verwey-Overbeek (DLVO) theory was applied to assess solid matrix and colloids interaction.

2.2 Materials

High purity QS (Carlo Bernasconi AG, Bern, Switzerland) with grain size distribution 1% <0.1mm, 45% 0.1-0.2 mm, 53% 0.2-0.315 mm, and 1% >0.315 mm was used. Residual iron oxides were removed from the quartz surface by treating 500 g QS with 10M HCl (32%) for 48 hours (Carstens et al., 2017). Subsequently, the QS was rinsed intensively with ultrapure water and air dried at room temperature.

The interface chemical composition of the HCl-treated quartz sand was tested by X-ray photoelectron spectroscopy (XPS; Axis Ultra DLD, Kratos Analytical, Manchester, UK). Quantification of survey spectra revealed predominantly Si (about 26 atomic %) and O (about 64 atomics %) and C (about 9 atomic %) witin the outmost interface layer. Further, some Al (about 1 atomics %) and traces of Fe, Ca, and Na (< 0.5 atomics %) and minor amounts of N (about 0.1 atomics %) were found. The considerable amount of C should be ascribed to adventitious carbon, i.e., C compounds sorbed to the interface from the surrounding air (e.g., Barr and Seal, 1995). For more information on XPS, please see, e.g., Woche et al. (2017).

Pure goethite was obtained from Bayferrox (Lanxess Bayferrox 920 Z; high chemical purity, Cologne, Germany) with a specific density of 4 g cm^{-3} and specific surface area of 12 m^{2}g^{-1} as provided by the manufacturer. The point of zero charge (PZC) of the goethite as measured by electrophoretic mobility of light scattering (Zeta-PALS, Brookhaven Instruments Crop., Holtsville, USA) was at pH 8.8. Following Carstens et al. (2017, 2018), 37 mg L^{-1} of goethite colloid was brought into suspension by sonication in ultrapure water using a ultrasonic bath (Bandelin, RK 106, Berlin, Germany) at an energy of 35 kHz,.

The goethite of Bayferrox was also used to coat the HCl-cleaned QS. According to Carstens et al. (2018), 1 g goethite powder was dispersed in 100 ml ultrapure water by sonication (VW UCR 200, Allpax GmbH & Co.Kg, Germany) for 5 minutes and afterwards shaken in an overhead shaker (Heidolph, Reax 2, Schwabach, Germany) for 24 h. Thereafter 100g of HCl-cleaned QS was added and the suspension was shaken for another 24 hours. Subsequently, the produced GCQS was rinsed with ultrapure water until the effluent was clear and finally the powder was air-dried at room temperature. To compare the amount of iron on the surfaces, XPS measurements was conducted for a goethite-coated quartz sand grain. Laser microscopy and surface topography of QS and GCQS were measured by CLSM. In order to have different percentages of GCQS in the solid matrix of the columns, the prepared GCQS was mixed in 2%, 5%, and 7.5%, respectively, with QS.

Dissolved OM was prepared from Pahokee Peat FA Standard II provided by the International Humic Substances Society (IHSS, St. Paul, MN, USA). According to XPS measurement the material contained no residual sodium. So, FA did not change ionic strength in the experiment. 1.0 mg of fulvic acid diluted with 50 ml distilled H_2O to obtain 20 mg L^{-1}of DOM and then DOM solutions of 0.25 mg DOM L^{-1} and 1.0 mg DOM L^{-1} were prepared from 20mg L^{-1}.

Organic matter coated goethite (OMCG) colloids were prepared by mixing different ratios of stock solutions of goethite colloid, hydrated $CaCl_2$ and fulvic acid .In order to separate the DOM from the OMCG, the suspension was centrifuged at 6000g for 6 hours (Fischer Scientific, Cryofug 6000i and 8500i, Schwerte, Germany).

2.3 Characterization of the solid and colloidal phases

The electrophoretic mobility of OMCG colloids were measured by phase analysis light scattering technique (Zeta-PALS, Brookhaven Instruments Corp., Holtsville, USA). After gentle shaking suspension, 1.6 ml of the OMCG suspension was transferred in a cuvette and after immersion of the electrode, the zeta potential was measured as arithmetic means of 10 replicated runs and each partitioned in 20 cycles via Smoluchowski’s equation (Elimelech et al., 1995).

The concentration of organic carbon (OC) in suspension was measured by a TOC analyzer (Liqui TOC II, Elementar Analysensysteme, Hanau, Germany).

Organically complexed Fe along with poorly and well crystalline Fe in (hydr) oxides of QS and GCQS were determined by the dithionite-citrate method (Carter & Gregorich, 2006). The extracted Fe in the supernatant was diluted with distilled H_2O and measured by ICP-OES (Varian ICP 725, r, Agilent Technologies, Santa Clara, CA, USA).

2.4 Effluent analysis

The OMCG colloids in the effluent of the column experiments were determined by UV-vis spectroscopy (Varian Carry 50 UV-Vis Spectrophotometer, Varian, Palo Alto, CA, USA). The maximal intensity for detecting OMCG colloids via UV-vis spectroscopy was at 440 nm to determine C/C_0. Colloid breakthrough curves were calculated from constant prepared concentration and displayed as C_0 which was constant for the individual experiments and C measured from every 3ml of fluid.

2.4 DLVO calculations

The sum of electrostatic and van der Waals interactions forms the classic DLVO approach (Verwey and Overbeek, 1948). The method of calculation followed the description outlined in Goebel et al. (2013). Electrostatic interactions were estimated from zeta potential and solution ionic strength. Van der Waals interaction was calculated via sessile drop method (SDM) contact angle measurements with a CCD-equipped microscope (OCA 15, DataPhysics, Filderstadt, Germany) in order to approximate surface free energies of OMCG colloids and sand grains (Bachmann et al., 2000). The surface free energy was calculated with three known liquids, ultrapure water, glycerol and iodobenzene. For measuring OMCG colloid SDM samples, the samples were air-dried on soda-lime glass slides (Menzel-Gläser, precleaned, Gerhard Menzel GmbH, Brunswick, Germany) and QS SDM samples were disturbed on double-sided adhesive tapes covering glass slides. Contact angle was measured by CCD-equipped microscope by placing 1 µl of know liquid on the soda-lime glass slides and the drop shape analysed with SC20 software (DataPhysics, Filderstadt, Germany).

3. Results and discussion

As previous research did not focus on the relative contribution of microscale roughness and charge heterogeneity of the solid matrix on the colloid immobility, a simulated solid matrix was used, allowing for assessing the effect of microscale roughness and charge heterogeneity on the OMCG colloids mobility which have different nanoscale roughness properties. For that total colloid retention and release at different proportions of GCQS in the solid matrix under continuous flow and flow interruption conditions are analyzed.

3.1 OMCG colloid breakthrough under different flow conditions

Flow conditions and surface heterogeneities significantly affected on OMCG colloids transport in the solid matrix.

The OMCG colloids were highly mobile under continuous flow conditions, while colloid mobility decreased during flow interruption phases of 2, 18, and 112 h specifically after five days (Fig. 1). In contrast, Henderson et al. (2012) and Borthkur et al. (2021) described that flow interruption led to increase in the mobility of colloidal Fe oxides in porous media due to establishment of reducing condition in the column, leading to reductive dissolution. However, under our experimental conditions, reducing conditions could be ruled out due to aerobic conditions in the saturated conducted columns, and also Carstens et al. (2017), using a similar experimental approach, demonstrated that flow interruption decreased the mobility of Fe oxide colloids in the columns filled by QS As compared to pure QS, there was higher retention of OMCG colloids in the GCQS matrixes (Fig. 1), because of the presence of hydroxyl group of iron oxides on the coated QS. The phase of flow interruption in two different concentrations of OMCG colloids (i.e. percolation with 0.25 mg L^{-1} DOM as compared to percolation with 1.0 mg L^{-1} DOM) showed lower mobility in colloid with low amount of OM loading on the goethite. More information regarding the effect of different OM loading on goethite will be given in Section 3.2.

In order to predict the movement of colloids in the columns under flow interruption, several assumptions may be considered, including (i) straining in the pore throats (Bradford et al., 2003), (ii) retention on the immobile flow zones (Gao and Saiers, 2006; Morales et al., 2009), (iii) and retention at locations with attractive DLVO interactions, i.e. secondary minima and hetero-domain locations (Bradford and Torkzaban, 2012; Shen et al., 2012). Straining in the pore throats at resuming flow is related to the colloid size. Bradford et al. (2005, 2007) and Johnson et al. (2010) showed that inorganic colloids strained in the pore throats during flow interruption could not be detached from the surface after re-rinsing due to aggregation the inorganic colloids in the pore sizes with too small for passage during the rinsing process. In these pores, the colloids likely aggregate with the solid phase via cation bridge at presence of Ca^{2+} (Chekli et al., 2013), which has a concentration of 0.3 mM in the background solution of our experiment. However, the particle sizes of the OMCG colloids did not change after flow interruption (Table 1). Hence, immobilization of the colloids in small pores of the matrix appears to be unlikely due to remained stable particle sizes during the phase of flow interruption.

Considering the immobile flow zones as another issue for the OMCG colloids retention, the findings of Gao and Saiers (2006) and Morales et al. (2009) showed that inorganic colloids can be retained on the immobile flow zones of the solid matrix through gravitational settling. However, Carstens et al. (2017), using the same solid matrix of QS as in our study, showed that trapping and straining of OMCG colloids in the immobile flow zones were not a critical value for colloid retention during flow interruption. The authors reported that re-rinsing of OMCG colloids with $CaCl_2$ released more colloids into suspension under flow interruption than were detached from immobile flow zones. It can be assumed that colloid immobility in the flow zones did not occur also in the presence of GCQS matrix due to higher release of colloids after flow interruption of the 7.5% GCQS (i.e. 102 mg Kg^{-1} Fe_d) as compared to QS (see also Carstens et al., 2017).

Hence, it seems likely that the colloids in the phase of flow interruptions were retained on the surface with attractive DLVO interaction such as secondary minima which is in the outwards of energy barrier (Shen et al., 2012) and hetero-domains locations with surface roughness and charge heterogeneity characteristics (Bradford and Torkzaban, 2012). Experiments in Table 2 presented the percentage of total amount of deposition and elution of OMCG colloids in phases 1 and 2 before and after flow interruption, respectively as those depicted in (Fig. 1). Phase 2PV represents the percentage of colloids injected during the last pore volume before flow interruption. The results showed deposited colloids in the locations with attractive interaction after 2h of interruption partly released into suspension. It can be assumed that colloids released into suspension likely deposited in the secondary minimum during phase 1 and re-establishment of flow after flow interruption led to release colloid into outflow (phase 2) due to higher drag of Brownian diffusion. The studies (Bradford et al., 2009; Torkzaban et al., 2010 and Shen et al., 2012b) showed inorganic and organic colloids retained on the secondary minima are loosely bound as compared to hetero-domains locations and can thus be easily detached from the surface into solution after re-establishment of flow during flow interruption phase. The results in phase 2 (Table 2) represented, decrease in re-mobilization of colloids after 18 and 112 h of flow interruption revealed the assumption of colloid retention in the hetero-domain locations. Study (Carstens et al., 2017) showed colloid retention in hetero-domain locations after 18 and 112h of flow interruption. Retention at hetero-domain locations originating from surface roughness and charge heterogeneity. Charge heterogeneity is originated from the presence of patches on the surface. In our study changes on the solid matrices of QS and GCQS showed by XPS measurements. The results by XPS measurements clearly showed the presence of trace of Fe in the amount of (0.23 atomic %) on the surface of QS and around (12.0 atomic %) on the surface of GCQS. The presence trace of Fe on HCl-cleaned quartz surfaces observed by (Johnson and Pazmino, 2010; Carstens et al., 2017) who reported the influence of charge heterogeneity of QS matrix on colloid retention. The report (Kim et al., 2008) showed with increasing iron oxide-coated sand the amount of colloid retention increased on the surface. Thus, it could be assumed that charge heterogeneity originated from hydroxyl group of iron oxide was an effective factor on control colloid mobility in QS and GCQS. As it was known the amount of trace of Fe on GCQS was higher than QS, hence higher OMCG colloid retention can be assumed.

Microscope images by CLSM showed the presence of surface roughness on the surface of sand grains (Fig. 2a.b). The measurements showed that the surface topography is clearer in GCQS matrix than QS matrix due to shaking GCQS during coating process that produced sand grains with different surface roughness. The study by (Zhang et al., 2016) showed the importance of surface roughness on the surface of QS and GCQS on decrease mobility of goethite colloid through increasing favorable site for retention with decreasing the energy barrier height. In general, the results suggested that colloids retained in hetero-domain originating from surface roughness and charge heterogeneity are rarely irreversible and sorption in phase 1 is strong enough, thus Brownian diffusion is un-able to release more colloids in phase 2 into suspension. However, increasing the phase of flow interruption enhanced the duration of retention on the locations.

3.2 Effect of surface roughness and charge heterogeneity of the matrix on colloid mobility

Colloid mobility is affected by both, surface roughness (microscale roughness) and charge heterogeneity of the solid matrix, which was unraveled by XPS measurements and CLSM image. Changes in OMCG colloids mobility with goethite colloid loading with 1.0 mg L^{-1} DOM showed that at absence of charge heterogeneity when using acid-washed QS as matrix, still 10% of the OMCG colloids were retained, as is indicated by the horizontal line (Fig.3a). This retention can be referred to the effect of surface roughness of the sand grains on the colloid retention. The presence of microscopic surface roughness of the porous media can reduce or eliminate energy barrier on the unfavorable site and provide attachment conditions for colloid retention (Bradford and Torkzaban, 2015). Burdick et al. (2005) and Bradford and Torkzaban (2012) stated that microscale roughness enhances colloid retention on the surface via increasing interaction energy between the colloids and the matrix surface and decreasing hydrodynamic drag. This observation may help explain the importance of colloid retention in surface topography of sand grains.

When the experiment was carried out with a more complex surface matrix with different percentages of GCQS, the amount of colloid retention increased with an increasing amount of Fe_d (Fig. 3a). It seems there was a linear increase of colloids retention with Fe_d. In the matrix GCQS there was an additional retention of OMCG colloids on the surface due to charge heterogeneity. Assuming Fe_d to indicate an increasing charge heterogeneity by sorbed goethite on the QS. An addition of goethite coating on the surface up to 102 mg Kg^{-1} Fe_d resulted in

100% of colloid retention on the surface (Fig. 3a). Hence, the colloid mobility could be considered to be due to both physical heterogeneity (i.e. surface roughness) and chemical heterogeneity (i.e. charge heterogeneity) (Bradford and Torkzaban, 2015). But as was also shown by Song et al. (1994), a minor amount of charge heterogeneity on the surface solid matrix has a strong impact on the deposition of inorganic colloids. The observation on colloid mobility in the presence of charge heterogeneity implies that the presence of goethite patches increased colloid retention due to increased amount of electrostatic attraction between (hydr) oxides Fe with negatively charged OMCG colloids.

However, flow interruption lead to a further increase in the retention of OMCG colloids as compared to continuous flow, irrespectively of the Fe_d contents, as is indicated by the area between the two diagonal lines in (Fig. 3a). Flow interruption led to an increase in retention of colloids close to 25% even in the absence of goethite coating on the QS matrix with its microscale surface roughness. With increasing GCQS content the amount of OMCG colloids retention due to flow interruption on the surface increased (Fig. 3a). It can be assumed that there are two process of colloid retention on the GCQS, i.e fast retention and slow retention. The fast retention of OMCG colloid on the GCQS was due to charge heterogeneity during continuous flow, while retention due to microscale roughness of the sand grains is a slow process under flow interruption. However, at highest goethite loading of the QS, i.e. 102 mg Kg^{-1} Fe_d, all fast retention due to charge heterogeneity was already responsible for complete colloid retention.

This observation showed changes of charge heterogeneity in the presence of positive patches on QS had a greater influence on colloid retention and release compare to microscale roughness. However, the retention of colloids in porous systems can be also affected by the nanoscale surface roughness of the colloids themselves (Fig. 3a.b). Here, we manipulated the surface roughness of the OMCG colloids by sorption of different amounts of OM (i.e. percolation with 0.25 mg L^{-1} DOM as compared to percolation with 1.0 mg L^{-1} DOM). The amount of colloid retention with 0.25 mg L^{-1} DOM on the surface of QS was 15% higher than with 1.0 mg L^{-1} DOM on the same matrix, as is indicated by the upwards shift of the horizontal base line in the case of the lower OM addition (Fig. 3b). At 0.25 mg L^{-1} DOM solution, 25% of the OMCG was retained under continuous flow conditions in the matrix QS, being similar to the retention after 112 h of flow interruption in case of the 1.0 mg L^{-1} DOM treatment (Fig. 3a.b). So, OMCG colloids in different amounts of OM behaved differently in breakthrough curves despite having the same zeta potential charge in the value (-31 mv). At smaller DOM concentrations in suspension the surface roughness of the OMCG colloids revealed a lower nanoscale roughness height, while at the larger DOM concentration higher nanoscale roughness properties were created. The sorption isotherm (Fig. 4) of OMCG colloid showed the amount of DOM adsorbed on goethite colloid surface resulted in different nanoscale roughness height. The results quantified that the less cover of OM around goethite colloid in the presence 0.25mg L^{-1} DOM than to 1.0 mg L^{-1} DOM. As colloid retention is favored at lower nanoscale roughness height, colloids with a smaller OM are retained to greater extent. According to Tipping and Higgins (1982) and Philippe and Schumann (2014) a more complete OM coverage of goethite colloid at higher DOM concentrations resulted at higher nanoscale roughness height with larger repulsive interaction. Hence, OMCG colloids with the 1.0 mg L^{-1} DOM concentration had higher electrostatic repulsion properties despite having the same zeta potential value at lower OM loading on goethite colloid, leading to a higher release of the colloids in the effluent.

Also when using 0.25 mg L^{-1} DOM, most of the OMCG colloids retention under continuous conditions was due to fast reaction caused by charge heterogeneity (Fig. 3b). Additional slow retention originating from microscale roughness and initiated by flow interruption was of minor importance. Furthermore, the OMCG colloids with 0.25 mg L^{-1} DOM were completely retained already at smaller goethite loading of the QS as compared to the 1 mg L^{-1} DOM treatment (i.e. 80 mg Kg^{-1} Fe_d *vs.* 102 mg Kg^{-1} Fe_d). This observation is likely due to stronger aggregation of colloids at low OM surface coverage that was neutralized earlier on the solid matrix.

3.4 Calculation of DLVO interaction energy for the explanation OMCG colloids mobility

The DLVO model is using for the prediction of the behavior of colloids in porous systems. The soil properties and surface free energy of QS, GCQS and OMCG colloids used for the DLVO model are given in the Table 3, and Fig. 5 shows the DLVO data between QS matrix and OMCG colloids. The DLVO interactions of OMCG colloids with 0.25 mg L^{-1} DOM showed deeper secondary minima as compared to colloids with 1.0 mg L^{-1} DOM due to weaker Lewis acid-base interactions (Table 3). So, the OMCG colloids at 1.0 mg L^{-1} DOM with higher nanoscale roughness height had lower electrostatic attractions with surfaces, thus impeding their retention. According to Bradford and Kim (2012) the shallow deposition of particles in secondary energy minimum is reversible and colloids are able to be released into suspension. Bradford et al. (2016 and 2017) showed that nanoscale roughness with increased height in nanoscale roughness properties via changes on the interaction energy curve exert a tendency to release colloids with shallow secondary minima into suspension. The changes of interaction energy strongly depend on the roughness fraction and height of nanoscale roughness (Zhang et al., 2008; Bendersky and Davis 2010; Bradford et al., 2017). Deposition in shallow secondary minimum is fast and can be released into suspension easily, while interactions in deeper secondary minimum is slow and colloids are attached on the surface for longer times and releasing into suspension is time-depending.

Summarizing, surface roughness properties were the relevant parameter to predict colloid mobility in QS matrix compare to electrostatic interaction. The results showed different breakthrough behavior curve of OMCG colloids despite having the same zeta potential characteristics.

4. Conclusions

This study recognized the relative importance of surface roughness and charge heterogeneity on the mobility of OMCG colloids in the matrix QS and GCQS under continuous flow and after flow stagnation. Flow interruption strongly increased the retention at the uncharged QS matrix which was related to microscale surface roughness. Increasing GCQS content led to higher colloid retention and results clearly indicate that most of the retention was caused by charge heterogeneity. Fast deposition already occurred during continuous flow, whereas the additional retention at flow interruption is related to slow retention driven by microscale roughness. The use of two different concentration of DOM revealed that the retention of OMCG colloids is a stronger at low OM loading of the goethite colloids than at high one under both, continuous flow and flow interruption. Thus, a lower nanoscale colloid surface roughness of the OMCG colloids facilitated their retention related to microscale surface roughness of the QS matrix. Furthermore, the increase in colloid retention during flow interruption at rising GCQS contents can be completely assigned to surface roughness, showing that the lower nanoscale surface roughness facilitates a fast colloid retention related to surface charge heterogeneities under continuous flow conditions, which is not further increased by flow stagnation. The results on the QS were confirmed by DLVO theory.

This observation indicates that the rate of colloid deposition is proportional to the presence of patch-wise chemical heterogeneity and also surface roughness. Furthermore, the total colloid deposition rate in the column increases with time as favorable sorption sited are being filled gradually.

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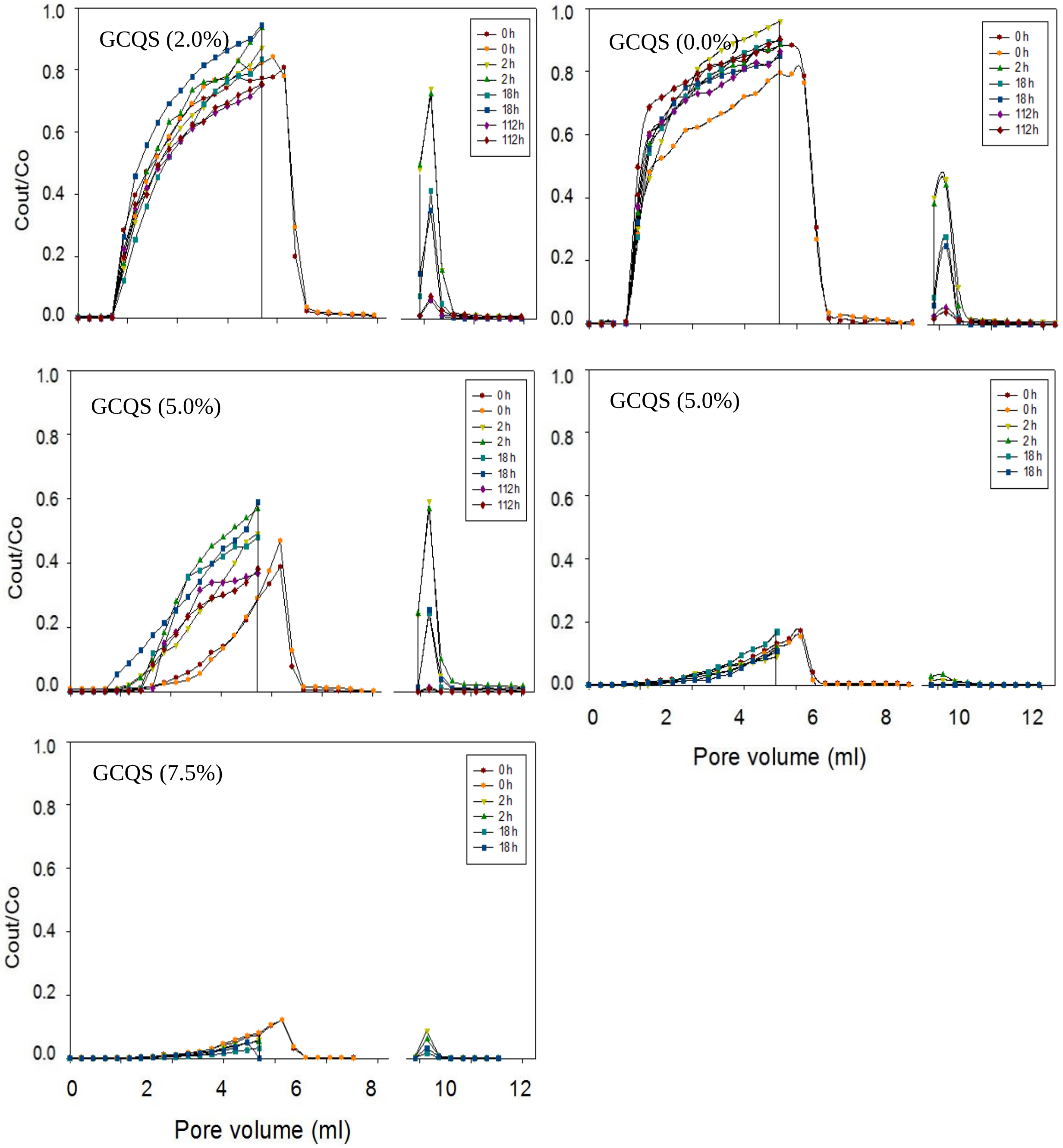

Fig. 1. Breakthrough curves of OMCG colloids released for 0,2,18 and 12 h of flow interruption in columns filled with quartz sand (QS) and goethite coated quartz sand (GCQS) at different addition of organic matter coated goethite (OMCG) colloids. The figures in the left side represent goethite colloid loading with 1.0 mg L^{-1} dissolved organic matter (DOM) in three variants of goethite added on QS (2.0, 5.0 and 7.5%) and in the right side goethite colloid loading with 0.25 mg L^{-1} DOM at two variants (QS (GCQS, 0.0%) and 5.0% goethite added on QS). The experiment of OMCG colloid with loading 1.0 mg L^{-1} DOM on GCQS (0.0%) was published by (Carstens et al., 2017). Results are depicted in two replicates.

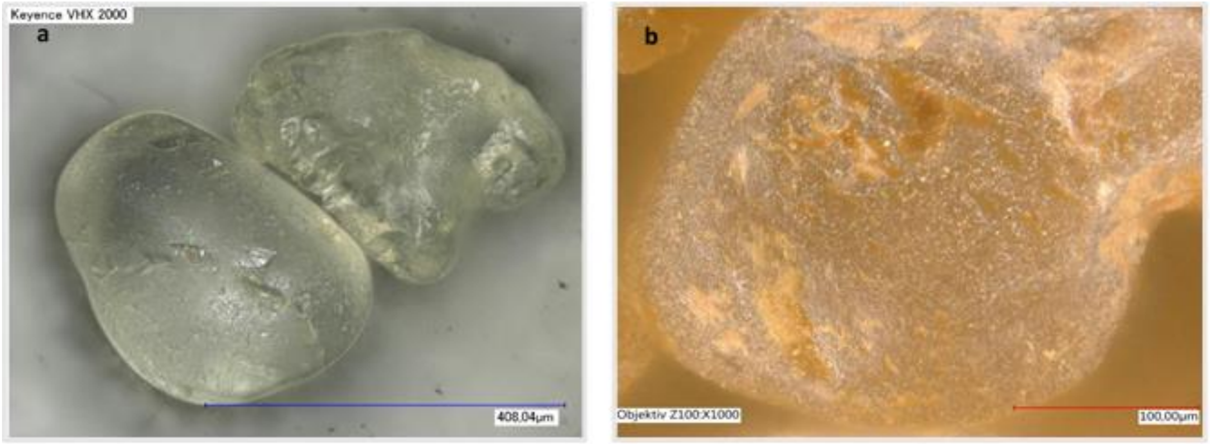

Fig. 2 a. b. Laser microscopy cross section and surface topography of a) quartz sand (QS) and b) goethite coated quartz sand (GCQS) measured by CLSM.

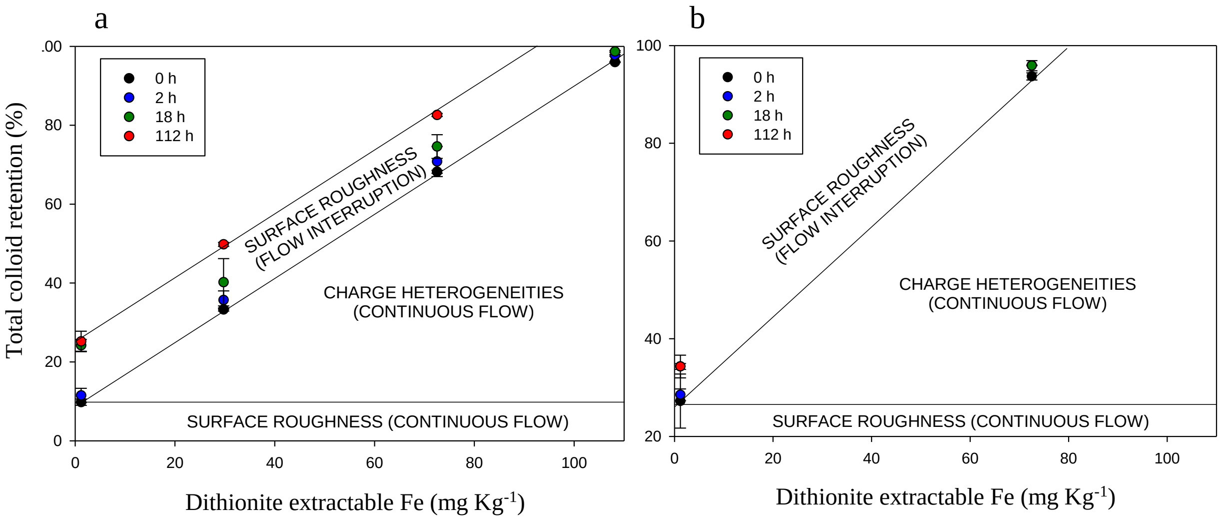

Fig. 3 a.b. Total colloid retention in the column before and after flow interruption(Phase 1 +2) in % in the different percentage of goethite added to quartz sand (QS) as a function of dithionite extractable Fe . Results represents at two different concentrations of dissolved organic matter (DOM) coated on goethite colloid, a) loading with 1.0 mg L^{-1} DOM, b) 0.25 mg L^{-1} DOM.

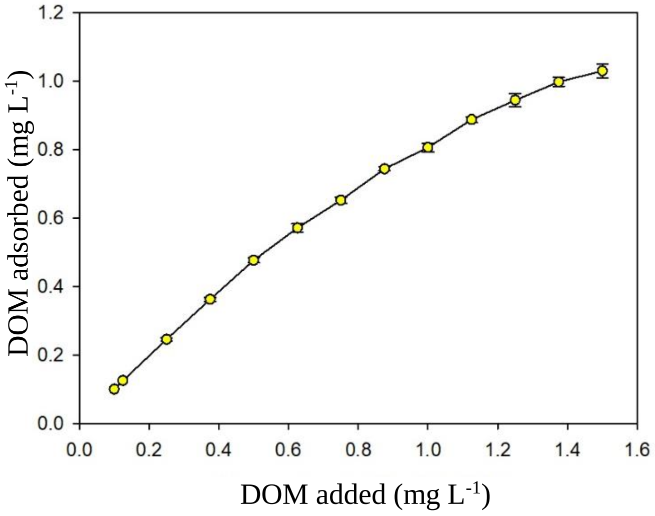

Fig. 4. The mass amount of dissolved organic matter (DOM) adsorbed on the goethite colloid. Results are depicted as arithmetic means of three replicates, with error bars depending the range.

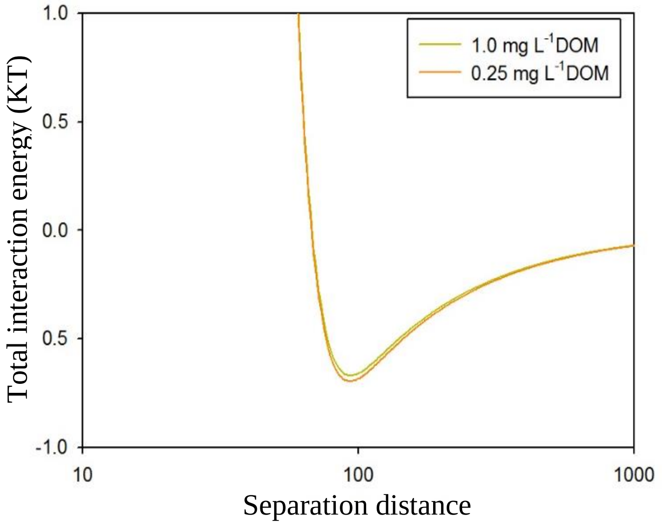

Fig. 5. Derjaguin-Landau-Verwey-Overbeek (DLVO) interaction between quartz sand (QS) and organic matter coated goethite (OMCG) colloids at two different concentrations of OM loading added on goethite colloids. The inserted plot depicts a zoom into the secondary minima.

Table 1. Particle size (nm) of organic matter coated goethite (OMCG) colloids at two different concentrations of dissolved organic matter (DOM) under flow interruption phases.

Time (h)	**Particle size (nm)**	
	OMCG colloid 1*	**OMCG colloid 0.25****
0	443.62± 11.0	457.0±15.24
2	484.4 ± 13.1	462.7 ± 11.8
18	474.4 ± 4.7	478.3 ± 9.3
112	456.70± 4.7	472.83± 10.8

*Organic matter coated goethite (OMCG) colloid loading with 1.0 mg L^{-1} DOM/** OMCG colloid loading with 0.25 mg L^{-1} DOM.

Table 2. Mass balance for different phases of experiment. Data is given in percent of total colloids injected except for phase 2PV (pore volume) which is the percentage of colloids injected in the last pore volume and released before flow interruption. Phase 1 the amount of colloids released before flow interruption and phase 2 shows colloids released after interruption. Total 1+2 is the sum of phase 1 and phase 2 in the total amounts of colloids released. Phase 2PV is colloids released after interruption. Results represents a) organic matter coated goethite (OMCG) colloid loading with 1.0 mg L^{-1} DOM and b) OMCG colloid loading with 0.25 mg L^{-1} DOM in the matrix goethite coated quartz sand (GCQS).

	GCQS(%)	Time (h)	Phase 1	Phase 2	Total 1+2	Phase 2PV
a	2	0	53.90	12.44	66.34	85.96
		0	53.99	13.16	67.16	91.01
		2	52.39	9.68	62.07	66.22
		2	57.14	9.47	66.61	65.35
		18	50.10	3.73	53.83	25.75
		18	62.25	3.50	65.75	24.10
		112	48.88	0.85	49.73	5.59
		112	49.58	1.10	50.68	7.58
	5	0	25.99	5.37	31.36	37.49
		0	25.49	6.71	32.20	46.29
		2	18.94	6.45	25.39	44.21
		2	26.03	6.95	32.98	47.30
		18	20.32	2.08	22.40	14.26
		18	26.23	2.22	28.45	15.44
	7.5	0	2.20	1.74	3.94	11.98
		0	2.39	1.76	4.15	12.18
		2	1.82	0.68	2.50	4.73
		2	1.55	0.50	2.05	3.45
		18	0.95	0.15	1.10	1.07
		18	1.21	0.27	1.48	1.86
b	0	0	64.73	13.57	78.30	93.46
		0	54.05	13.18	67.23	90.36
		2	65.55	7.15	72.70	48.74
		2	63.76	6.50	70.27	44.58
		18	62.78	2.31	65.08	15.94
		18	63.54	2.74	66.28	18.89
		112	62.39	0.99	63.37	6.80
		112	67.23	0.79	68.03	5.54
	5	0	4.33	2.72	7.05	18.44
		0	3.54	2.04	5.58	14.13
		2	3.62	0.37	3.99	2.60
		2	3.58	0.54	4.12	3.73
		18	5.08	0.08	5.16	0.54
		18	3.03	0.05	3.08	0.32

Table 3. Sessile drop method contact angles and inferred surface free energies for for quartz sand (QS), goethite and organic matter coated goethite (OMCG) colloids. θ = contact angle for the fluids indicated, γ^{LW}= van der Waals free energy, γ^{+}=Lewis acid free energy, γ^{-}= Lewis base free energy.

Material	θ_{Water} (°)	$\theta_{Glycerol}$ (°)	$\theta_{Iodobenzene}$ (°)	γ_s^{LW}	γ_s^{+}	γ_s^{-}
QS	23.4±3.9	51.9±6.4	0.0±0.0	39.7	0.0	66.40
Goethite	28.4±2.3	63.6±10.6	39.0±2.6	31.35	0.29	79.41
OMCG colloid 1*	41.06±2.8	73.75±7.1	28.75±1.28	34.96	1.92	73.31
OMCG colloid 0.25**	39.4±3.4	59.73±4.3	30.27±2.70	34.47	0.01	55.81

*Organic matter coated goethite (OMCG) colloid loading with 1.0 mg L^{-1} DOM/** OMCG colloid loading with 0.25 mg L^{-1} DOM.

3. Study II

Drying and Rewetting Cycles Amplify the Preferential Retention of Hydrophobic DOM in Soils

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Contribution: I contributed to the conceptualization of the study. Designed the experiments, conducted the laboratory analysis. I evaluated the data and compiled the tables and figures. Contributed to the manuscript writing. Prepared for the journal: Vadose Zone Journal.

Highlights:

- DOC retention in disturbed subsoil is increased by cycles of drying and rewetting
- Drying enhances the preferential retention of more hydrophobic DOM fractions
- This preferential retention is promoted by lower soil OM loadings prior to drying
- During a second drying/rewetting, the retained DOM is relatively more hydrophilic
- This indicates that drying amplifies the formation of multilayer OM coating structures

Abstract

Dissolved organic matter (DOM) is one of the most mobile components of the global carbon cycle. Most previous DOM transport studies have been conducted under high water saturation levels, which is a very limited mode of operation compared to real hydrologic conditions in soils. Therefore, the present study aims to systematically compare DOM retention in disturbed subsoil via column breakthrough experiments that were either conducted at full water saturation or with two consecutive cycles of drying and rewetting. Column effluent DOC and DON as well as the specific UV absorption at 280 nm (SUVA) were determined. Results showed that the total quantity of DOC retention was higher in the variants with drying and rewetting cycles, and that the DOM leached by rewetting was more strongly depleted in hydrophobic fractions. This was especially the case for a further set of experiments in which the soil surfaces had a lower OM loading before drying. During the second drying and rewetting cycle, the released DOM was less depleted in hydrophobic fractions than after the first drying in both OM loading variants. Sessile drop contact angle data showed a marked decrease of soil wettability and surface free energies after DOM percolation, in particular after drying. We conclude that cycles of drying and rewetting lead to an increased DOM retention in soils, with an amplified preferential retention of more hydrophobic fractions. Furthermore, the retained DOM in subsequent drying cycles becomes relatively more hydrophilic, indicating the formation of distinct OM coating layer structures.

Keywords: drying/rewetting; dissolved organic matter mobility; OM coating structure; soil water repellency; surface free energies

1. Introduction

Broadening the knowledge on the mobility of DOM in soils is crucial in context of soil carbon sequestration as well as the co-transport of contaminants (Tipping et al., 2012; Yang et al., 2012; Cheng and Saiers, 2015). DOM transport and retention processes in soils occur in the context of drying and rewetting cycles, which are expected to become more pronounced as global change leads to more irregular regional precipitation patterns (Kim et al., 2012).

In general, rewetting of soils after dry periods leads to an increase in DOM concentrations, likely due to reduced microbial decomposition and release of dead microbial biomass (Kalbitz et al., 2000; Bailey et al., 2019). In column transport experiments, it has been shown that cycles of drying and rewetting facilitate DOM retention in soils (Arye et al., 2007; Lamparter et al., 2014). However, systematic research on the effects of drying and rewetting cycles on the formation of mineral-organic associations and on the composition of DOM remains scarce (Kaiser et al., 2015; Olshansky et al., 2018).

From previous research, several processes by which drying and rewetting affect the formation of mineral-organic associations are known. An important effect of drying is that both the DOM concentration and the ionic strength in the constricting water volume is rising, leading to more favorable conditions for DOM sorption onto soil minerals (Weng et al., 2005; Setia et al., 2013). The sorption strength of organic acids onto iron oxide minerals is enhanced by drying, as it leads to a transformation of outer-sphere to inner-sphere sorption complexes (Kang et al., 2008). Furthermore, OM molecules retained on soil particles are subjected to a re-orientation by drying: Their hydrophilic moieties turn towards the soil mineral surfaces, while their hydrophobic moieties become oriented towards the pore space (Horne and McIntosh, 2000). This leads to an increase of soil water repellency of dried soil surfaces, which can potentially affect water flow patterns during phases of rewetting (Arye et al., 2007) and thereby protect OM from remobilization. Moreover, changes in wettability affect soil surface free energies, which in turn play an important role in the interactions of soil particles (Calero et al., 2017).

During its movement through the soil, the composition of DOM is affected by the preferential sorption of more aromatic components onto soil minerals, especially onto metal oxide phases. This has been shown to occur in water saturated columns (Guo and Chorover, 2003) and field experiments (Kaiser et al., 2004; Leinemann et al., 2016). Moreover, the preferential sorption of DOM components in column experiments with phases of flow stagnation was affected by prior OM loading: at lower previous OM loadings, more hydrophobic DOM was retained, whereas higher previous OM loadings led to the retention of more hydrophilic DOM (Carstens et al., under review). This is in good agreement with findings that OM coatings on soil minerals are more hydrophobic at closer proximity to the mineral surfaces (Gao et al., 2020). In batch experiments with soils that were relatively depleted in metal oxide mineral phases, the preferential sorption of more hydrophobic DOM components under consecutive cycles of drying and rewetting was comparable to the preferential sorption under fully saturated conditions (Olshansky et al., 2018). For soils that are richer in metal oxides, it remains an open question how the formation of OM layer structures comparable to those described in Gao et al. (2020) is affected by cycles of drying and rewetting under flow conditions.

Based on these considerations, we developed the following hypotheses concerning the effects of drying and rewetting on transport and retention of DOM in subsoil material rich in metal oxide mineral phases:

(1) In experiments involving drying and rewetting cycles, the total DOC retention is higher than in experiments that are conducted under continuously full water saturation;

(2) During drying, more hydrophobic components of DOM are preferentially retained on the soil surfaces, especially at lower OM loadings on the soil surfaces prior to drying,

(3) In a second drying and rewetting cycle, the retained DOM is more hydrophilic than in the first cycle, both at lower and higher previous OM loadings,

(4) DOM retention affected by drying leads to a stronger decrease in soil wettability and surface free energies than DOM retention under fully water saturated conditions.

In order to test these hypotheses, breakthrough experiments were conducted using columns filled with disturbed Cambisol subsoil. Effluent DOM was analyzed for total DOC and DON, and the aromaticity was determined via SUVA measurements. Subsequent to the column experiments, sessile drop contact angles of the column fillings were measured in order to determine the effects of DOM retention on soil wettability and surface free energies.

2. Materials and Methods

2.1 Soil

Soil samples were taken in 50 cm depth from the BvC horizon of a dystric Cambisol under *Fagus sylvatica* (L.) forest in the Grinderwald forest, NW of Hannover, Lower Saxony, Germany. The samples were air-dried, sieved with a 2 mm mesh and thoroughly mixed. The following soil parameters were determined in triplicates: soil texture was analyzed via wet sieving (sand fractions) and sedimentation (clay and silt fractions) according to Stoke’s Law. For pH measurements, 4.0 g soil were mixed with 10 ml 0.01 M $CaCl_2$ solution, shaken for 1 hour and measured with a pH-meter (PH-100ACT, Voltcraft, Switzerland). Soil organic carbon was measured with a Vario TOC Cube (Elementar, Langenselboldt, Germany). The content of of low and high crystalline Fe and Al oxide minerals were determined via sodium dithionite and ammonium oxalate extraction and subsequent measurements via ICP-OES (Varian ICP 725 Optical Emissions Spectrometer, Agilent Technologies, Santa Clara, CA, USA), according to McKeague and Day (1966). The specific surface area was measured via the BET (Brunauer-Emmett-Teller) method (Brunauer et al., 1938) on a Nova Surface Area + Pore Size Instruments analyzer (Quantachrome Instruments, Oedelzhausen, Germany).

2.2 Dissolved organic matter

The extraction of dissolved organic matter (DOM) was conducted as described in Poggenburg et al. (2016). Water-soluble DOM was extracted from Oi horizon material taken from a *Fagus sylvatica* (L.) forest on a dystric Cambisol, located in close proximity to the soil sampling site in the Grinderwald forest. The Oi horizon material was air-dried, ground and mixed with ultrapure water (1/10 v/w). The suspensions were shaken for 16 hours and filtered through 2 mm filters and subsequently centrifuged for 10 minutes at 3000 rpm. The suspensions were decanted, pressure filtrated at 2 bar through 142 mm cellulose nitrate filters, and then filtrated at 6 bar through 0.45 µm filters (Whatmann Filter Nr. 41, Merck, Darmstadt, Germany). The DOC and DON concentrations of the filtrates were determined in six replicates at a Vario TOC Cube (Elementar, Langenselboldt, Germany). The SUVA of the DOM was 0.019 ± 0.001 L mg C^{-1} cm^{-1}, and the C/N ratio was 9.3 ± 0.7, 1 (each given as mean of eight replicates and standard deviation). The DOM solution was shock frozen in liquid nitrogen and stored at 253 K; it was thawed directly before the experiments.

2.3 Breakthrough column experiments

The disturbed Cambisol subsoil samples were filled into 12 cm long semicircular plexiglass columns (diameter: 2 cm), which featured removable lid from top to bottom. At the bottom of the columns, a 1 cm layer (2.7 g) of pure, acid-washed quartz sand (Carlo Bernasconi AG, Bern, Switzerland; grain size distribution: 98% between 0.1 and 0.315 mm) was filled to provide a buffer between the column outlet and the soil packing. The quartz sand was washed in 10 M HCl solution for 48 hours in order to remove residual oxide mineral phases. Above the sand, a 5 cm thick layer of soil (12.4 g) was filled, followed by another 1 cm layer of quartz sand (2.7 g) at the top, in order to protect the packed soil bed from disturbance by the droplet impact. The DOC retention in the acid washed quartz sand was negligible, amounting to $1.3 \pm 0.8\ 10^{-3}$ mg in a column packed to a height of 2.5 cm with the sand. The solid matrix materials were filled in small portions into columns that were previously filled with 0.3 mmol $CaCl_2$ solutions, following the wet-packing method (Saiers and Hornberger, 1996) to exclude air bubbles and thereby achieving full water saturation. The pore volume (PV) of the packed beds amounted to 5.0 ml. The flow columns were integrated into an experimental setup including a peristaltic pump (Type 202, Watson Marlow, Falmouth, UK) and a fraction collector (Ultrorac 2070, LKB, Bromma, Sweden).

The column breakthrough experiments were conducted either under full water saturation, or with two consecutive cycles of drying and rewetting. An overview of the experimental variants given in (Fig. 1). Each variant consisted of four percolation pulses, (i) percolation of DOM at 180 mg l^{-1} DOC, (ii) leaching with DOM-free solution, (iii) percolation of DOM at 180 mg l^{-1} DOC, (iv) leaching with DOM-free solution. For all input solutions, background ionic concentration was 0.3 mmol $CaCl_2$ and pH was kept constant at pH 4.0 (adjusted via HCl addition), comparable to the natural pH in the sampled soil horizon (pH 4.2; Table 1). Both the variants with and without drying were conducted for a higher and a lower soil OM loading each, achieved by conducting the DOM percolation pulses for either 15.0 PV or 2.5 PV, respectively. Thus, in total, four different column experiment variants were applied, in two replicates each. During the percolation phases, ponding water levels were established above the solid matrix packings to maintain full water saturation and to achieve constant water infiltration rates due to constant hydraulic gradient. Flow velocity was kept at constant rate of 1.1 cm min^{-1}.

In the variants with drying and rewetting cycles, the columns were opened by removing the lid and put into an oven to dry at 40°C. The small sample volume that allowed fast drying and the brief total duration of the experiments were intentionally chosen to avoid any meaningful impacts of microbial activity on the results. Subsequent to drying, the DOM rinsing phases (ii) and (iv) were conducted equivalent to the variants without drying. At the end of the first and second leaching phases after drying, soil water saturation was determined by weight.

2.4 Effluent measurements

The column effluents were collected in glass vials (in portions of 3 ml) and measured with UV-Vis photospectrometry at 280 nm (Varian Carry 50 UV-Vis Spectrophotometer, Varian, Palo Alto, CA, USA) in a quartz cuvette (High Precision Cell, 10 mm, Hellma Analytics, Mühlheim, Germany). Total DOC and DON were determined with a Vario TOC Cube (Elementar, Langenselboldt, Germany). The UV-Vis measurements were conducted immediately after the column experiments. Samples for DOC and DON analysis were frozen at 253 K and thawed for measurements in portions.

Breakthrough curves and total quantities of DOC retention were calculated from DOC measurements. The specific UV absorbance (SUVA) was calculated by dividing the absorption at 280 nm by the DOC concentration (Leinemann et al., 2016). In order to show the SUVA results in breakthrough curves, the effluent SUVA results were divided by the SUVA of the added DOM. The "percent of potential SUVA" is the percentage of the effluent SUVA normalized by the SUVA value of the added DOM, both weighted by both the effluent volume and DOC concentration. Thus, a value of 100% would represent the case that the effluent SUVA signature would be identical to that of the added DOM; values below 100% show a depletion in hydrophobic components. The percent of potential SUVA was calculated for each glass vial filling by

$$Percent\ of\ potential\ SUVA = V_{eff} * DOC_{eff} * \frac{SUVA_{eff}}{SUVA_{added}}$$

with $SUVA_{eff}$ = SUVA of the effluent [l mg C^{-1} cm^{-1}], V_{eff} = volume of the effluent [ml], DOC_{eff} = DOC concentration of the effluent [mg l^{-1}], and $SUVA_{added}$ = SUVA of the added DOM [l mg C^{-1} cm^{-1}]. For depiction of C/N ratios in the breakthrough curves, the C/N ratios of the effluent DOM were divided by the C/N ratios of the added DOM.

2.5 Contact angles and surface free energies

Soil samples for sessile drop method contact angle measurements were prepared by distributing the soil particles evenly on double-sided adhesive tapes covering glass slides, following the procedure established by Bachmann et al. (2000). Contact angles of soil samples were measured with a CCD-equipped microscope (OCA 15, DataPhysics, Filderstadt, Germany). The initial contact angle was determined by placing a 1 µl drop of liquid on the prepared samples and analyzing the drop shape with the SCA20 software (DataPhysics, Filderstadt, Germany). Each measurement was replicated five times and is given as arithmetic mean of these measurements. From contact angle data, surface free energies can be derived. The underlying principle is the interrelation of solid and liquid interfacial properties through the solid-liquid contact angle, described by the van Oss-Chaudhury-Good equation (van Oss et al., 1988):

$$(1+\cos\theta)\ \gamma_l\ = 2(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^{+}\gamma_l^{-}} + \sqrt{\gamma_s^{-}\gamma_l^{+}}\ )$$

with θ = solid-liquid contact angle (°), γl = liquid surface free energy (J m-2), γs = solid surface free energy (J m-2). 'LW' denotes the non-polar Lifshitz-van der Waals component, '+' the electron-acceptor (acid) component, and '-' the electron-donator (base) component. To calculate the three unknown variables γ_s^{LW}, γ_s^{+} , and γ_s^{-}, contact angles of the solid surfaces must be determined with three different liquids with known surface free energy components. For the present work, ultrapure water, glycerol and iodobenzene were applied.

3. Results

3.1 Effects of drying and rewetting at high prior soil OM loadings

In this variant, the effluent DOC reached $C/C_0 = 1$ after approximately 5.5 PV (Fig.2), during which total DOC retention amounted to 3.29 ± 0.09 mg (given as mean and standard deviation of four replicates). The SUVA of the initial DOM breakthrough was very low, showing a strong depletion of hydrophobic compounds, and steadily increased (Fig. 2). Furthermore, C/N ratios during the initial breakthrough showed a slight enrichment of DON as compared to the added DOM (Fig.3). When the effluent DOC stabilized at $C/C_0 = 1$, both the SUVA and the C/N ratios were very similar to that of the input solution.

Subsequent to DOM percolation, a DOM-free leaching phase was conducted either immediately after percolation or after drying the soil material. In the continuously water saturated variant, the total quantity of DOC leached from the soil amounted to 1.23 ± 0.06 mg (Fig. 2; given as mean and range of two replicate experiments), while the DOC quantity was reduced by 39.8 % in the variants that were dried and then rewetted during the leaching phase. The DOM leached from the water saturated columns was more hydrophilic (86.2 % of potential SUVA; Fig.4) and had a lower C/N ratio (0.92 ± 0.01; Fig.3) than the added DOM. These trends were amplified by the drying-rewetting processes: The percent of potential SUVA was reduced to 71.8 %, and the C/N ratio was lower, 0.83 ± 0.04.

Subsequently, a second DOM percolation phase was conducted (Fig.2). For both variants, the SUVA was immediately similar to that of the added DOM, while the initial DOM breakthrough showed a slight depletion in DON in both variants. The second leaching phase showed much stronger differences between the variants, though. Under full water saturation, both the quantity of leached DOC (1.21 ± 0.02 mg) and the reduction caused by drying and rewetting (49.6 %) was comparable to the first leaching. In contrast to the first variant, the percent of potential SUVA was comparable in both variants, whereas the C/N ratio was reduced by drying and rewetting.

3.2 Effects of drying and rewetting at low prior soil OM loadings

In this variant, the DOC in the column effluent did not reach $C/C_0 = 1$ (Fig.6), implying that not all sorption sites accessible under the given flow conditions were occupied by DOM. The total DOC retention during percolation amounted to 1.42 ± 0.21 mg (given as mean and standard deviation of four replicates). Equivalent to the high OM loading variant, the DOM in the column effluent had a lower SUVA (Fig.6) and was depleted in DON as compared to the added DOM (Fig.7).

Subsequently, a DOM-free leaching phase was conducted either immediately after DOM percolation or after drying the soil material. The total quantity of released DOC in the fully water saturated variant was comparable to that in the higher OM loading variant (1.27 ± 0.15 mg; given as mean and range of two replicates), while the reduction after drying and rewetting was lower, at 23.3 % (Fig. 6). In fact, after drying, the DOC leached by the rewetting pulse slightly surpassed $C/C_0 = 1$ for one effluent vial in both replicates. Therefore, the total DOC release after drying was actually higher than in the higher OM loading variant. The quality of leached DOM showed further clear differences: The effluent DOM was a lot more enriched in hydrophilic components, especially after drying, which reduced the percent of potential SUVA to 23.6 % (Fig. 4). And notably, subsequent to drying, the effluent was depleted in DON as compared to the added DOM (Fig. 3).

The second leaching phase led to a DOC release of 1.41 ± 0.06 mg, and drying led to a reduction by 14.9 %, a slightly lower percentage than during the first leaching (Fig. 6). The quality of DOM in the fully water saturated variant was comparable to the values observed for the high OM loading variant. In contrast, after drying, it was again strongly depleted in hydrophobic fractions, having a potential SUVA of 33.5 %. As in the first leaching phase of the lower OM loading variant, the effluent of the fully saturated columns was enriched in DON, whereas the effluent of the dried and rewetted variants was depleted in DON.

3.3 Effects of OM coating formation on soil water repellency and surface free energies

Prior to DOM percolation, the disturbed Grinderwald soil was so strongly hydrophilic that no measurable contact angles formed (Table 2). Contact angles measured subsequent to the column experiments showed an increase in soil water repellency in each case. For the variants that were continuously water saturated, the contact angle for water was 46.7 ± 6.8° for the lower OM loading variant and 52.0 ± 6.8° for the higher OM loading variant. In the variants with drying and rewetting cycles, soil water repellency increased more strongly, to 61.2 ± 6.1° and 61.5 ± 7.1° for the lower and higher OM loading variants, respectively.

The surface free energies calculated from contact angle data showed only minor changes in the Lewis acid components of free energy due to DOM percolation (Table 2). By contrast, the Lewis base parameters were reduced considerably, in particular after phases of drying and rewetting. For both water saturation variants, the base parameter decreased more strongly for the higher OM loading variants.

4. Discussion

4.1 Drying and rewetting increases the quantity of DOC retention

In general, the retention of DOM in the Cambisol subsoil samples used in the present study was likely related to the high contents of dithionite and oxalate extractable Fe and Al oxide mineral phases (Table 1), which are known to have a high affinity for DOM sorption (Kaiser and

Guggenberger, 2000; Kleber et al., 2005; Schneider et al., 2010). In each of the experimental variants, cycles of drying and rewetting led to an increase in total DOM retention as compared to the fully water saturated variants, confirming hypothesis 1. Several factors were likely responsible for this and will be discussed in the following.

First of all, the loss of water volume during the drying process led to an increase in DOM concentration and ionic strength, factors that generally promote the sorption of DOM on metal oxides (Weng et al., 2005) and via cation bridging on clay minerals (Setia et al., 2013). Specifically, drying and wetting cycles enhanced the interactions between carboxyl functional groups of DOM and soil minerals, dominated by Ca^{2+} bridging (Olshansky et al., 2018). Furthermore, batch experiments have shown that drying leads to an increase in sorption strength of organic acids on iron oxide mineral phases: while at high water saturation, outer-sphere sorption is common, an alteration of the coordination to inner-sphere complexes occurs due to drying (Kang et al., 2008).

Moreover, the shrinking water recedes into fine pores (Kemper and Rosenau, 1984) and thereby promotes diffusion of DOM into immobile flow zones that were not used for the solution flux under saturated conditions (Jarvis, 2007; Bijeljic et al., 2010). Specifically, Albalasmeh and Ghezzehei (2014) had shown the movement of DOM to soil particle contact points during drying. Retention of DOM in small pores on soil mineral surfaces can result in high resistance towards remobilization into the pore fluid (Kaiser and Guggenberger, 2007).

In this context, it must also be considered that during rewetting, the water saturation did not reach 100 % again (Table 3). This was likely due to the fact that air was trapped in the pore space during the downwards advancement of the water front (Hallet et al., 2001). Additionally, the re-orientation of OM molecules during drying that makes the hydrophobic parts face toward the pore space (Horne and McIntosh, 2000), thereby increasing soil water repellency, may have impeded a higher water saturation (please see 4.4. for the topic of soil water repellency). Under the partly saturated conditions after drying, DOM retention at air water interfaces likely occurred (Lenhart and Saiers, 2004; Morales et al., 2011), contributing to the decrease of effluent DOC as compared to the fully saturated variants.

In summary, drying likely promoted DOM retention by changing the solution chemistry in the shrinking water layers, by leading to an increase in sorption strength, and by facilitating sorption in parts of the pore space that were protected from hydrodynamic drag during the rewetting.

4.2 Drying and rewetting amplifies the formation of multilayer OM coating structures

The quality of leached DOM, especially after drying, made it possible to draw the conclusion that distinctly structured OM coating layers (Kleber et al., 2007; Gao et al., 2020) formed in the different experimental variants. In general, the presence of air water interfaces under the partly water saturated conditions after drying likely did not affect the quality of leached DOM significantly, as Lenhart and Saiers (2004) reported that DOM retention at air water interfaces did not lead to changes in the composition of effluent DOM.

In the higher OM loading variants, effluent SUVA results (Fig.4) implied that during the second drying, a more hydrophilic layer of DOM was retained on the more hydrophobic coating that formed during the first drying process. In the lower OM loading variants, more hydrophobic OM coatings were formed, especially in the columns with drying and rewetting. In fact, the relatively high DOC release after drying might have been related to a strong hydrophilicity of the outer coating layers, which were thus easily remobilized by rewetting. During the second percolation/leaching cycles, relatively more hydrophilic OM coating layers formed on the initial coatings. Again, the total depletion in hydrophobic DOM was much stronger in the drying variants. Hence, the different characteristics of the OM coatings that formed during the first percolation/leaching cycle directly influenced the characteristics of the respective second OM layers.

Thus, in summary, the released DOM was depleted in hydrophobic components in each experimental variant. In our experiments, the depletion in hydrophobic components was always stronger (i) in the variants with drying and rewetting as compared to the continuously water saturated variants, (ii) in the lower OM loading variants as compared to the higher OM loading variants, and (iii) in the first leaching phase as compared to the second (Fig.4). These findings confirmed hypotheses 2 and 3. Therefore, it can be said that each of our experimental variants showed clear evidence for the formation of a coating structure with more hydrophobic DOM components closer the soil mineral surfaces and more hydrophilic components in the outer layers.

These findings were in agreement with previous research showing that soil mineral surfaces have a high affinity towards the sorption of more hydrophobic DOM fractions (Mikutta et al., 2007; Schneider et al., 2010; Kramer et al. 2012), and that OM coating layers in closer proximity to soil mineral surfaces are more enriched in hydrophobic components (Kleber et al., 2007; Mikutta et al., 2009; Gao et al., 2020).

The stronger retention of more hydrophobic DOM components caused by drying might have been related to the higher DOM concentrations, as (i) hydrophobic components are more competitive when sorption sites become increasingly limited (Kaiser et al., 1996), (ii) larger and more hydrophobic DOM clusters favoring the retention might have formed, and (iii) patches of sorbed hydrophobic OM may have increased interactions with remaining hydrophobic DOM through H bonding or van der Waals forces (Avneri-Katz et al., 2017; see Gao et al., 2020, for a review). In conclusion, our results clearly showed that the formation of layered coating structures was amplified by cycles of drying and rewetting.

4.3 C/N ratios of retained DOM are affected by drying and rewetting

For each experimental variant, the C/N ratios during the first DOM percolation phases were reduced as compared to the added DOM (Fig.3 and 7). This was in agreement with the finding that more N-rich DOM components were less prone to retention on soil minerals (Kaiser et al., 2004). In contrast, during the second percolation phase, C/N rations were increased in both the lower and the higher OM loading variants (in the latter, the ratio stabilized around that of the added DOM when C/C_0 reached 1).

During the leaching phases, the C/N ratios in the effluent were relatively similar throughout all experimental variants of the fully water saturated columns (Fig.5). In each case, there was a slight enrichment in DON as compared to the added DOM, again in agreement with the preferential transport of DON reported by Kaiser et al. (2004). For the variants including cycles of drying and rewetting, the results were more complex. In the high OM loading variant, there was an increase in the DON enrichment during the second leaching phase, indicating that the OM coating layer formed during the second drying was containing less N that the first layer that formed during the first drying. It was notable that in the lower OM loading variant, the C/N ration after drying was higher than the ratio of the added DOM. Thus, the results indicated that the respective experimental conditions favored an enrichment of N-rich DOM components in the surface-near, hydrophobic coating layer.

In summary, the present study showed mixed results concerning the enrichment of DON in different OM coating layers (Fig.5). Previous studies on the N content of OM coating layers came to differing results. Whereas some studies found an enrichment of N at closer proximity to the mineral surfaces (Hatton et al., 2012; 2015; Du et al., 2014), others did not (Mikutta et al., 2009; see Gao et al., 2020, for a review). As the characteristics of retained DON were not the focus of the present study, no clear conclusions could be drawn from these findings. However, our results indicate that the distribution of N within OM coating layers were influenced by cycles of drying and rewetting, thus representing a promising topic for future research.

4.4 Drying and rewetting decrease soil wettability and surface free energies

The high wettability of the Cambisol subsoil prior to DOM percolation (Table 2) was in agreement with the well-established fact that barren surfaces of almost all soil minerals are known to be hydrophilic (Giese et al., 1996). An increase in soil water repellency subsequent to DOM percolations is a common effect of OM coating formations (Roberts and Carbon, 1972; Lamparter et al., 2014). That the contact angle for the higher OM loading variants was a little higher than for the lower OM loading variants under continuously water saturated conditions was in agreement with findings that soil water repellency is related to the soil OM content (Scott, 2000).

This may likewise be the explanation for the increase in soil water repellency after cycles of drying and rewetting (confirming hypothesis 4), which led to both a higher quantity of total DOC retained in the soil as well as to the retention of more hydrophobic DOM components. A decrease of wettability facilitated by drying of DOM onto soil particles was previously reported by Arye et al. (2007) and Lamparter et al. (2014). However, the strongly preferential retention of more hydrophobic DOM components caused by drying in the lower OM loading variants was not reflected in the contact angle results. In this context, it must be considered that the DOM leaching after drying likely affected soil water repellency (Arye et al., 2007).

While the Lewis acid components of the surface free energies were barely affected by OM sorption on the soil surfaces, the Lewis base parameters were reduced significantly (Table 2). This was in principle comparable to Jouany (1991) and Calero et al. (2017), who reported comparable effects on the different free energy components originating from the sorption of humic acids. The strongest reduction of the Lewis base parameter, to 26.7 mJ m^{-2}, occurred for the high OM loading variant after drying. Thus, it was deceeding the critical threshold of 28.9 mJ m^{-2} below which clay minerals have hydrophobic surface properties (van Oss and Giese, 1995). Notably, the lowest Lewis base parameters were found for the higher OM loading variant, despite the fact that drying in the low OM loading variant led to the retention of much more hydrophobic OM (see 3.3). This underscored the complexity of how the quantity and quality of OM coatings affect soil surface free energies (Calero et al., 2017).

In general, a decrease of soil surface free energies leads to stronger hydrophobic attraction forces between particle surfaces (Vogler, 1998; van Oss, 2006), and thereby affects several processes in soils. For instance, it can enhance aggregate stability (Calero et al., 2017) and reduce colloid mobility (Goebel et al., 2013). Thus, our finding that drying considerably enhanced the decrease in surface free energies elucidates the relevance of cycles of drying and rewetting on various soil processes.

5. Conclusions

A direct comparison of DOM retention in column flow experiments was conducted between variants that were subjected to cycles of drying and rewetting and variants that were continuously water saturated. Drying and rewetting cycles led to (i) a higher quantity of DOC retention, (ii) a stronger preferential retention of hydrophobic components, especially at lower previous soil OM loadings, (iii) a relatively lesser preferential retention of hydrophobic components in a second cycle of drying and rewetting, and (iv) a stronger decrease of soil wettability and surface free energies.

These findings have implications for transport and retention processes of DOM in the environment. While it is well established that the downwards percolation of DOM leads to an enrichment in hydrophilic components due to the preferential retention of more hydrophobic components, the present study indicates that cycles of drying and rewetting might play a crucial role for those changes in DOM composition. Moreover, our results indicate that the formation of distinct OM coating structures with more hydrophobic layers in closer proximity to the mineral surface and more hydrophilic outer layers is likewise amplified by drying and rewetting processes in soils.

With regard to the assumption that global change leads to more irregular regional precipitation patterns, the importance of drying and rewetting cycles and their repercussions for the quantity and quality of DOM retention in soils will likely increase in the future.

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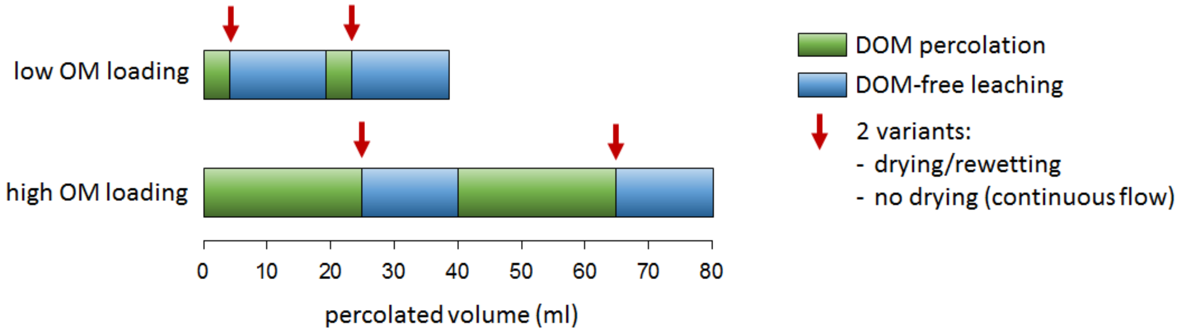

Fig. 1. Experimental approach for the column breakthrough experiments. In the ‘high OM loading variant’, DOM was percolated in two pulses with 75 ml each; in the ‘low OM loading variant’, in two pules with 12 ml each (in both variants at a concentration of 180 mg/l DOC). The background ion concentration (0.3 mM $CaCl_2$) and pH (4.0) were constant in both the DOM percolation and DOM-free leaching phases. The red arrows indicate the points at which either a drying/rewetting or no drying (i.e., continuous flow) were conducted after both DOM percolation pulses. This led to a total of four experimental variants, each conducted in two replicates.

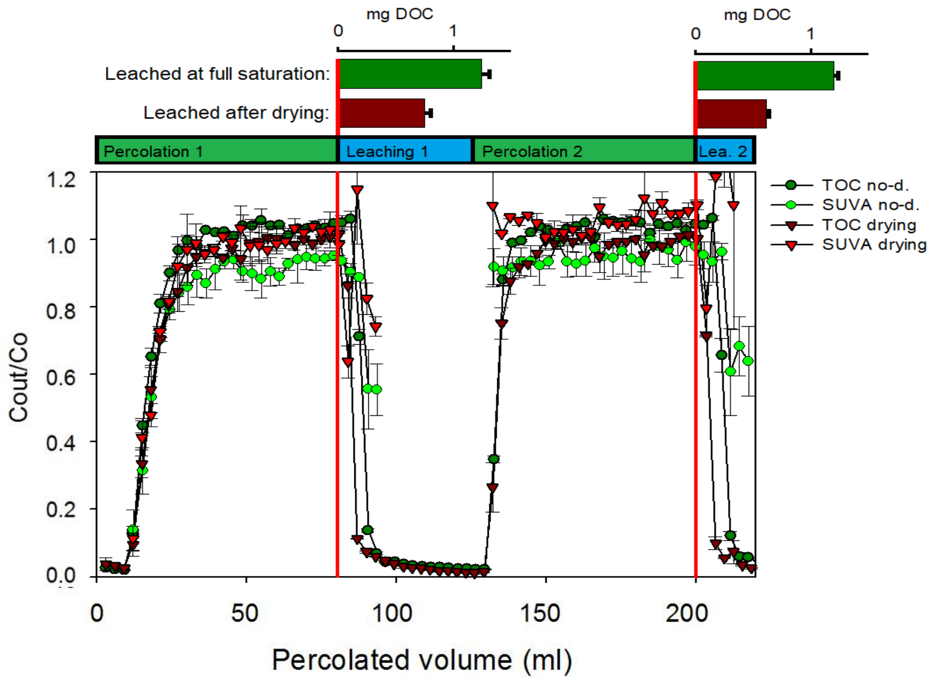

Fig. 2. Breakthrough of DOC and SUVA ratios for the high OM loading experiments, given as mean of two replicates and the range. “no d.” refers to the continuously water saturated variants, “drying” to the variants with drying and subsequent rewetting. Vertical red lines indicate the time points of the drying. The bar diagrams above show the quantity of leached DOC, either at full water saturation or during rewetting after drying. (SUVA results shown for DOC $C/C_0 > 0.05$; values below that scatter considerably due to proximity to the detection limits).

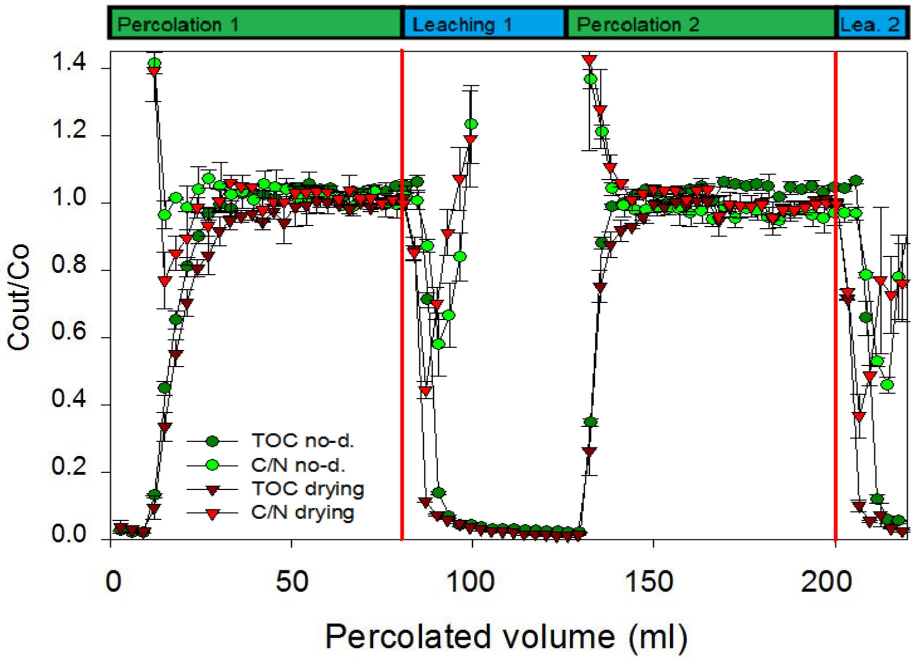

Fig. 3. Breakthrough of DOC and C/N ratios for the high OM loading experiments, given as mean of two replicates and the range. "no d." refers to the continuously water saturated variants, "drying" to the variants with drying and subsequent rewetting. Vertical red lines indicate the time points of the drying. The bar diagrams above show the quantity of leached DOC, either at full water saturation or during rewetting after drying. (C/N ratio results shown for DOC $C/C_0 > 0.05$; values below that scatter considerably due to proximity to the detection limits).

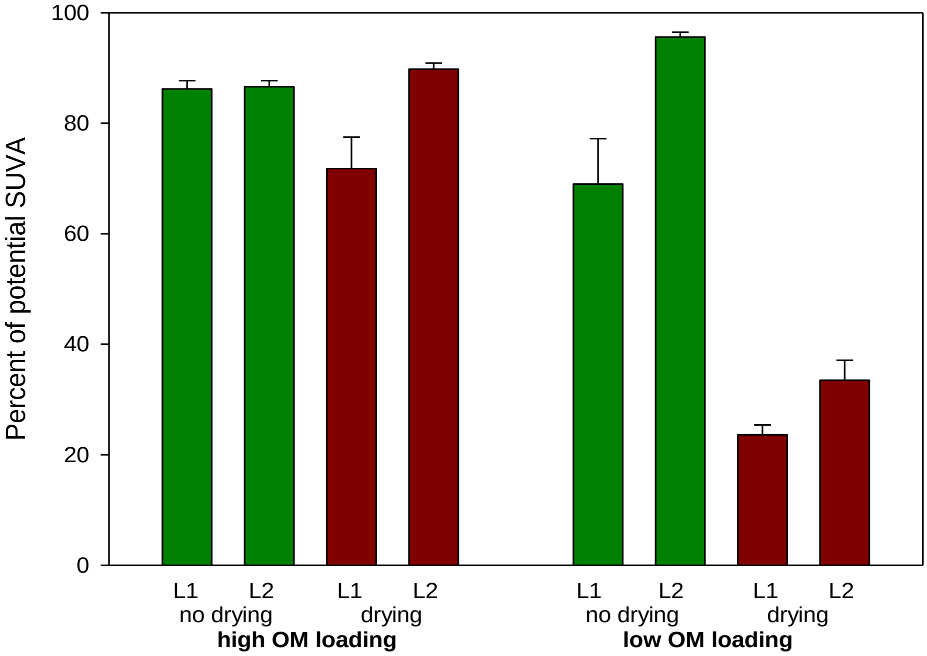

Fig. 4. Percent of potential SUVA for the effluent DOM of the high OM loading and low OM loading variants, given as mean of two replicates and the range. “no drying” refers to the experiments at continuously full water saturation, “drying” to the experiments with drying and rewetting cycles. “L1” and “L2” refer to the first and second leaching phases, respectively.

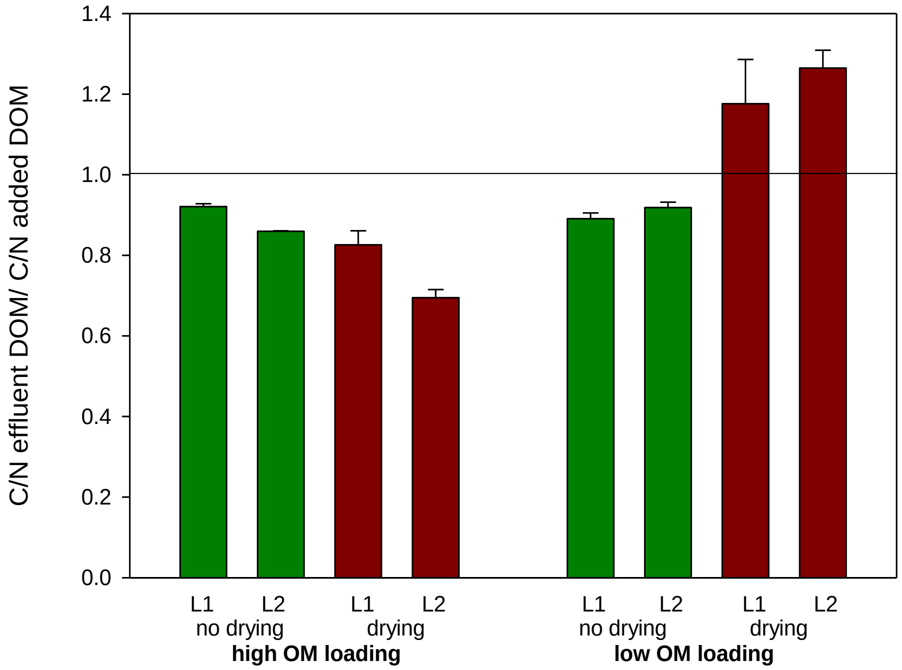

Fig. 5. Effluent DOM C/N ratios for the high OM loading and low OM loading variants, given as mean of two replicates and the range. "no drying" refers to the experiments at continuously full water saturation, "drying" to the experiments with drying and rewetting cycles. "L1" and "L2" refer to the first and second leaching phases, respectively.

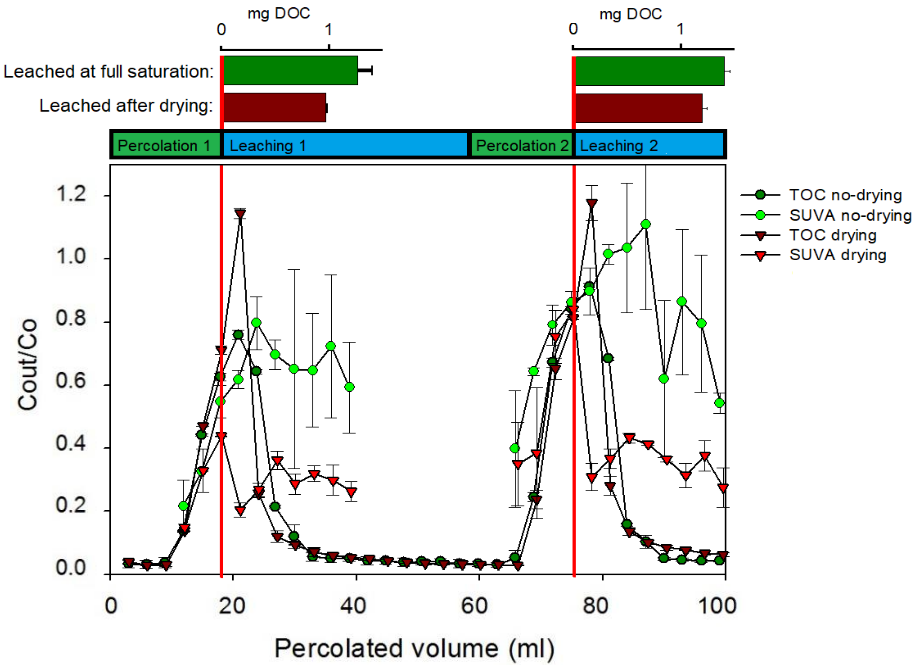

Fig. 6. Breakthrough of DOC and SUVA ratios for the low OM loading experiments, given as mean of two replicates and the range. "no d." refers to the continuously water saturated variants, "drying" to the variants with drying and subsequent rewetting. Vertical red lines indicate the time points of the drying. The bar diagrams above show the quantity of leached DOC, either at full water saturation or during rewetting after drying. (SUVA ratio results shown for DOC C/C_0 > 0.05; values below that scatter considerably due to proximity to the detection limits).

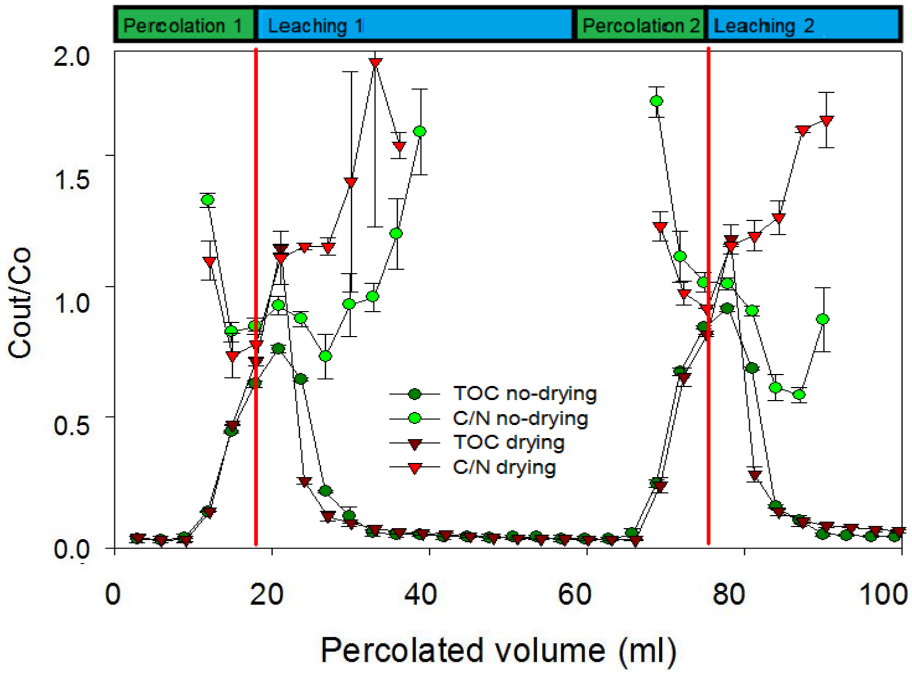

Fig. 7. Breakthrough of DOC and C/N ratios for the low OM loading experiments, given as mean of two replicates and the range. “no d.” refers to the continuously water saturated variants, “drying” to the variants with drying and subsequent rewetting. Vertical red lines indicate the time points of the drying. The bar diagrams above show the quantity of leached DOC, either at full water saturation or during rewetting after drying. (C/N ratio results shown for DOC $C/C_0 > 0.05$; values below that scatter considerably due to proximity to the detection limits).

Table 1. Basic parameters of the disturbed soil sample, measured after air-drying and sieving <2 mm. Data for each measurement is given as the mean of three replicates and standard deviation.

SSA	**pH ($CaCl_2$)**	**Sand**	**Silt**	**Clay**	**SOC**	**Fe_o**	**Fe_d**	**Al_o**	**Al_d**
$m^2\ g^{-1}$		**%**			**$mg\ g^{-1}$**				
1.7± 0.1	4.2 ± 0.0	93.0±0.7	5.7± 0.6	1.3± 0.1	0.06±0.01	3.3± 0.5	16.9± 1.5	4.1± 0.5	5.8± 0.4

Table 2. Sessile drop method contact angles and inferred surface free energies for the Cambisol subsoil before DOM percolation and after the different variants of OM loading and drying and rewetting variants. θ = contact angle for the fluids indicated, γ^{LW}= van der Waals free energy, γ^{+}=Lewis acid free energy, γ^{-}= Lewis base free energy.

Soil treatment	**θ_{Water} (°)**	**$\theta_{Glycerol}$ (°)**	**$\theta_{Iodobenzene}$(°)**	**γ_s^{LW}**	**γ_s^{+}**	**γ_s^{-}**
Before DOM percolation	0.0 ± 0.0	57.2 ± 3.3	0.0 ± 0.0	39.7	0.6	88.0
High OM loading – no drying	52.0 ± 6.8	64.4 ± 6.4	0.0 ± 0.0	39.7	0.0	39.2
High OM loading – drying	61.5 ± 7.1	67.3 ± 5.4	0.0 ± 0.0	39.7	0.2	26.7
Low OM loading – no drying	46.7 ± 6.8	59.2 ± 7.8	0.0 ± 0.0	39.7	0.4	42.1
Low OM loading – drying	61.2 ± 6.1	70.3 ± 4.5	0.0 ± 0.0	39.7	0.1	30.2

Table 3. Soil water saturation at the end of the respective leaching phases after drying.

Variant	**Leaching1**	**Leaching2**
high OM	98.8 %	93.0 %
loading	90.8 %	90.0 %
low OM loading	88.6 %	84.2 %
	94.6 %	94.5 %

4. Study III

Interactive Control of Organic Matter Loading of Colloidal and Solid Iron oxide on Lead Mobility in a Model Sand

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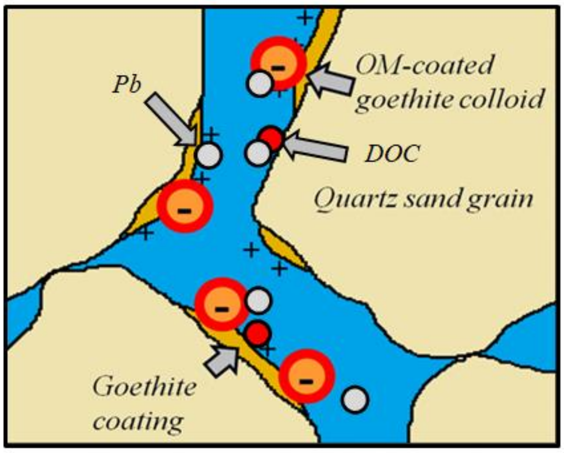
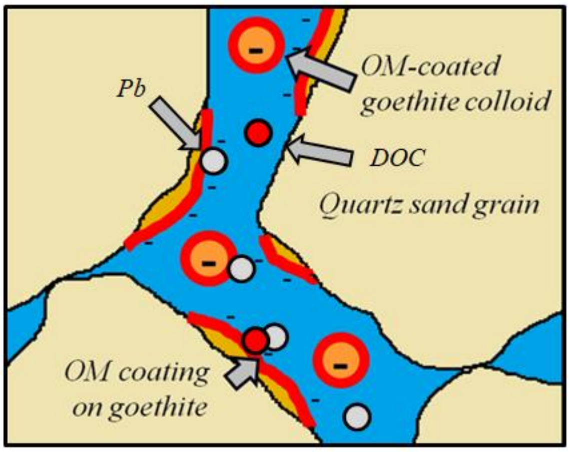
Contribution: I contributed to the conceptualization of the study. Designed the experiments, conducted the laboratory analysis. I evaluated the data and compiled the tables and figures. I wrote the manuscript. Prepared for the journal European of Soil Science.

GRAPHICAL ABSTRACT

Before preconditioning surface with DOM



After preconditioning surface with DOM



Highlights:

- Iron oxide colloids are highly mobile in a negatively charged solid matrix.
- Dissolved organic matter (DOM) leads to lead (Pb) immobility despite the presence of goethite colloids.
- DOM preconditioning on goethite coated quartz sand (GCQS) modifies surface characteristics through charge reversal from positive to negative and organic matter coated goethite (OMCG) colloids mobility increase with surface modification.
- Colloid mobility as predicted by classic Derjaguin-Verwey-Landau-Overbeek (DLVO) theory is controlled by electrostatic interactions.

Abstract

The mobility of lead (Pb) in soils can be significantly affected by co-transport and co-retention with goethite colloids and dissolved organic matter (DOM) extracted from either Oa horizon material under spruce or Oi horizon material under beech. This study aimed at assessing the magnitude of Pb transport affected by DOM and organic matter coated goethite (OMCG) colloids in pure quartz sand (QS) and goethite coated quartz sand (GCQS), and depending on GCQS surface loading by organic matter (OM). Double-pulse experiments with goethite colloids and DOM extracted from soil Oa and Oi horizons were conducted in saturated QS and GCQS columns with Pb^{2+}, OMCG colloids, and Pb + OMCG colloids . The retention of ionic and complexed Pb was more pronounced in GCQS than in pure QS, and Pb mobility was less in the presence of OMCG colloids due to co-retention as compared to Pb^{2+}. A preconditioning of the GCQS surface by OM coatings increased mobility of OMCG colloids while the transport of Pb^{2+} was not affected by co-transport of OMCG colloids. The type of DOM used to produce the OMCG did not significantly affect the mobility of the colloids. This is assumed to be due to a selective sorption of hydrophobic compounds on goethite coating, leading to a similar type of OM associated with the goethite. OM conditioning of goethite by OM led to a charge reversal from positive to negative charge and made the GCQS less attractive for OMCG colloids and more attractive for Pb^{2+} retention. Classic Derjsguin-Verwey-Landau-Overbeek (DLVO) calculations revealed that an increasing ionic strength in suspension through ionic Pb^{2+} injection decreases the depth of secondary minima. This suggests a decreasing colloid mobility via decreasing electrostatic repulsion at increasing ionic strength. We conclude that DOM via sorption onto solid matrix and coating iron oxide enhances the Pb retention. Simultaneous injection of OMCG colloids and Pb decreased colloid mobility in the matrix GCQS prior to preconditioning, while following preconditioning OMCG colloid mobility increased strongly due to the predominance of electrostatic repulsion.

Keywords: Complex Pb-DOM, Pb immobility, Goethite colloid, competitive ions

1. Introduction

Lead (Pb) is a prevalent heavy metal, which causes serious environmental problems. Its widespread use in chemical, petrochemical and metallurgical industries, vehicular emission, smelting, burning of coal, and lead-acid batteries has resulted in extensive environmental contamination, human exposure and significant public health problems in many parts of the world (Hong et al., 1994; Roszyk and Szerszen, 1998; Dong et al., 2000; Jeong and Kim, 2019). Pb is characterized by a low p_K value (Sherene, 2010), and is considered immobile in soil at pH > 6 (Herms and Brümmer, 1984), while it has a high tendency to form metal hydroxo complexes, e.g. with goethite (Kooner, 1993; Avena and Koopal, 1998; Xiong et al., 2015). Ionic Pb^{2+} shows particularly a high affinity towards OM due to form complexes with carboxylate and hydroxyl groups of OM (Gustafsson et al., 2011). This usually leads to steadily increasing Pb contents in OM-rich soil surface horizons (van Erp and Van Lune, 1991; Yanai et al., 2004). Hence, Pb^{2+} concentrations in soil solution are usually low.

This high affinity of Pb towards soil solid phases leads to soil contamination on the one hand, but it protects Pb to migrate into the groundwater on the other hand (Jensen and Ledin, 1999). However, protonation at low pH increases Pb solubility, as was shown for Pb bound to kaolinite (Illera et al., 2004). In addition, a number of other factors, including the ionic strength, concentrations of colloidal and dissolved organic matter (DOM) and mineral colloids as well as flow velocity have been shown to affect Pb mobility (Kretzschmer and Schaefer, 2005; Yin et al., 2016). Decreasing ionic strength general increases Pb mobility, and monovalent cations in soil solution are increasing the mobility of colloids more strongly than divalent cations due to the expansion of double layer repulsion between colloids and grain surfaces (Grolimund et al., 1996; Grolimund and Borkovec, 2005, 2006). As for numerous other contaminants, co-transport of Pb with organic and mineral colloids is a common process that increases its mobility (Foerstner et al., 2001; Denaix et al., 2001; Roulier et al., 2008).

Associations of Pb with mobile iron oxides and OM play a key role for Pb mobility in soils (Elimelech and Ryan, 2002; Bradl, 2004; Kaste et al., 2006). Typically, goethite does not appear as pure mineral in soils, but sorption of OM and co-precipitation of dissolved Fe with OM lead to the formation of OM-goethite complexes (Gu et al., 1994;). The opposite charge of iron oxides and OM leads to an attraction of both components in the presence of electrostatic forces (Carstens et al., 2017; Dultz et al., 2018). Under moderately acidic soil conditions, Fe oxides have a net positive charge, as their point of zero charge (PZC) is at pH > 7 (Kretschmar et al., 1997), so it can adsorb negatively charged materials such as mineral colloids (Loveland et al., 2002), viruses (Foppen et al., 2006), and OM (Hassellöv and von der Kammer, 2008). At moderately acidic pH, being typical for soils of humid climate zones, adsorption of OM onto the Fe oxide's surfaces can turn the net positive charge of iron oxides to negative (Herrera Ramos and McBride, 1996). This formation of OM coated Fe oxides assert a key influence on the mobility of Fe oxide colloids in soils, as the associated charge reversal can decrease the colloid-colloid collision (Kretschmar et al., 1997). Hence, colloids with negative charge are highly mobile in a negatively charged matrixes (Förstner et al., 2001; Huynh and Chen, 2011; Li et al., 2013).

Dissolved OM is the most mobile OM form in soil, and shows a wide concentration range from about 0.5 to 60 mg dissolved organic carbon (DOC) L^{-1} in the soil solution (Nelson et al., 1992; Fiedler and Kalbitz, 2003; Cory et al., 2004). During the downward transport of DOM from the organic layer and topsoil to subsoil, primarily sorptive retention to soil minerals decreases the DOC concentration considerably (Kalbitz et al., 2000; Kaiser and Kalbitz, 2012). Sorption of DOM to Fe oxides not only affects DOM transport in soil (Deb and Shukla, 2011), but may also mobilize mineral colloids adsorbed on the partially positively charged solid matrix (Abudalo et al., 2010; Yang et al., 2010a; Carstens et al., 2018). However, the extent to which the surface charge of mineral colloids are modified by OM coverage strongly depends on the composition of DOM that is adsorbed. So DOM mobilized in the humus layer (Oa horizon) under Norway spruce (*Picea abies* L. Karst) contains much lignin-derived phenols with high contents of carboxylic groups, while DOM leached from the litter layer (Oi horizon) under European beech (*Fagus sylvatica*) is rather rich in polysaccharides (Kaiser and Guggenberger, 2000). The affinity of the former towards Fe oxides is much higher than that of the latter (Gu et al., 1994; Kaiser et al., 1997).

While studies on the effect of OM on colloid mobility are multiple (Kretzschmar and Sticher, 1997; Jansen et al., 2005; Li et al., 2013), the effect of OM preconditioning of the solid matrix on Pb transport in heterogeneous matrices is still unclear. In order to address this, a detailed analysis of the charge dynamics and their effects on attractive and repulsive forces between colloids is necessary (Xiong et al., 2015). The DLVO (Derjaguin-Landau-Verwey-Overbeek) theory describes forces of different direction, e.g. steric, electrostatic and van der Waals interactions, between the dispersed particles and is able to describe colloid mobility in soils and aquifers (Kuhnen et al., 2000; Tosco et al., 2012). Kretzschmar and Sticher (1997), Tosco et al. (2012), and Carstens et al. (2017) predicted the mobility of negatively charged inorganic colloids in sand matrix with the DLVO theory. Using DLVO, Bradford et al. (2009) showed that transport of negatively charged Fe oxide colloids through negatively charged soil matrix is due to repulsive electrostatic energy barrier between colloids and the solid matrix surface.

The mobility of Pb thus strongly depends on the stability of colloids, such as goethite, to which they can be adsorbed, whose mobility, in turn, is affected by a complex interrelationship of the charges and the resulting attractive and repulsive forces, depending on the amount and composition of OM. Finally, the retention of these complexes is also controlled by the zeta potential (ζ) of the solid soil matrix, which also varies depending on the mineral composition and the preconditioning of OM. To elucidate the underlying processes and to quantify the consequences of colloidal and solid OM-mineral complexes for Pb mobility for column experiments with modification of the ζ of both, the colloidal goethite and the solid soil matrix, by OM sorption. Here, we studied the mobility of colloidal goethite and colloid-associated Pb, where the ζ of the colloids was modified by percolation with two types of DOM, i.e. derived from an Oa horizon under spruce and an Oi horizon under beech. The experiments were conducted in columns packed artificially with QS or GCQS with different surface loading of OM. With this principle approach, we aimed at testing the following hypotheses. First, in the presence of negatively charge OMCG colloids, Pb transport is increased due to co-transport. Second, conditioning of positively charged GCQS with negatively charged DOM increases the mobility of negatively charged OMCG colloids, but decreases the mobility of Pb. Third, the complex behavior of colloid mobility depending on the ionic strength of the Pb can be predicted with the DLVO theory.

2. Materials and Methods

2.1 Overview of the column experiments

Experiments with goethite colloids, ionic Pb^{2+} ($PbCl_2$) and organic matter (OM) extracted from soil Oa and Oi horizons were conducted in semicircular plexiglas columns with a height of 12 cm and inner diameter of 2 cm. Experiments were conducted in quartz sand (QS) and goethite coated quartz sand (GCQS) columns under water-saturated conditions , where 27 g of QS or GQCS were added to a height of 10 cm to obtain a porosity of 39%. The experiments were performed in three different variants. An overview of experimental series and given results shows in Table 1. Either ionic Pb^{2+} ($PbCl_2$), OMCG (organic matter coated goethite) colloids, and Pb + OMCG colloids were injected into saturated columns with QS and GCQS at a flow velocity of 1.09 cm min^{-1}. The column experiments were performed with artificially produced QS in a single pulse experiment and GCQS in triple pulse experiments. The experiments in GCQS included injection of an initial OMCG colloid and Pb^{2+} pulses either separately or simultaneously in the column followed by percolation with Oa-DOM or Oi-DOM with a concentration of 20 mg DOC L^{-1} in order to determine whether DOM coatings on the GCQS affect the mobility and immobility of colloids and Pb, respectively. DOM percolation ended when the DOM concentration in the effluent equaled that of the influent (C/C0=1), and in the third pulse second injection of Pb^{2+} and OMCG colloids pulses added in the column. The concentration of ionic Pb^{2+} in the column experiment was set to 10 mg L^{-1}, and the pH of the solution was adjusted to 4.5 to avoid the precipitation of $Pb(OH)_2$ at pH above 5 (Fadzil et al., 2016). The background electrolyte ($CaCl_2 \times 2H_2O$) and goethite concentrations were 0.303 mM and 37 mg L^{-1}, respectively. The background electrolyte and goethite concentration are comparable to the column experiment by Carstens et al. (2017) and were constant in suspension until performance of the column experiments. The experiments were done in two replicates.

2.2 Materials used for experiments

Pure standardized goethite (Lanxess Bayferrox 920 Z, high chemical purity, Cologne, Germany) was used throughout the experiment. According to information of the manufacturer, the density and surface area of goethite were 4 g cm^{-3} and 12 m^2 g^{-1}, respectively. The point of zero charge (PZC) of the goethite was determined to be 8.8 via ζ measurements (Zeta-PALS, Brookhaven Instruments Crop, Holtsville, USA). Following Carstens et al. (2017), the goethite was brought into suspension by sonication in ultrapure water using an ultrasonic bath (Bandelin, RK 106, Berlin, Germany) at an energy of 35 kHz, 2 x 240 W. The used concentration of goethite was 37 mg L^{-1} in 0.303 mM $CaCl_2$ solution.

High purity QS was obtained from Carlo Bernasconi AG (Bern, Switzerland) with a grain size distribution of 1% for <0.1mm, 45% 0.1-0.2 mm, 53% 0.2-0.315 mm, and 1% >0.315 mm (Carstens et al., 2017). To remove iron oxide coatings from the surface of the quartz sand, 500 g quartz sand was treated with 10 M HCl (32%) for 48 hours to produce HCl-clean QS. Subsequently, the QS was rinsed intensively with ultrapure water and air dried at room temperature.

The method of Scheidegger et al. (1993) with some modifications by Carstens et al. (2017) was used to coat the QS with 2 g goethite powder in 200 ml ultrapure water by sonication for 5 minute. The suspension was shaken in an overhead shaker (Heidolph, Reax 2, Schwabach, Germany) for 24 hours. Thereafter, 50 g more HCl-cleaned QS was added and the suspension was shaken for another 24 hours. The produced GCQS was rinsed with ultrapure water until the runoff was clear and subsequently air-dried at room temperature. This stock GCQS was thoroughly mixed with QS at a ratio of 1:10 to obtain the GCQS used for the column experiments.

Dissolved OM was extracted from the Oa horizon of a Haplic Podzol under Norway spruce (*Picea abies* L. Karst) and the Oi horizon of a Eutric Cambisol under European beech (*Fagus sylvatica*). For the Oa DOM, 150 g of Oa horizon material was mixed with 750 ml deionized water and for the Oi DOM, 70 g Oi horizon material was mixed with 700 ml deionized water on a horizontal shaker at 1,000 rpm at 22°C for 16h. Subsequently, the suspension was centrifuged in 3000 g for 15 min (Fischer Scientific, Cryofug 6000i, Schwerte, Germany), and the extracts were pressure filtered through 0.7µm glass fiber filter (Whatman, GF 92, Munich, Germany) and 0.45µm cellulose nitrated membrane filter (G, Sartorius AG, Goettingen, Germany). The DOC concentration of the filtered extracts, as measured by a TOC-Analyzer (liquiTOC II, Elementar Analysensysteme, Hanau, Germany) were 118.1 mg DOC L^{-1} for the Oa DOM and 1458.6 mg DOC L^{-1} for the Oi DOM. To prevent microbial activity, the stock solutions were stored in the freezer at -20°C until processing. The solutions were stored in a small units in the original concentration. Samples were thawed slowly in a refrigerator one day before starting the experiment and adjusted to DOC concentrations used in the experiment by diluting the stock solutions with distilled water.

To produce OMCG colloids, Oa DOM and Oi DOM with concentrations of 0.02, 1.0, 2.0, 5.0, and10.0 mg DOC L^{-1}, respectively, were added to the goethite colloid suspensions (37 mg L^{-1} goethite, 0.303 mM $CaCl_2$). The different DOC concentrations were selected in order to know the effect of DOM loading on goethite ζ. For the preparation of the dissolved Pb^{2+} in the suspension of the OMCG colloids, from a $PbCl_2$ stock solution concentrations of 1.0-10.0 mg L^{-1} were prepared for ζ and particle size analyses (see section Analytical methods). The concentration of goethite (37 mg L^{-1}) and $CaCl_2$ x $2H_2O$ (0.303 mM) were kept constant in all experiments.

2.3 Analytical methods

The surface charge (SC) of OM was determined by an automatic titration according to (Böckenhoff and Fischer, 2001) in a polytetrafluoroethylene cell of a particle charge detector (PCD) (PCD 03 pH, Mütek, Germany). In the titration cell a streaming potential is induced by an oscillating piston, and the electro kinetic signal resulting from distortion of counter ions from the particle surfaces is recorded by two Au electrodes. For quantification of the negative SC the cationic polyelectrolyte polydiallyldimethyl-ammonium chloride (poly-DADMAC; Mütek, Germany) and for the positive SC the anionic polyelectrolyte sodium polyethylene sulphonate (PES-Ms; Mütek, Germany) were added with a syringe pump until PZC. For determination of SC properties of Oa DOM and Oi DOM, 10 ml solution with 0.125 mg DOC L^{-1} and 0.0625 mg DOC L^{-1}, respectively, were transferred into titration cell.

Exchangeable cations (Ca, Mg, K, Na, Al, Fe and Mn) were determined with the $BaCl_2$ method (Hendershot and Duquette, 1986). 0.5 g of the air-dry solid matrix (QS , GCQS) as well as Oa DOM and Oi DOM were mixed with 30 ml 0.1 M $BaCl_2$. The suspension was shaken for 2 hrs in an end-over-end shaker, subsequently centrifuged and passed through Whatman No.41 paper filter. The cations extracted were measured by inductively coupled plasma optical emission spectrometry (ICP-OES; Varian ICP 725 Optical Emissions Spectrometer, Agilent Technologies, Santa Clara, CA, USA).

For characterization of the structure of Oa DOM and Oi DOM, aliquots of the extracts were freeze-dried (CHRIST, Alpha 1-4 LD plus, Osterode am Harz, Germany). From the freeze-dried samples, KBr pellets were prepared and measured by Fourier transform infrared spectrometry (FT-IR; TENSOR 27; Bruker Optik GmbH, Ettlingen, Germany). In the attenuated total reflectance (ATR) method, spectra of KBr pressed pellets (1 mg sample, 300 mg KBr) were recorded in the range of 400 to 4000cm^{-1}.

The electrophoretic mobility of OMCG colloids was measured by phase analysis light scattering technique (Zeta-PALS, Brookhaven Instruments Corp., Holtsville, USA). After gently shaking the suspension, 1.6 ml of suspension were transferred in a cuvette and directly after immersion of the electrode the ζ was determined from arithmetic means of 10 replicate runs and each partitioned in 20 cycles via Smoluchowski’s equation (Elimelech et al., 1995).

The particle size of the colloids was determined by dynamic light scattering (Zeta-PALS, Brookhaven Instruments Corp., Holtsville, USA). 3 ml of suspension transferred into standard acryl cuvette, and the hydrodynamic diameter was determined at 20°C at a wavelength of 658 nm and a scattering angle of 90° and the diameter evaluated by the software BIC (Brookhaven Instruments Corp., Holtsville, USA).

The Pb concentrations in the effluent of the columns was determined by ICP-OES (Varian ICP 725 Optical Emissions Spectrometer, Agilent Technologies, Santa Clara, CA, USA) after dissolving colloid by sodium dithionite. The goethite colloid and DOM concentrations in the effluent were measured by UV-vis spectroscopy with a maximal extinction of 440 nm for the goethite colloids and of 350 nm for DOM (Carstens et al., 2018). 50 µl Sodium dithionite was added in each effluent for dissolving the colloids after measuring by UV-vis in order to measure Pb associated with the colloids by ICP-OES. The breakthrough and retention curves were calculated based on two replicate column runs.

2.6 DLVO approximations

The classic DLVO approach to calculate the total interaction energy between colloids and solid matrix includes electrostatic and van der Waals interactions. Electrostatic interactions were estimated from ζ and solution ionic strength. Van der Waals interaction was calculated from surface free energies of OMCG colloids and sand grains. The surface free energies were determined via sessile drop method (SDM) contact angle measurements with three liquids with known surface free energies, i.e. ultrapure water, glycerol and iodobenzene (reference, year). For that, OMCG colloid samples were prepared by air-drying on soda-lime glass slides (Menzel-Glaeser, precleaned, Gerhard Menzel GmbH, Brunswick, Germany) and quartz sand were prepared by distributing sand grains on soda-lime glass sides using double-sided adhesive tapes. Contact angles were measured with a CCD-equipped microscope (OCA 15, DataPhysics, Filderstadt, Germany) after dropping 1.0 µl of each of known liquids separately on the prepared slides and subsequently the SCA20 software (DataPhysics, Filderstadt, Germany) was used to analyze the drop shapes.

3. Results and discussion

This study aims at identifying the control of OM sorption and related surface charge of OMCG colloids and the surface matrix on the mobility of Pb and colloidal goethite. To unravel the complex interactions, we first focus on the effect of Pb^{2+} and DOM on the ζ and particle size of goethite. Then we elucidate the effects of solid matrix manipulation, i.e. coverage of the QS with goethite and also the effect of OM sorption on GCQS, on the Pb and colloid mobility. Finally, we applied the DLVO theory to explain the mechanisms of the colloid retention depending on surface charge and activation energy.

3.1 Zeta potential and particle size of goethite depending on DOM

Since the pH of the experimental conditions is below the PZC of goethite at pH 8.2 (Carstens et al., 2017), the ζ of the goethite is positive (Fig. 1). It turned to negative values at addition of 0.05 mg DOC L^{-1} Oa DOM and 0.3 mg DOC L^{-1} Oi DOM, and ζ became more negative with increasing DOC concentration up to 1.0 mg DOC l^{-1} (Fig. 1 a.b). With further addition of the DOM, ζ remained stable. We assume that this is because all available sorption sites for DOM on the iron oxide surfaces are occupied and thus, no further DOM could be adsorbed, as was also reported by Kretschmar and Sticher (1997) and Foerstner (2001) upon sorption of dissolved humic acid on hematite and goethite. The particle size of the colloidal goethite changed in line with the ζ (Fig. 1 c, d). While it was 597.5 ±11.4 nm for pure goethite, it increased to 921.7 ± 6.1 nm at addition of 0.02 mg DOC L^{-1} Oa DOM (Fig. 1 c) and to 704.4 ± 4.4 nm at addition of 0.1 mg DOC L^{-1} Oi DOM (Fig. 1 d). At higher DOC concentration, the particle size decreased again and reached a constant level of about 450 nm at 1.0 mg DOC L^{-1} for both Oa DOM and Oi DOM. This observation is in accordance of the findings of Herrera Ramos and McBride (1996) and Carstens et al. (2017) reporting that colloid-colloid collision increased at addition of DOC at low concentration. This is due to the presence of both positive and negative charge at small surface loading of goethite by OM. With increasing OM loading more negative surface charge repulsive interactions likely increased between colloids (Herrera Ramos and McBride, 1996; Kretschmar and Sticher, 1997). The response of the ζ of goethite on the sorption Oa DOM and Oi DOM were similar, but a higher concentration of Oi DOM than of Oa DOM was needed to perform the change of charge of the goethite. According to Gu et al. (1994) and Kaiser et al. (1997) preferably organic molecules enriched in aromatic and carboxylic groups are sorbed to goethite, and likely the same type of OM was associated with the goethite. As DOM derived from Oa DOM is richer in these compounds than that extracted from Oi DOM (Evanko and Dzombak, 1999; Meier et al., 1999; Zhou et al., 2001), this explains the necessity of a higher DOM concentration for the change of charge of the goethite in the case of the Oi DOM.

The ζ and the particle size of the Oa-OMCG colloids and Oi-OMCG colloids were expected to be also affected by Pb^{2+} addition. As Pb^{2+} was added together with the complex OMCG colloids, it is assumed that the Pb^{2+} addition should change the SC of OM in order to turn the ζ of colloidal goethite. However, Pb^{2+} additions of 1.0-10.0 mg L^{-1} of did not change the negative charge of the OMCG (Fig. 2). According to Table 2, showing the surface charge of Pb^{2+}, Oi-DOM and Oa-DOM, it appears that the amount of Pb^{2+} in the solution was too less to overcome the changes of ζ around colloids. This finding is in contrast to the report of Herrera Ramos & McBride (1996), who showed that 0.1-10 mM polyvalent cations (Ca^{2+} and Al^{3+}) in solution can turn the ζ of colloidal goethite coated with humic acid from negative to positive. Similarly, Tipping et al. (1981) reported that 10-50 mM Ca^{2+} in solution led to a charge reversal of humic acid coated colloidal goethite. Therefore, the low amount of charge of Pb^{2+} (0.096 meq L^{-1} positive charge) sorbed within the slipping plane of the OMCG surface was likely insufficient to turn the zeta potential to a positive value (Table 2).

3.2. Mobility of Pb and OMCG colloids in quartz sand and goethite coated quartz sand

In the column experiments, the selected concentrations of 10 mg Pb^{2+} L^{-1} and 1 mg DOC L^{-1} were based on ζ and particle size results reported in the previous chapter. A DOC concentration of 1 mg L^{-1} was chosen for both types of DOM, because at this concentration all positive sorption sites of goethite were occupied by DOM. The HCl-cleaned QS used in this experiment had a negative charge with some patches of positive charge including Fe and Al oxides on its surface and exhibited a ζ of -24.8 ± 7.8 (Carstens et al., 2017). At application of Pb^{2+} to the column, two thirds of injected Pb^{2+} were mobile at pH 4.5 (Fig. 3 a). The results could be partly attributed to the low pH under the experimental conditions. At pH <5, the competition between Pb^{2+} and H^+ could decrease the amount of Pb^{2+} adsorption on the solid matrix. At low pH, protons are increasingly competing with Pb^{2+} to reach the surfaces, and the ions $PbOH^+$ and Pb^{2+} were less susceptible to be sorbed. It seems that low pH is likely responsible for the small amount of Pb retention on the QS matrix. Gundersen and Steinnes (2003) and Sherene (2010) showed a general increasing mobility of heavy metal with decreasing pH. Another factor leading to Pb^{2+} mobility in the QS matrix is the effect of ionic strength. According to Acosta et al. (2011), at high concentration of $CaCl_2$ the mobility of Pb^{2+} in sandy soil increased due to Ca^{2+}has a higher affinity to negatively charged surface than Pb^{2+} in sandy soil, increasing Pb^{2+} mobility. Thus, higher contents of competing cations (H^+ and Ca^{2+}) resulted in the mobility of Pb^{2+} in QS.

In another experiment, Oa-OMCG and Oi-OMCG colloids were injected in the separate HCl-cleaned QS columns to study the transport of iron oxide carrying negative surface coatings through negatively charged porous media. Fig. 3b shows OMCG colloids to be highly mobile in QS. This echoes results of others. So, Kretschmar and Sticher (1997) and (Foerstner et al. (2001) reported high mobility of humic acid-coated hematite colloid and goethite colloid in a QS system, and Carstens et al. (2017) presented similar results on the mobility of goethite coated with fulvic acid in a QS matrix. Here, we showed that also loading of colloidal goethite with natural OM (Oa-DOM and Oi-DOM) increases the mobility of the iron oxide due to the presence of electrostatically repellence on the solid matrix and OMCG colloids (Carsten et al., 2021). Therefore, the transport of OMCG colloids in the solid matrix controlled by electrostatic repulsion between OMCG colloid and QS.

Further, Pb + OMCG colloids were simultaneously injected in order to determine whether the presence of highly mobile colloids lead to an increase in Pb mobility. According to Fig. 3 c, the OMCG colloids did not have an effect on the Pb mobility under the given solute conditions. This result contradicts the hypothesis of an enhanced Pb mobility by co-transport. The results showed that a larger amount of Pb was retained in the presence of OMCG colloids, which likely was related to complex formation with DOM. Therefore, the amount of mobilized Pb at presence of OMCG colloids was less as compared to ionic Pb (Fig. 3 a). We rather consider that changes of zeta potential in the double layer of OMCG colloids controlled Pb^{2+} mobility in the solid matrix. These results inferred from Section 3.1 (Zeta potential and particle size of goethite depending on DOM). The results indicated that addition of Pb^{2+} in suspension solution did not change the colloid’s SC (Fig. 2). A possible explanation could be Pb^{2+} did not penetrate into the double layer thickness of OMCG colloids to reverse the SC of OMCG colloids. Thus, it could be assumed that OMCG colloid had a weak bonding with Pb^{2+} to mobilize Pb^{2+} in QS matrix. This study was in contrast with findings Tang and Weisbord (2009) and Kaste et al. (2005) who presumed that strong association of Pb^{2+} with iron oxide colloids was a pathway for its transport in porous media. Furthermore, chemical property of solution was a controlling factor to reduce mobility of Pb^{2+} in the presence of mobile colloid. The presence of divalent cation of Ca^{2+} in higher concentration in a solution acted as a competitive ion with Pb^{2+}. Then, it impeded the less mobility of Pb^{2+} in the column. Papini et al. (1999) reported a decreasing sorption of Pb^{2+} to humic acids coated colloid with increasing ionic strength's solution through cationic elements. In general, in the mobility of colloidal Pbthe ratios of Ca^{2+}/Pb^{2+} and OMCG colloid/Pb^{2+} controlled the amount of Pb^{2+} transport in the QS matrix. for the effect of competitive ion on sorption sites and for forming complexation with OMCG colloids should be considered.

In the column experiments with GCQS with partially positively charge surfaces the surface was modified with DOM in order to determine whether DOM coatings on GCQS has an effect on the mobility. As for the experiments with pure QS, either Pb^{2+}, OMCG colloids, and Pb + OMCG colloids were injected to the columns to determine the mobility of the substances separately and simultaneously. At injection of Pb^{2+} in pulse 1 the concentration of total Pb^{2+} in the effluent was less in the GCQS system as compared to the QS system (Fig. 4 a). The likely reason is the presence of hydroxyl groups (OH^-) of iron oxide on the surface of GCQS, which led to electrostatic attraction with Pb^{2+} and $PbOH^+$ ions. This fits to results of Xu and Axe (2005), who reported a higher Ni adsorption to sand coated with goethite than to uncoated sand due to higher surface reactivity. Lai et al. (2000, 2002) showed that Pb^{2+} and Cd^{2+} ions can enter the pores of goethite coated quartz sand or having a complex with hydroxyl groups of GCQS. Thus, the results could be partly attributed to the potential of (oxy) hydroxides of GCQS matrix for adsorption Pb^{2+} on the GCQS matrix.

In pulse 2, electrostatic attraction of DOM to GCQS led to a change of surface charge of the goethite colloids to negative charge through OM sorption. In pulse 3, Pb^{2+} was injected to a solid matrix that was uniformly negatively charged due to OM sorption. Despite this favorable negative charge of the OM conditioned GCQS, Pb was quite mobile (Fig. 4 a). Probably the addition of ionic Pb^{2+} in the form of dissolved ion had higher tendency to be mobilized in the column than to be retained on the surface. This competition is even more pronounced at $pH < 5$ (Papini et al., 1999; Klitzke et al., 2008). Also Kalbitz and Wennrich (1999) reported a higher mobility of metal in soil with high DOC concentrations at low pH. However, Pb^{2+} had a partly retention on the surface of solid matrix after DOM preconditioning, but the content of Pb^{2+} retention on the surface through complexation with DOM was less than of expectation. It is likely, there was not enough time for injected Pb^{2+} to form complexation with DOM.

By injection of OMCG colloids, into the columns filled with GCQS, the breakthrough curve in pulse 1 showed immobility of OMCG colloids (Fig. 4 b), caused by electrostatic retention between OMCG colloids and the hydroxyl group of GCQS (Hanna, 2007; Li et al., 2013; Carstens et al., 2018). In pulse 2, DOM was percolated to change the positive surface charge of the GCQS to negative values. Subsequently, in pulse3 OMCG colloids showed highly mobility (Fig. 4 b) due to electrostatic repulsive forces caused by the negative charge on both surfaces, the colloids and the solid matrix. Carstens et al. (2018) reported that preconditioning with fulvic acid enhanced the transport of negatively charged OMCG colloids in GCQS. This study showed that natural DOM causes the same behavior regarding electrostatic interactions on OMCG colloids.

When Pb + OMCG colloids were applied together, in pulse 1 they were less mobile than when injected individually (Fig. 4 c). This observation is likely related to the effect of increasing ionic strength in a solution with Pb^{2+} addition in decreasing OMCG colloid mobility. The calculated ionic strength quantified that presence of Pb^{2+} increased the ionic strength from 0.91mM to 1.045 mM. Likely, this decreased the mobility of OMCG colloids in the suspension. And in the case of Pb^{2+}, probably a part of Pb^{2+} had a complexation with DOM coated on the surface OMCG colloids. At presence of DOM in pulse 2, the partially positively charged of GCQS surfaces turned negative. In pulse 3, applying the same procedure as in variant 1, the mobility of the OMCG colloids was close to 100%, while Pb mobility decreased. In pulse 3, the goethite colloids were mobile after DOM percolation, because electrostatic repulsion caused by negative surface charge on OMCG colloids was stronger than the attraction caused by ionic strength in pulse 1. But mobility of colloidal Pb in pulse 3 did not increase despite the presence of high mobile colloids in the solid matrix. Principally, there are the same mechanisms controlling the Pb mobility in the matrix GCQS as there were in the matrix QS. But in GCQS matrix there was extra addition of DOM on the surface of GCQS (pulse 2), which led to higher retention of Pb on the surface. It seems, higher amount of DOM (20 mg L^{-1}) on the surface of GCQS acted as an adsorptive for Pb^{2+}complexation which impeded Pb^{2+} mobility in GCQS matrix after DOM preconditioning. Thus, it could be assumed that the higher amount of Pb^{2+} formed complexation with DOM than to be mobilized with mobile OMCG colloids. Less mobility of Pb^{2+} in the variant (1 and 3) was due to higher concentration of DOM in the suspension either on coated on the solid matrix or coated on goethite colloid surfaces.

The less mobility of Pb^{2+} in the presence of DOM in the solid matrix fits to a study of Velimirovic et al. (2020), who showed that humic acid-coated goethite was an effective *in situ* substance for remediation of aquifers from contaminated materials. The observations by Zhao et al, (2007) and Li and Zhou (2010) showed that the influence of organic acids on retention of metal (Cu and Cd) through adsorption and complexation. Another study by Covelo et al. (2007) showed due to higher accumulation of soil organic matter in the upper layer of soil, the top soil is more prone to be contaminated with metal. The results are in the line with the hypothesis that a condition of the GCQS with negatively charged DOM increases the mobility of negatively charged OMCG colloids, but decreases that of dissolved ionic Pb^{2+}. This observation showed that Pb^{2+} transport is related to factors (i) the amount of concentration of dissolved Pb^{2+} in the suspension, (ii) Pb^{2+} complexation with DOM, (iii) weak bonding of Pb^{2+} with OMCG colloids to be mobilized in the solid matrix. In general, OM considered as a crucial factor with a great influence on metal mobility through forming a stable complex.

3.3 Applicability of the DLVO theory

The column experiments results showed that ζ and ionic strength were two important factors in controlling the mobility of OMCG colloids in QS and GCQS matrixes. The sum of electrostatic and van der Waals interactions can be evaluated by the classic DLVO approach (Grasso et al., 2002; Tosco et al., 2012). Electrostatic interaction energies between the surfaces are predicted by the zeta potential and can be attractive or repulsive, while van der Waals interactions are always attractive, and can be quantified via free surface energies derived from SDM contact angle measurements (Goebel et al., 2013) explained in Table 3. Van der Waals interactions are stronger in the presence of attractive electrostatic interaction and leads to favorable attachment conditions in the primary minima (Bradford et al., 2017). Primary minima is an attractive force which favors to coagulation of particles over dissociation of particles (Bradford et al., 2006a). The repulsive electrostatic interaction results in an unfavorable attachment condition, which is involving an energy barrier. Outwards of the energy barrier caused by the attractive van der Waals interactions there exists a secondary minima. Fig. 5 shows the presence of energy barrier between solid matrix and OMCG colloids. The interaction energies between OMCG colloids and solid matrix show that there was colloid retention in the presence of positive charge GCQS, while colloid mobility increased at presence of negatively charged QS and OM-coated GCQS. Ionic strength also had a decreasingly effect on the colloid mobility in the QS and GSQS matrixes. Pb^{2+} addition in the solution increased the value of ionic strength from 0.91mM to

1.045mM mM. Therefore, the depth of secondary minima decreased in the higher ionic strength. Decreasing in the depth of secondary minimum led to higher retention of colloids on the surface (Fig. 6a, b). The influence of ionic strength on mobility stated by (Zhou et al., 2011) who showed high ionic strength decreased the mobility of colloids in soil matrix through shrinking electric double layers. With increasing ionic strength the depth secondary minimum increases towards a more negative value (Brinker and Scherer, 1990; Tosco et al., 2012). In general, DLVO energy derived from surface properties and ionic strength was able to predict the general trend in the mobility of OMCG colloids in the solid matrix.

4. Conclusions

This study investigated the behavior of Pb^{2+} and OMCG colloids in the model sands. To better understand the underlying mechanism on mobility of OMCG colloids and Pb^{2+}, the samples were studied in separately or together in different solid matrix under experimental conditions (pH 4.5 with $CaCl_2$ at concentration 0.3 mM and DOM derived from Oi and Oa horizon). The results showed that DOC through coating on goethite colloid increased colloid mobility through electrostatic repulsion with negatively charged solid matrix, although OM coating on solid matrix was effective in Pb^{2+} retention through electrostatic attraction on the surface despite the presence of mobile colloid in the suspension. The chemical conditions of suspension had a relative importance on OMCG colloids $^{+}$mobility. The prediction of OMCG colloids mobility by DLVO theory showed colloids mobility were effected by Pb^{2+} when ionic concentrations outcompeted than electrostatic interaction.. We conclude that the behavior of Pb^{2+} transport was complicated when organic matter appears on the solid matrix. Thus the further studies should be considered under more complex natural material to consider the effect of soil organic matter on the mechanism of transport into groundwater.

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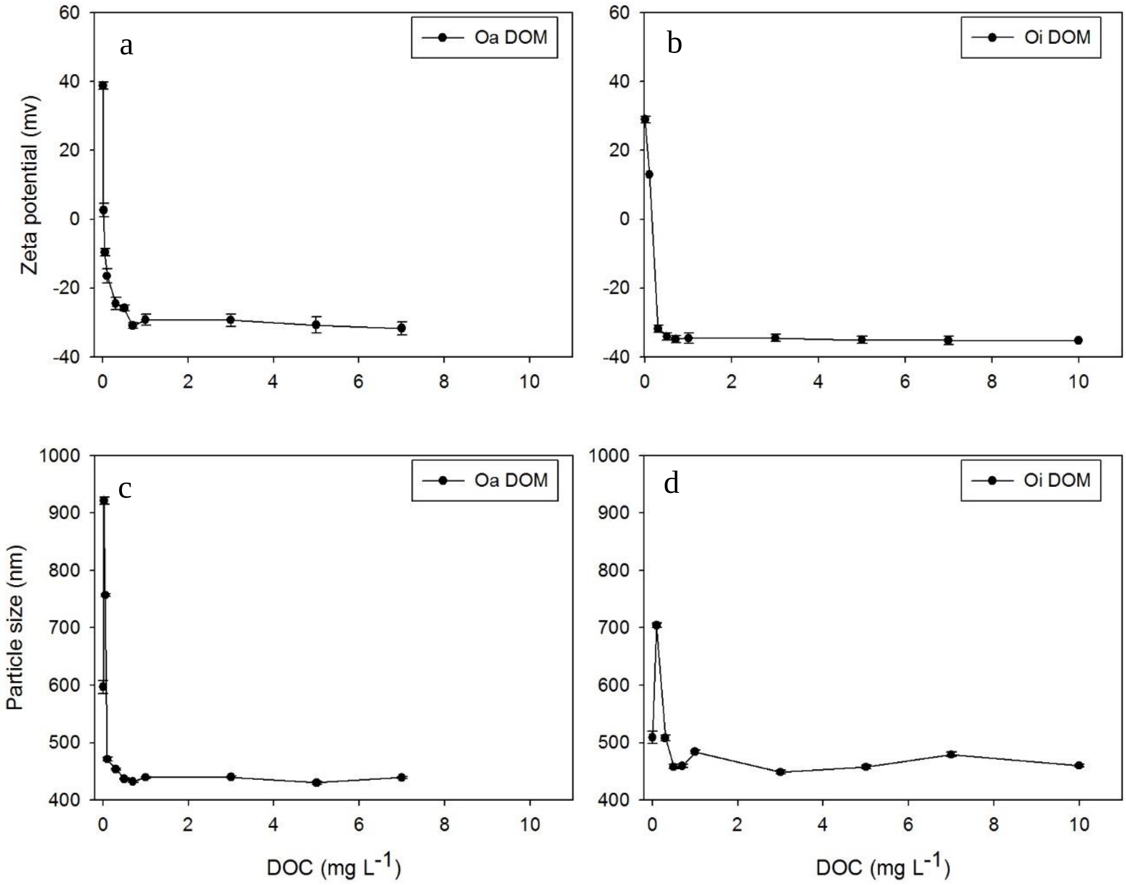


Fig. 1 a.d. Modification of zeta potential and particle size of goethite colloids by DOM (dissolved organic matter). a) Changes of zeta potential in the presence Oa DOM (DOM derived from Oa horizon under spruce), and b) in the presence of Oi DOM (DOM derived from Oi horizon under beech) ; c) changes of particle size in the presence of Oa DOM, and d) in the presence of Oi DOM.

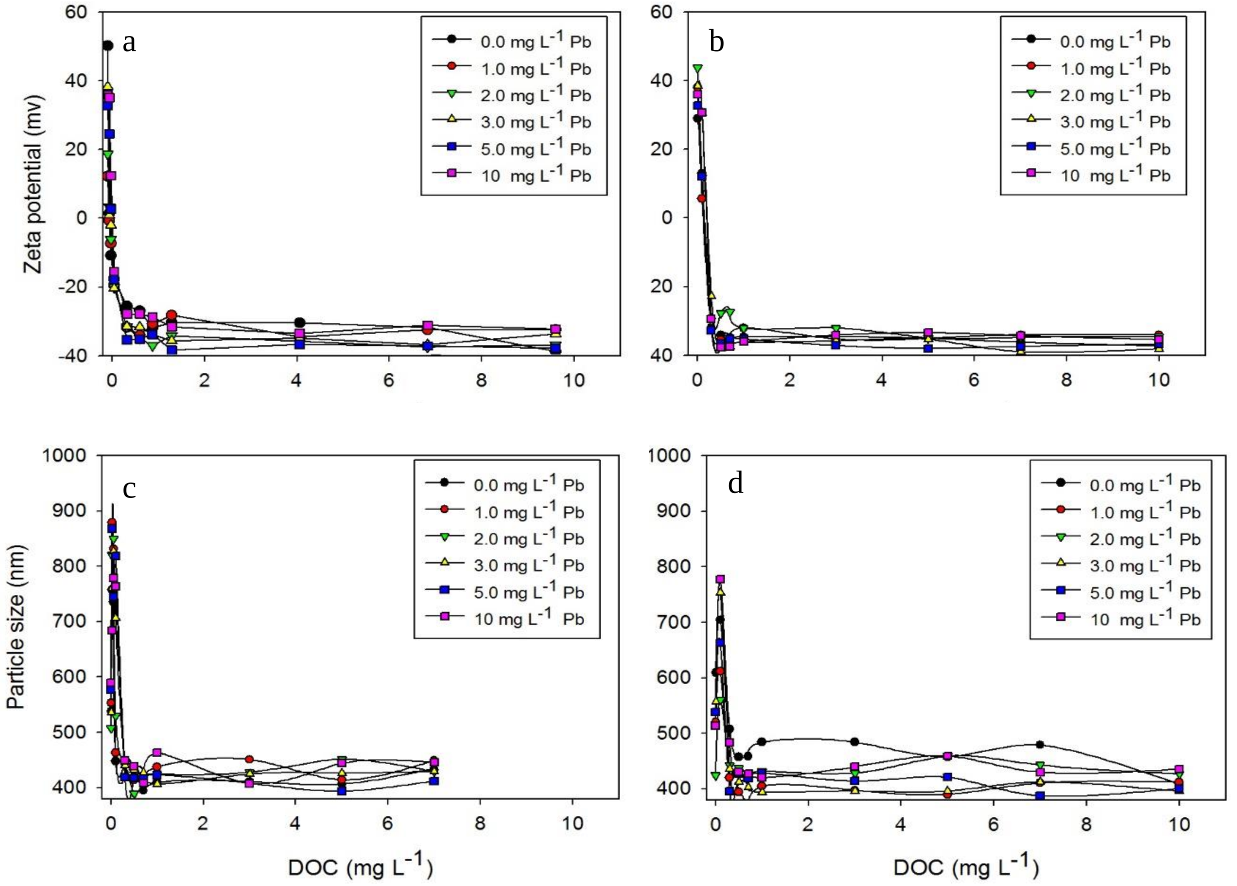


Fig. 2 a.d. Influence of Pb on changes of zeta potential and particle size of OMCG (organic matter coated goethite) colloids. a) Changes of zeta potential in the presence of Oa-OMCG colloid (goethite coated with DOM extracted from Oa horizon under spruce), b) Oi-OMCG colloid (goethite coated with DOM extracted from Oi horizon under beech); c) changes of particle size in the presence of Oa-OMCG colloid, d) Oi-OMCG colloid.

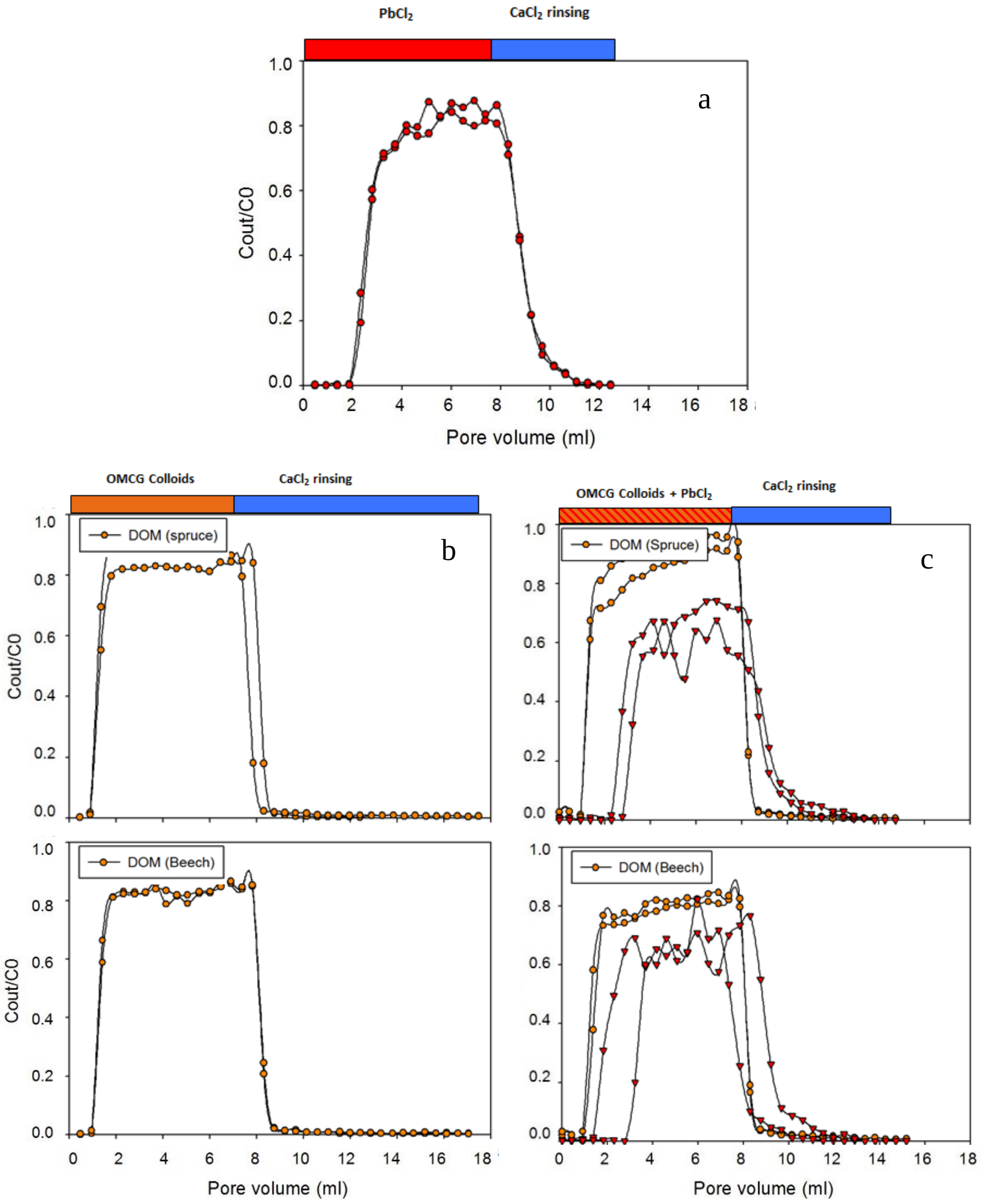
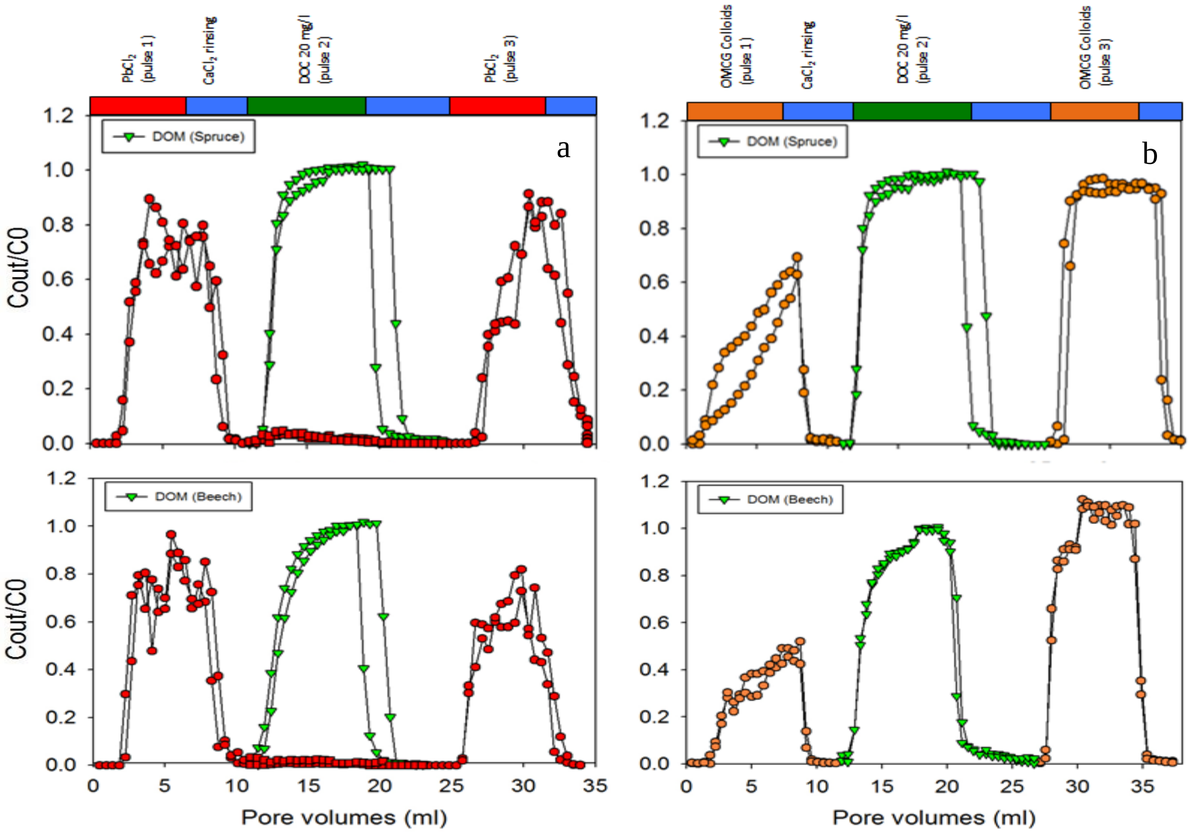


Fig. 3 a.c. Breakthrough curves of a) Pb, b) OMCG colloids (Oa OMCG and Oi OMCG colloids) and c) Pb+OMCG (Pb+ Oa OMCG and Pb+ Oi OMCG colloids) released in quartz sand (QS) solid matrix in a single pulse experiment. Results are depicted in two replicates. The samples of dissolved organic matter (DOM) extracted from Oa horizon under spruce (Oa DOM) and Oi horizon under beech (Oi DOM), OMCG colloids represent goethite coated with DOM extracted from Oa and Oi horizons. The experiments conducted at pH 4.5.



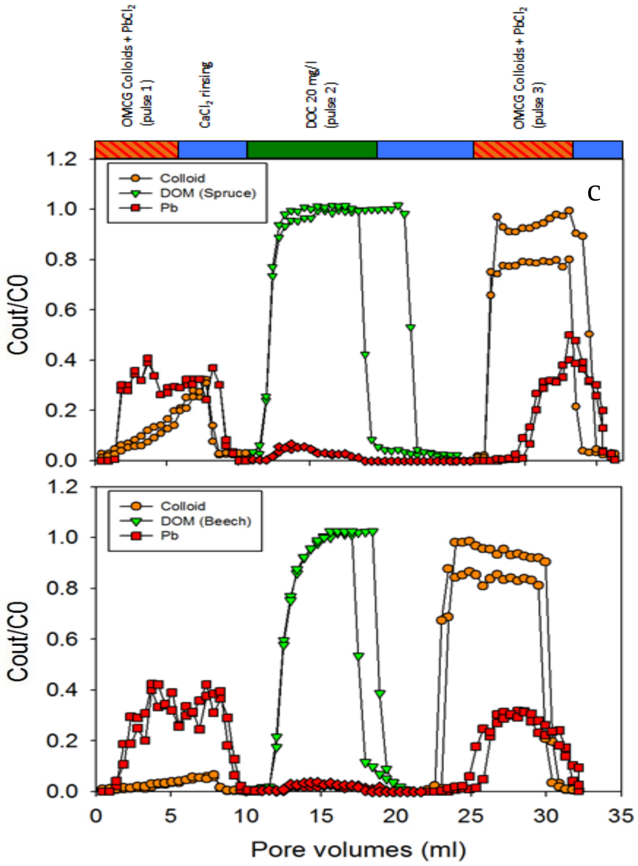


Fig. 4 a.c. Breakthrough curves of a) Pb, b) OMCG colloids (Oa OMCG and Oi OMCG colloids) and c) Pb+ OMCG (Pb+ Oa OMCG and Pb+ Oi OMCG colloids) released in goethite coated quartz sand (GCQS) solid matrix in triple pulse experiments. Results are depicted in two replicates. The samples of dissolved organic matter (DOM) extracted from Oa horizon under spruce (Oa DOM) and Oi horizon under beech (Oi DOM), OMCG colloids represent goethite coated with DOM extracted from Oa and Oi horizons. The experiments conducted at pH 4.5.

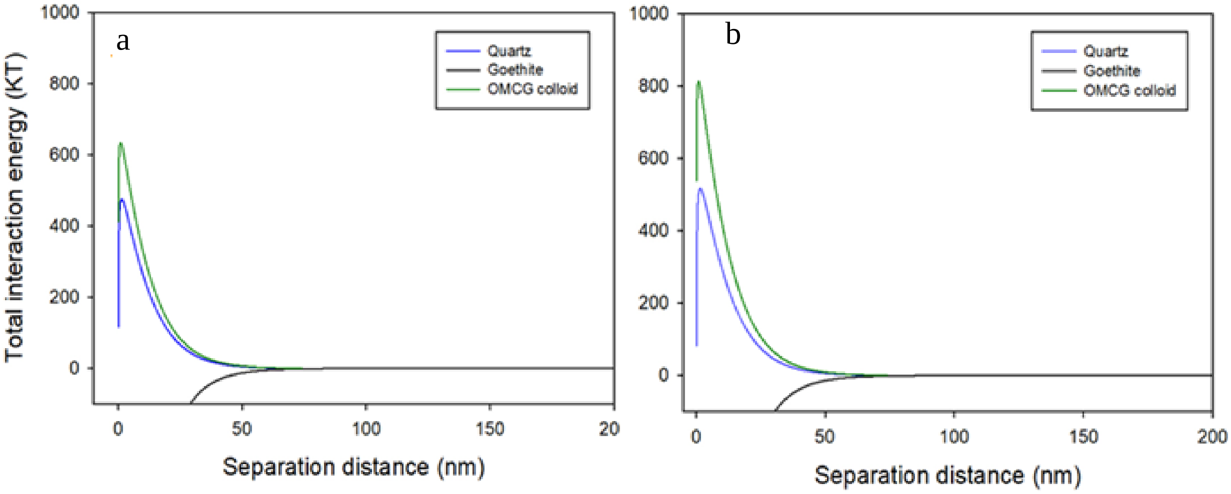


Fig. 5 a.b. Total interaction energy between Oa OMCG and Oi OMCG (organic matter coated goethite) colloids and the solid surfaces; quartz sand (QS) stands for the uncoated sand, goethite for goethite coated on QS (GCQS), and OMCG coated stands for dissolved organic matter (DOM) preconditioning on GCQS surface. a) Oa DOM (DOM derived from Oa horizon under spruce) and b) Oi DOM (DOM derived from Oi horizon under beech. KT is the product of Boltzmann constant (K) and temperature (T). The data are depicted in the presence of energy barrier.

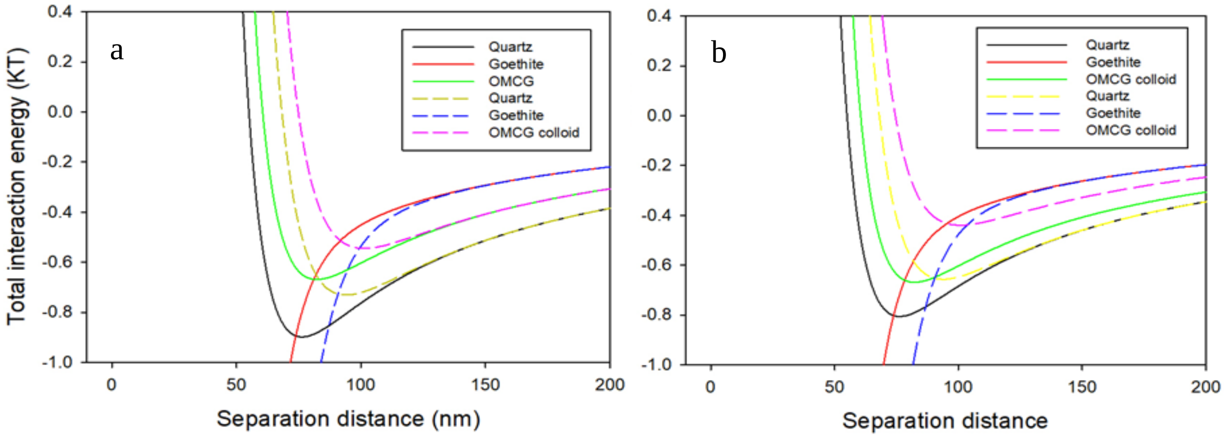


Fig. 6 a.b. Total interaction energy in the presence of secondary minimum between Oa OMCG and Oi OMCG (organic matter coated goethite) colloids and the solid surfaces; quartz sand (QS) stands for the uncoated sand, goethite for goethite coated on QS (GCQS), and OMCG coated stands for dissolved organic matter (DOM) preconditioning on GCQS surface. a) Oa DOM (DOM derived from Oa horizon under spruce) and b) Oi DOM (DOM derived from Oi horizon under beech. KT is the product of Boltzmann constant (K) and temperature (T).). Dash lines stand for DLVO interactions in the absence of Pb. The data are depicted in the presence of secondary minimum.

Table 1. Overview of the experimental series in the matrices quartz sand (QS) and goethite coated quartz sand (GCQS) with three different variants, Pb, OMCG colloids and Pb+OMCG colloids. Dissolved organic matter (DOM) extracted from Oa horizon under spruce (Oa DOM) and Oi horizon under beech (Oi DOM). Breakthrough of colloids and Pb are shown as percent of the input into the columns in two replicates with mean and the range of two replicates. Pulse 1 shows the injection of an initial suspensions and pulse 2 shows the second injection of suspensions after DOM preconditioning on the GCQS surface.

Solid matrix	**DOM**	**Variant**	**Colloid-pulse 1**	**Mean/ range**	**Pb-Pulse 1**	**Mean/ range**	**Colloid-Pulse 2**	**Mean/ rang**	**Pb-Pulse 2**	**Mean/ range**
QS	Oa	Pb			77.3	78.3				
		Pb			79.4	1.1				
		Colloid	84.1	81.9						
		Colloid	79.7	2.2						
		Pb+ Colloid	86.3	88.6	62.9	60.8				
		Pb+ Colloid	90.9	2.3	58.6	2.1				
	Oi	Pb			77.3	78.3				
		Pb			79.4	1.1				
		Colloid	88.6	87.6						
		Colloid	86.5	1.1						
		Pb+ Colloid	80.4	80.6	62.9	65.5				
		Pb+ Colloid	80.8	0.2	68.1	2.6				
GCQS	Oa	Pb			60.6	66.7			51.9	56.9
		Pb			72.9	6.2			61.9	5.0

	Colloid	45.7	38.9			95.4	95.2		
	Colloid	32.1	6.8			95.0	0.2		
	Pb+ Colloid	18.2	16.7	37.2	37.4	105.2	101.1	28.4	27.2
	Pb+ Colloid	15.2	1.5	37.7	0.2	97.0	4.1	26.0	1.2
Oi	Pb			62.4	67.2			50.7	57.6
	Pb			72.0	4.8			64.6	6.9
	Colloid	34.8	36.1			100.6	100.5		
	Colloid	37.4	1.3			100.4	0.1		
	Pb+ Colloid	3.4	3.7	36.1	36.3	95.2	93.8	21.9	23.9
	Pb+ Colloid	4.0	0.3	36.5	0.2	92.4	1.4	25.9	2.0

Table 2. Calculated charge of lead (Pb) and measured surface charge (SC) of dissolved organic matter (DOM) extracted from Oa horizon under spruce (Oa DOM) and Oi horizon under beech (Oi DOM). The samples quantified at target pH 4.5 for Oa DOM and pH 5.5 for Oi DOM suspensions at pH 5.0 for Pb^{2+}

	Concentration (mg L $^{-1}$)	**SC (mmol $_c$ g $^{-1}$ C)**		**SC (meq L $^{-1}$)**
		pH 4.5	**pH 5.5**	**pH 5**
Pb	10.0			0.096
Oa DOM	0.125	-5.60		
Oi DOM	0.0625		-4.08	

Table 3. Zeta potential and sessile drop method contact angles (θ) and inferred van der Waals free energy (Y_s^{LW}) for quartz sand (QS), goethite, and organic matter coated goethite (OMCG) colloids.

Material	**Zeta potential (mv)**	**θ_{water}(◦)**	**$\theta_{Glyceroler}$(◦)**	**$\theta_{Idobenzener}$(◦)**	**Y_s^{LW}**
QS	-24±7.8	23.4±3.9	51.9±6.4	0.0±0.0	39.7
Goethite	+50.1±7.0	28.4±2.3	63.6±10.6	39.0±2.6	31.40.3
Oa-OMCG[1]	-30.2±3.1	39.7±5.5	64.9±4.6	31.5±3.1	35.61
Oi-OMCG [2]	-32.5±5.3	33.0±3.0	65.3±3.8	26.5±3.1	34.04

1) Goethite coated with DOM extracted from Oa horizon under spruce, 2) Goethite coated with DOM extracted from Oi horizon under beech.

5. Study IV

Additional results and information on the experiments

In Study IV, additional experimental data will be shown and discussed. It is directly connected to the experiments of Study III.

Abstract

The mobility of lead (Pb) in soils and sediments is related in very complex ways to iron oxides and organic matter (OM), both in the form of coatings on the solid matrix or in a colloidal or dissolved state in the pore solution. However, systematic studies on the complex interactions of Pb with goethite and OM under flow conditions remain scarce. The goal of this study was to assess the mobility of Pb^{2+} and OMCG colloids in a disturbed natural soil material and also depending by loading OM on soil surface to assess the of transport in Pb^{2+} and OMCG colloids. In the present study, triple pulse breakthrough experiments in a $CaCl_2$ background solution were conducted using columns filled with disturbed subsoil Cambisol that was rich in natural iron oxide coatings. In the first pulses, three different solutions containing either Pb, OMCG colloids, or Pb plus OMCG colloids were percolated. In the second pulse, dissolved OM (DOM) was percolated to form coatings on the solid matrix. In the third pulse, the three different solution variants were percolated again to assess the effect of surface modification on the mobility of the Pb and the colloids. Results show that the simultaneous percolation of OMCG colloids and Pb leads to an increase in Pb mobility in the disturbed soil as compared to the Pb mobility in the absence of colloids. The percolation of soil surface with DOM and subsequently rinsing it with $CaCl_2$ in pulse 2 leads to Pb re-mobilization from soil due to competitive sorption with Ca^{2+}. Sorption of DOM onto the solid matrix leads to an increase in OMCG colloid mobility and a decrease in Pb mobility in pulse 3. We conclude that in the disturbed natural soil material with high OM loading on the surface, Pb^{2+} was easily adsorbed and the transport of Pb^{2+} in the column decreased. However, in this study the ratios of Ca^{2+}/Pb^{2+} in solution controlled mobility of Pb^{2+} in the solid matrix.

Key words: colloidal goethite, column experiments, dissolved organic matter, DLVO, Pb mobility, sorption

1. Introduction

The mobility of heavy metals in soils and their transport into ground water is a crucial environmental topic. Adsorption and desorption of heavy metal to soil particles is affected by chemical speciation of the heavy metals, the composition of the soil matrix, and the composition of the soil solution with respect to pH, ionic strength (Kamrani et al., 2018; Bai et al., 2020). Sorption of heavy metal on the solid matrix is a competitive sorption between cations in the soil solution that can compete with heavy metal for sorption sites (Gutierrez and Fuentes, 1991). The ions of Mg^{2+} and K^{+} (in the high concentrations) and Ca^{2+}, are the most competitive ions with heavy metals, and may lead to a release of heavy metal from solid matrix into outflow (Elrashidi and O'Connor, 1982). Particularly the presence of colloids in the soil solution enhance the mobility of heavy metals (Roulier et al., 2008). With respect to Pb, its association with mobile iron oxides plays a key role for its mobility in soils (2001; Bradl, 2004).

OM with hydrophilic and hydrophobic components have reactive absorption sites for the retention of heavy metals on the surface of soil. The retention's behavior of lead (Pb) and copper (Cu) by the solid soil matrix is the result of complexation with OM (Kile et al., 1999). Retention of Pb^{2+} on the sorption sites of solid matrix not only controlled with OM components but also oxy (hydroxides) of Fe, Al and Mn had a role for metal adsorption on the surface of solid matrix. The presence of different sorption sites on the surface of solid matrix provides chemical bonding with different interactions with heavy metal (Sparks, 2003).

Information concerning mobility of goethite colloids in the solid matrix and loading OM on the surface of colloid and solid matrix explained in Study III.

Still, there are unknown questions regarding complexity the combination of colloid-DOM-Pb in the solid matrix on the mechanism mobility of Pb^{2+} and colloid. The objective of this study was hence to unravel mobility and retention of Pb in soil at presence of DOM and to assess the sorption behavior of Pb to DOM and the solid soil matrix in the presence of mobile colloids. We hypothesized that (i) Pb mobility enhances in the presence of OMCG colloids, (ii) OM loading on the soil matrix inhibits Pb mobility through electrostatic attraction, while it enhances colloid mobility through electrostatic repulsion.

2. Material and Methods

Saturated semi-circular plexiglass columns with a height of 12 cm and inner diameter of 2 cm were filled with sandy Cambisol subsoil under beech forest at the Grinderwald experimental site (Carstens et al., 2018) north of Hanover, Germany. The sample was taken from the Bw horizon at a depth (35-65 cm). The porosity of the disturbed natural soil under saturated condition was 39%. According to Table 1 the soil is characterized by sandy texture and low concentrations of organic carbon. At a glance, column experiments in three pulses with three different variants were conducted. The variants were Pb^{2+}, OMCG colloids, and Pb^{2+} + OMCG colloids in order to assess the mobility of substances separately and simultaneously in the column injected to determine whether the presence of highly mobile colloids lead to an increase in Pb mobility. The pulses included the following: First, Pb^{2+}, OMCG colloids, and Pb^{2+} + OMCG colloids were added in a 0.3 mM $CaCl_2$ as background solution, Then, in the second pulse Oi DOM (under European beech (*Fagus sylvatica*)) with concentration of 100 mg L^{-1} dissolved organic carbon (DOC) was added in order to determine whether OM coatings on the disturbed soil formed by DOM sorption affect the mobility and immobility of Pb and OMCG. DOM percolation ended when the DOM concentration in the effluent equaled that of the influent (C/C0=1) and then preconditioned DOM rinsed with $CaCl_2$ to remove any un-bonded of DOM from surface. In the third pulse second injection of Pb^{2+} and OMCG colloids pulses added in the column. The analysis of outflow in DOM, OMCG colloid determined by UV-vis and Pb measured by inductively coupled plasma optical emission spectrometry (ICP-OES; Varian ICP 725 Optical Emissions Spectrometer, Agilent Technologies, Santa Clara, CA, USA). Information regarding experimental methods, DLVO calculations and producing Oi DOM presented in Study III. Soil texture was analyzed via wet sieving (sand fractions) and sedimentation (clay and silt fractions) according to Stoke’s Law. Soil organic carbon was measured with a Vario TOC Cube (Elementar, Langenselboldt, Germany). The content of low and high crystalline Fe and Al oxide minerals were determined via sodium dithionite and ammonium oxalate extraction and subsequent measurements via ICP-OES (Varian ICP 725 Optical Emissions Spectrometer, Agilent Technologies, Santa Clara, CA, USA), according to McKeague and Day (1966).

3. Results and Discussion

The breakthrough curves of outflow for three different variants Pb, OMCG colloids, Pb + OMCG colloids are depicted in Fig. 1 and 2. The breakthrough curves for Pb and for OMCG colloids can be divided to two parts. In pulse 1, mobility or immobility at heterogeneous surface of the solid matrix can be assessed, while in pulse 3 mobilization and immobilization from the soil matrix after DOM preconditioning can be elucidated. The results of the first variant (Pb injection in the absence of OMCG colloid) showed 80% retention of Pb in the column (Fig.1a). During the second pulse with the DOM percolation and then rinsing with $CaCl_2$, 66% of Pb retained in the first pulse was remobilized in the effluent. Thereafter, in the third pulse Pb was completely retained by the soil surfaces modified by OM sorption. The re-mobilization of Pb^{2+} in the second pulse was due to higher concentration of Ca^{2+} in the suspension that makes it more competitive than Pb^{2+} for sorption sites. Likely, the most part of Pb^{2+} was bound as an outer-sphere complex (ionic bond) and could be easily exchanged with the competitive ion of Ca^{2+} in high concentration.

The complete retention of the added Pb^{2+} in the third pulse was due to DOM percolated on the surface of Cambisol material. Impellitteri et al. (2002) and Tang et al. (2013) illustrated that the presence of OM on the surface of solid matrix decreased mobility of heavy metal especially Cu and Pb. Likewise, Huang and Weber (1997) showed complexation and retention of heavy metals is particularly strong with DOM in the solid matrix. Hence, in the conducted experiment, OM coated on the soil material showed a high affinity to retain Pb^{2+} on the surface.

In the second variant (OMCG colloid injection) all colloids were retained by the heterogeneous surface of the Cambisol material (Fig. 1b). However, after preconditioning of the soil surface by OM sorption, the OMCG mobility strongly increased and 90% of the injected colloids were found in the effluent. The immobilization of colloids in the first pulse was due to electrostatic attraction between the negatively charged colloids and oxy (hydroxides) of Al and Fe (Table 1) that are positively charged at the given pH of 4.5. The next part probably is the effect of microscale roughness heterogeneity on colloid retention on the solid matrix. The reported study by Bradford et al. (2017) stated that microscale roughness properties on the surface of soil solid matrix led to the retention of the inorganic colloids on the surfaces The investigations in study (I) showed that the surface of HCl-cleaned QS had a potential to retain 10% of colloid on the surface with microscale roughness properties. I assumed that the Cambisol materials have even higher physical heterogeneities for colloid retention on the surface than the QS due to increase in the grain size distribution of Cambisol materials. Thus, properties of physical and chemical heterogeneities in the first pulse led to immobility of the OMCG colloids on the surface while electrostatic repulsion in the third pulse increased mobility in the column.

The results of the third variant (Pb + OMCG colloids) illustrated that in the first pulse only 3% of injected OMCG colloids were found in the effluent and the percentage of Pb^{2+} mobility in the first pulse was 40% in the presence of colloid (Fig. 2). In the second pulse, preconditioning DOM on the surface of Cambisol material and then subsequently rinsing with $CaCl_2$ led to re-mobilization of 43% of Pb^{2+} retained in the first pulse in the effluent. Thereafter, in the third pulse only 8% of the injected Pb and 75% of the OMCG colloids were found in the effluent. The most interesting findings in the behavior of Pb^{2+} transport in the soil solid matrix was re-mobilization of Pb^{2+} after $CaCal_2$ rinsing. The results clearly reveal that the affinity of metal toward DOM depends on the content of metal in the solution.

When comparing the third variant with the second variant concerning the OMCG mobility during the second pulse, this was less in presence of Pb (variant 3) than in its absence (variant 2). It was due to the higher cationic element in the solution caused by Pb^{2+}. The result of this cationic effect is explained by the DLVO theory. This fits to the findings of Zhou et al. (2011) and Tosco et al. (2012) concerning the effect of cationic elements on the depth of secondary minima and electric double layer. The cationic elements with changes on the ionic strength of solution decrease the depth of secondary minimum. According to Fig. 3, transport of OMCG colloids in the presence of Pb^{2+} decreased due to shrinkage of the electrical double layer. So, shrinkage of the electrical double layer decreased the depth of secondary minimum, which led to lower OMCG colloid mobility in the column.

OMCG colloids mobility on the heterogeneous surface before DOM preconditioning was lower than after DOM preconditioning due to higher sorption site with attractive interactions on the surface which is originating from hydroxyl groups (Table 1). The study by Carstens et al. (2018) stated the OMCG colloids were less mobile in the matrix goethite coated quartz sand due to the presence of hydroxyl groups of Fe on the surface. While electrostatic repulsion between OMCG colloid with GCQS matrix after DOM preconditioning increased OMCG colloid mobility.

However, the results of the third pulse in the third variant (colloid with Pb) showed that mobile OMCG colloids did not act as a carrier for transport of Pb. It was likely due to the formation of

Pb-OM complexes on the soil particle surfaces after DOM preconditioning. Jordan et al. (1996) and Bergkvist (2001) highlighted the importance of OM for Pb^{2+} retention even in the presence of mobile colloids in the solid matrix. Another study by Diagboya et al. (2015) stated that organic matter showed an immediate reactive with Pb^{2+} while the interaction of iron oxide colloids depends on the time of reaction.

Summarizing, goethite colloids and OM both played important roles on the mobility of Pb^{2+} in the matrix disturbed natural Cambisol. The effect of OM on Pb retention was higher than the effect of OMCG colloid on Pb mobility. Likely, this was due to the impact of various functional groups, particularly carboxylic groups, on the OM surface that led to a high capacity sorption to immobilize Pb^{2+}.

4. Conclusions

This study aimed at identifying the impact of goethite colloids and DOM preconditioning of the solid soil matrix on Pb and colloids mobility in the column experiments. Rinsing columns with $CaCl_2$ exhibited a competition between Ca^{2+} and Pb^{2+} and led to re-mobilization of Pb^{2+} from the soil matrix into effluent. However, after preconditioning the surface with DOM, Pb mobility decreased through form complexation of Pb^{2+} with OM. Pb was immobile in the solid soil matrix even in the presence of highly mobile colloids. Complexation of OM with Pb^{2+} outcompete with mobile colloids and colloid did not act as a shuttle for Pb^{2+} transport. Thus, OM and the concentration of competitive ion in solution are significant factors than mobile colloids to control the mechanism of mobility and immobility of Pb^{2+} in the soil surface.

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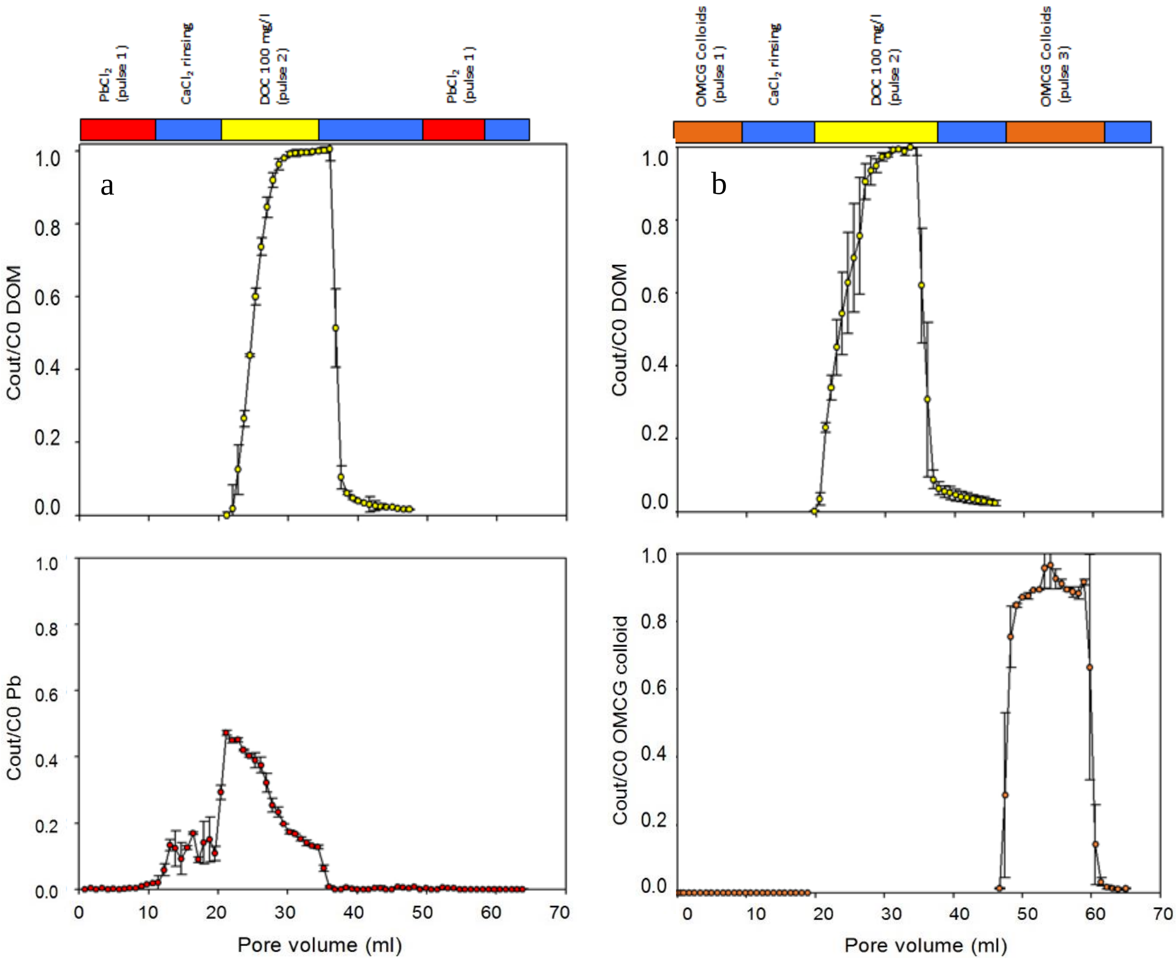

Fig. 1. Breakthrough curves in two different variants, injection of solutes of a) Pb, b) organic matter coated goethite (OMCG) colloids into columns filled with disturbed soil (n =2 with error bars indicating the range).

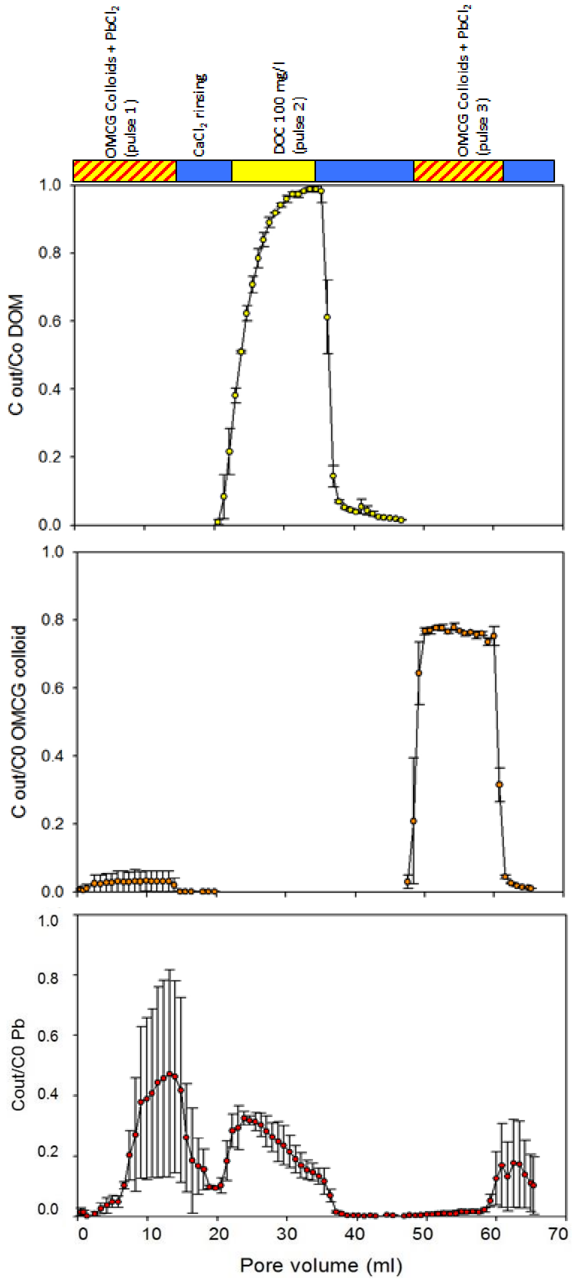

Fig. 2. Breakthrough curves in variant, injection of solute Pb + OMCG colloids into columns filled with disturbed soil (n =2 with error bars indicating the range).

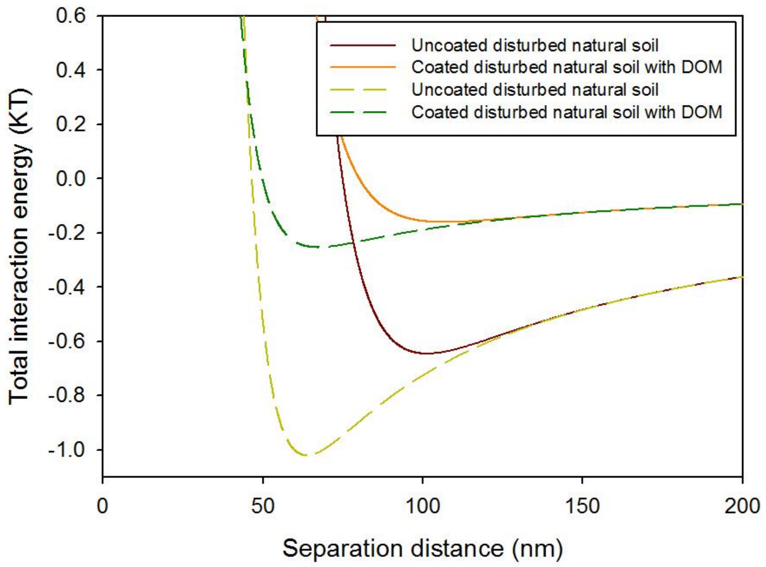

Fig. 3. Classic Derjagun-Verwey-Landau-Overbeek (DLVO) Interaction energies between OMCG (organic matter coated goethite) colloids and uncoated disturbed natural soil and coated disturbed natural soil with dissolved organic matter (DOM) derived from Oi horizon under beech. Solid lines indicate mobility in the presence of Pb, and dashed lines indicate DLVO interaction in the absence of Pb. The inserted plot is zoom into secondary minima.

Table 1. Chemical and physical properties in disturbed natural soil material (n = 3 with standard deviation).

Sand	**Silt**	**Clay**	**SOC**	**Fe_o**	**Fe_d**	**Al_o**	**Al_d**
%			**mg g^{-1}**				
93.0 ± 0.7	5.7 ± 0.6	1.3 ± 0.1	0.06 ± 0.01	3.3 ± 0.5	16.9 ± 1.5	4.1 ± 0.5	5.8 ± 0.4

Table 2. Sessile drop method contact angles θ for six replicate given as mean and standard deviations and inferred surface free energies of the Cambisol subsoil. θ = contact angle for the fluids indicated, γ^{LW}= van der Waals free energy, γ^{+}=Lewis acid free energy, γ^{-}= Lewis base free energy.

Sample	**θ_{Water} (°)**	**$\theta_{Glycerol}$ (°)**	**$\theta_{Iodobenzene}$ (°)**	**γ_s^{LW}**	**γ_s^{+}**	**γ_s^{-}**
Disturbed Cambisol	0.0 ± 0.0	57.2 ± 3.3	0.0 ± 0.0	39.7	0.6	88.0

6. Synthesis

6.1. Mechanisms inducing colloids retention during transport

Understanding of factors that influence OMCG colloids mobility in the solid matrix is needed for inducing mechanisms. The most important factors in inducting goethite colloids mobility include surface heterogeneities of solid matrix (study I) and coating OM on the surface of colloids (study III). Study III (Fig. 1) shows the repulsion between colloids particles through association with OM. The study shows that the mobility of iron hydroxide increased through coating with DOC extracted from soil Oa and Oi horizons. The mobility was the result of electrostatic repulsion between colloids caused by OM on the surface of colloids particles in a negatively charged solid matrix. Study III shows that the first addition of DOC on the surface of goethite colloids turned the surface charge to partially positive charge and led to aggregation of particles due to electrostatic attraction between positive and negative charges of particles. Addition again of DOC on the surface of goethite colloids turned the mixed negative-positive charge to completely negative charge. The data show that OMCG colloids were stable from concentration 1.0 mg DOC L^{-1} onwards with blocking all of sorption sites by OM (Fig.1, study III). This observation is in accordance with the findings of Herrera et al. (1996) and Carstens et al. (2017) who reported that interaction of colloidal particles decreased with increasing concentration of OM loading on goethite colloids due to the presence of repulsive interactions between colloids. Furthermore, in study I (Fig. 5) the addition of OM on goethite colloids in different concentrations from 0.1 mg DOM L^{-1} to 1.5 mg DOM L^{-1} led to a change in the surface roughness properties of OMCG colloids and formed a surface with different roughness properties despite having the same zeta potential (Table .1). Taking these different factors into consideration, the results reported in study I, with OMCG colloids in two different concentrations of DOM (0.25 mg DOM L^{-1} and 1.0 mg DOM L^{-1}), show that at lower concentration of DOM, the height of nanoscale roughness was lower. Lower height in roughness led to higher retention of OMCG colloids on the solid matrix despite having the same zeta potential charge (Table 1). Hence, modification of goethite colloids through OM coverage strongly changed stability and mobility of OMCG colloids.

Even with different DOM components conducted in studies I and III, fulvic acid, Oi-DOM and Oa-DOM, the zeta potential of OMCG colloids were similar (Table. 1). It could be assumed that in all three used DOM samples, there was a selective sorption of hydrophobic compounds on goethite coating, which led to a similar type of OM compounds adsorbed on the surface of goethite.

Table 1. The zeta potential of the three different types of dissolved organic matter (DOM) extracted from Oa horizon under spruce (Oa DOM), Oi horizon under beech (Oi DOM), and Pahokee Peat Fulvic acid coated on goethite colloid to produce organic matter coated goethite (OMCG) colloids. Oi-DOM and Oa-DOM added in concentration of 1.0 mg DOC L-1 on goethite colloid. Data show the mean of three replicates with standard deviation.

Zeta potential (mv)			
Fulvic acid 1*	**Fulvic acid 0.25****	**Oi-OMCG**	**Oa-OMCG**
-30.62±2.3	-31.99±3.1	-30.20±2.7	-32.57±4.3

* OMCG colloid loading with 1.0 mg L^{-1} DOM/** OMCG colloid loading with 0.25 mg $L^{-}1$ DOM.

In addition to the above information, surface properties of the solid matrix also had an influence on the OMCG colloids mobility. The solid matrices in our investigation included defined model soils (quartz sand and goethite-coated quartz sand) and natural disturbed subsoil material from a sandy Cambisol. In the following sections, the effect of complexity of the solid matrix on colloids mobility is represented.

(i) Effect of QS on OMCG colloids transport

With regard to changing the surface charge of goethite by OM loading, the results from Study III (Fig. 3) show that negatively charged OMCG colloids were mobile in the QS matrix. Similar results of OMCG colloids mobility in the QS matrix have been demonstrated by Foerstner et al. (2001) and Carstens et al. (2017). In their studies, the mobility of goethite colloids coated by humic acid- and fulvic acid was investigated, while the results in study III were obtained from goethite colloids coated by natural OM (Oi-DOM and Oa-DOM). Study III also demonstrated that differences in the components of DOM, either from Oa horizons or Oi horizons, did not alter the amount of OMCG colloids breakthrough in the QS matrix. This is probably due to a selective sorption of hydrophobic compounds on goethite coating. The results from study I indicate that the presence of microscale roughness on the surface of QS led to retention of 10% of OMCG colloids (Fig. 3a). As shown in study III, the amount of mobile OMCG colloids in the matrix QS did not reach 100% of breakthrough due to the presence of microscale roughness on the colloids. Studies I and III agree with Zhang and Bradford (2016) and Bradford et al. (2017) who considered the microscale roughness properties on the retention of inorganic colloids on the surface. In general, potential retention of OMCG colloids changed by modification of surface roughness properties, and by association with OM.

(ii) Mobility of OMCG colloids in the GCQS matrix

Mobility of OMCG colloids highly decreased in the GCQS matrix because of electrostatic attraction to the surface (study III, Fig. 4b). This result provides an indication about the transport of OMCG colloids under natural condition because the surface of solid matrix in the environment is covered by different percentages of amorphous and crystalline oxy (hydroxide) of Fe. Coating QS by goethite not only decreased OMCG colloids mobility via electrostatic attraction (study III), but also the combination of iron oxide on the QS matrix led to changes in the physical and chemical heterogeneities of the surface (study I). The later study demonstrates that by increasing goethite content on QS, the amount of OMCG colloid retention linearly increased with the amount of coating and reached 100% of retention at 102 mg kg^{-1} concentration of dithionite extractable Fe in study I (Fig. 3a.b). The studies by Bradford and Torkzaban (2012 and 2015) stated that minor changes of charge heterogeneity on the surface of solid matrix had a high influence on the retention of inorganic colloids compared to smooth surfaces. The results from study III are consistent with the results of Hanna (2007), Li et al. (2013), and Carstens et al. (2018) who reported immobility of OMCG colloids caused by electrostatic retention between OMCG colloids and the hydroxyl group of GCQS. Study I and study III addressed different hypotheses, but had the same background about retention OMCG colloid on the solid matrix. Hence, it can be deduced that surface heterogeneity through changes on electrostatic attraction had a decreasing effect on mobility of OMCG colloids.

(iii) Disturbed natural soil

We also studied OMCG colloids mobility transferred in a disturbed natural soil material (subsoil Cambisol, B_w horizon) in study IV (Fig. 1). The results indicate that OMCG colloids were immobile in the Cambisol matrix. The immobility can thus be assigned to changes of electrostatic interaction through coating of oxy (hydroxide) of Fe and Al on the solid matrix. The amount of colloid retention in the disturbed Cambisol was higher than in the GCQS matrix. This higher retention could be related to surface heterogeneities which increased via hydroxyl group of Fe and higher surface area in the disturbed natural soil (Table 1, study IV). The reports by Bosch et al. (2010) and Carstens et al. (2018) also showed a decrease in inorganic colloids mobility with increasing surface heterogeneities. The study on colloids mobility in the matrix disturbed natural soil material (Study IV) directly was related to Study I concerning surface heterogeneities on decreasing colloid mobility. Hence, properties of surface heterogeneity is a well-known mechanism that strongly affects colloid mobility. The results in the sections i, ii, and iii, are in the line with H1, OMCG colloids mobility in the solid matrix is predominately controlled by physical and chemical heterogeneities of the solid matrix, enhanced by charge heterogeneity on the surface of solid matrix.

Nevertheless, transport of OM through the soil profile has a significant influence on the mobility of OMCG colloids through reversing the surface charge of solid from partially positively charged to net negative values. Studies III and IV (Figs. 4 and 2, respectively) showed the mobility of OMCG colloids after DOM preconditioning on the solid matrix.

(iv) Preconditioning of GCQS and disturbed natural soil by DOM

DOM preconditioning is a major factor for the transport of OMCG colloids in the model sand (GCQS) and the disturbed natural soil material (Cambisol). Experiments in study III and study IV shows that DOM preconditioning on the surface of solid matrices increased mobility of OMCG colloids (Fig 4 in study III and Fig 1 in study IV). There are investigations on adsorption of OM to hydroxyl groups of Fe of solid matrix that led to increasing in the mobility of inorganic colloids (Kim et al., 1998 and Carstens et al., 2018). Adsorption of OM on the hydroxyl groups of Fe was through electrostatic attraction in soils. The study by Kaiser and Zech (1996) observed that the maximum capacity of soil for adsorbing OM is highly controlled by the content of iron and aluminum (hydro) oxides in soils. In addition, there was a positive relation between addition of OM, and iron and aluminum (hydro) oxides. Experiments in study III and study IV shows that the amount of OM coating on the solid matrix of disturbed natural soil was five times more than that in the GCQS matrix due to increasing content of (hydro)oxides of Fe (16.9 Fe_d in a disturbed natural soil vs 3.0 Fe_d in GCQS matrix).

6.2 Mobilization and immobilization of Pb^{2+} in porous media

Modification of Colloid-facilitated transport of Pb^{2+} in porous media through experimental conditions provides a comprehensive understanding on the transport mechanism under natural conditions. Study III examined the conditions of transport in the model sands (QS and GCQS), and Study IV examined the process of transport in a disturbed natural soil (sandy Cambisol). Study III (Fig. 3.c) examined the transport of colloidal Pb in the HCl cleaned-QS matrix. The results revealed that OMCG colloids did not act as a shuttle for the Pb^{2+} transport in the QS matrix.

The lower mobility of Pb^{2+} in the QS matrix in the presence of mobile colloids was due to higher Ca^{2+} content in the suspension, and protonation of OMCG colloid surface at low pH (4.5). Higher content of Ca^{2+} in the suspension led to Pb^{2+} release into suspension. Comparing Pb^{2+} in the form of dissolved and colloidal showed that Pb^{2+}mobility in the form of complex (with OMCG colloids surface) was lower. It seems, Pb^{2+}after release into suspension, it may builds complexes with DOM, which decreases the solubility of Pb^{2+} in the suspension and further lower release into outflow (Study III, Fig 3. b and c). The results of study I (Fig. 5) show only 80% of DOM injected at concentration 1.0 mg L^{-1} on goethite colloid had a complex with goethite colloid and the rest was in the solution. Hence, it can be concluded that Pb^{2+} had a potential to form complex with DOM in the solution.

To assess the effect of mobile colloids on Pb mobility in the more complex system, the colloidal Pb experiment was conducted in the GCQS matrix and a disturbed natural soil material (Study III and IV, Fig 4 and 2, respectively). The results show even under more complex solid matrix, OMCG colloids did not act as a shuttle for the transport of Pb^{2+}. Despite the presence of mobile colloids in a negatively charged solid matrix, the percentage of Pb^{2+} retention was even more in the disturbed natural soil after DOM preconditioning. This higher Pb^{2+} retention in the disturbed natural soil was because of higher OM loading on the surface of solid matrix. These results were in contrast to the findings of Papelis (2002) and Roulier et al. (2008) who reported that inorganic colloids (goethite colloid coated with humic acid) acted as a co-transport for Pb^{2+} in the negatively charged solid matrix. The results of study III and study IV also were in contrast to findings of Hassellov and von der Kammer (2008), who declared that the presence of goethite colloids enhanced Pb^{2+} transport from topsoil to subsoil. They found that iron (hydro) oxides nanoparticles efficiently outcompete accumulated OM on the topsoil to mobilize Pb^{2+}. Bergkvist (2003) stated that the presence of OM coating on the topsoil material led to a strong complexation with Pb^{2+} and decreased mobility of Pb^{2+} through movement into soil profile along with mobile inorganic colloids. The study by Kaste et al. (2006) showed that immobilization of Pb^{2+} on topsoil can happen over several decades and Pb^{2+} can form a strong complexation with O horizons. Therefore, the reason for Pb^{2+} retention was OM coating on the surface. It seems that OM coating on the surface of solid matrix had higher potential to form a stable complex with Pb^{2+} compare to mobilization of Pb^{2+} with mobile OMCG colloids in the solid matrix.

The results from studies III and study IV show the order of Pb^{2+} immobility in the solid matrix were as follows: soil> GCQS> QS. In addition, comparing Pb^{2+} mobility on the heterogeneous matrix of GCQS and disturbed natural soil before preconditioning showed the same order. Thus, it can be assumed that the physico-chemical heterogeneities of the solid matrix was another effective parameter in controlling Pb and colloid mobility. The results in study I show complexity on the surface of solid has a decreasing effect on colloid mobility. The results were in the line with studies of Lai et al. (2000, 2002) who showed Pb^{2+} and Cd^{2+} ions can enter the pores of solid matrix through interaction with hydroxyl groups of GCQS. In general, surface heterogeneity had an indirect role on controlling Pb^{2+} mobility which was highly dependent on OM coating on the surface of either solid matrix or colloid. Thus, supporting H2, preconditioning the surface of solid matrix with DOM increases mobility of OMCG colloids, while decrease mobility of Pb^{2+} despite the presence of mobile colloids in the solid matrix.

6.3 Impact of flow conditions and wetting-drying cycles on mobility

The process of transport and retention of OM and OMCG colloids were intensified in the context of flow conditions (study I) and the drying-rewetting cycle (study II). The general findings are consistent with increase of OMCG colloid retention with increase of flow interruption phase’s duration (Study I, Fig. 1). Study II illustrated the impact of drying-rewetting cycle on the preferential retention of DOM on the solid matrix. In these studies, mobility of OM and OMCG colloids under continuous flow conditions and fully saturated continuous flow conditions was tested to compare the results. In study I, the effects of surface roughness and surface charge heterogeneity on the mobility of OMCG colloids at flow interruption over periods of 2, 18 and 112 h were investigated. Study I shows higher retention of OMCG colloids on the GCQS matrix when flow interruption phase increases. Study I (Fig. 3a.b) showed that retention reached to about 100% after 5 days flow interruption and re-establishment of influent did not re-mobilize colloids, while colloids were highly mobile under continuous flow conditions. The previous experiments by Kretzschmar and Sticher (1997) and Foerstner et al. (2001) regarding mobility of OM-coated goethite and hematite colloids under continuous flow conditions in QS were in line with the results of study I. Carstens et al. (2017) described an increase in the amount of OMCG colloids retention under flow interruption phases in QS matrix. Study I provides information about flow interruption and continuous flow conditions in a complex matrix with surface roughness and surface charge heterogeneity properties. The results show charge heterogeneity of solid matrix promoted a fast retention mechanism and led to higher retention of colloids on the surface under continuous conditions, while retention mechanism on microscale roughness was a slow process under flow interruption. Supporting H3, flow interruption enhances retention of OMCG colloids on the surface with microscale surface roughness and surface charge heterogeneity.

The probable reason for colloid immobilization even after re-establishment of flow (study I) was through association of more hydrophobic components of DOM with goethite colloid on the surface of the solid matrix (Study II). Probably due to loss of water after flow interruption phase, DOM components had a sorption with iron oxide goethite through cation bridging with Ca^{2+}. This result agrees with study of Setia et al. (2013) who determined DOM retention with iron oxide after the cycle of drying.

Study II examined the impact of drying-rewetting on OM retention in a disturbed natural soil material. The results indicate the preferential retention of hydrophobic components on the solid matrix during the cycle of drying, and releasing of hydrophilic components into effluent. Findings of Kleber et al. (2005) and Schneider et al. (2010) showed that the cycles of drying and rewetting led to an increase in total preferential retention of DOM on the surface. To compare the effect of the drying-rewetting cycle under experimental and natural condition, the second cycle of drying-rewetting was conducted on DOM retention. The data in study II (Fig. 4) clearly indicate that during the second period of drying, the adsorption of DOM on the disturbed soil depends on the prior content of OM loading on the surface. The results show a relation between specific UV absorption (SUVA) with hydrophobic and hydrophilic components during the cycle of drying-rewetting. Results indicate during the second drying, more hydrophilic layer of DOM was retained on the more hydrophobic coating, which were formed during the first drying process, fitting H4, the affinity of hydrophilic and hydrophobic components for retention on the solid matrix is predominantly controlled by prior OM loading on the surface of solid matrix, and the cycle of frying-rewetting increases retention of hydrophilic components on the outer-layer of hydrophobic components in the solid matrix with higher prior OM loading. In the lower OM loading variants during the cycle of drying-rewetting, more hydrophobic OM coatings were formed and hydrophilic components released into outflow. In fact, the relatively high DOC release after re-wetting of the dry material might be related to a strong hydrophilicity of the outer coating layers, which were thus easily remobilized by rewetting. The study was in the contrast with the Lenhart and Saiers (2004) studies where DOM retention at air water interfaces did not lead to changes in the composition of effluent DOM.

In summary, the results clearly show that hydrophobic components have a strong complex with solid matrix. Hydrophilic component either were released easily after the first cycle of drying-rewetting or were formed an outer layer complex with surface during the second cycle of drying-rewetting. Probably, the mobility of colloids in study I after flow interruption was related to form complex of more hydrophobic components with goethite colloids during flow interruption phases, and OM coating caused less mobility of goethite colloids after flow interruption phases. Accordingly, the solubility and mobility of Pb^{2+} were related to the association with OM (studies III and IV). Likewise, it was reported by Refaey et al. (2014) that the OM complex caused the higher retention of Pb on the topsoil. Furthermore, the obtained results in studies III and IV show that after DOM preconditioning on the surface of solid matrix, the percentage of Pb^{2+} mobility was less in the presence of the mobile colloids. Presumably, the chance of Pb^{2+} to form complexes with hydrophobic DOM fractions increased even at low pH (4.5) with protonated aromatic and carboxylic components.

6.4 DLVO approach for prediction of Pb and colloid transports

The classic DLVO theory is able to predict a general trend in the transport and mobility of colloids in the solid matrix. The basic information needed for the DLVO approach are: zeta potential, ionic strength and surface free energy components. Study III showed the interaction between model sands with OMCG colloids and study IV showed the effect of interaction between a disturbed natural soil material and OMCG colloids. Both studies predicted the mechanism interactions of OMCG colloids mobility with solid matrix via DLVO theory. The studies of III and IV showed that OMCG colloids were highly mobile in a negatively charged solid matrix, while the presence of positive patches of Fe hydro (oxide) on the surface of negatively charged solid matrices (QS) decreased OMCG colloids mobility. The positive patches of Fe hydro (oxide) on the surface of QS led to retention of colloid in the primary minimum. The decrease in the mobility of OMCG colloids was more in the disturbed natural soil materials. It was due to increasing in the amount of hydro (oxides) of Fe and Al on the surface of disturbed natural soil. Electrostatic attractions between OMCG colloids and solid matrices had an increasingly trend with the amount of hydro (oxides) of Fe and Al on the surface of solid matrix. Prediction of OMCG colloids mobility with DLVO theory showed that the height of energy barrier decreased with less mobility of OMCG colloids in the solid matrix. The decrease in the mobility of OMCG colloids was due to reducing in the height of energy barrier in the interaction energy curves. (Fig. 5). This observation fitted clearly to the finding of Tosco et al. (2012) and Carstens et al. (2018) regarding decrease in the mobility of inorganic colloids with increase in the amount of hydro (oxides) of Fe on the surface of solid matrix. Hence, the results showed DLVO theory was able to predict the electrostatic interactions between OMCG colloids and solid matrix. Fits to H5, DLVO interactions is able to predict control mobility of OMCG colloids in the solid matrix.

DLVO theory was able to predict mobility of OMCG colloids in the solid matrix with changes in concentration of solution. The result in study III and IV (Fig. 6 and 2, respectively) showed that with addition of Pb^{2+} in the suspension, OMCG colloids mobility decreased due to decreasing in the electrical double layer thickness. Changes in the thickness of electrical double layer showed in the depth of secondary minimum. The results showed that the depth of secondary minima decreased with addition of Pb^{2+} in the suspension of OMCG colloids. This result agrees with studies Brinker and Scherer (1990) and Tosco et al. (2012) who observed the same increasing effect of addition of cationic elements in the suspension decreased mobility of goethite colloids. Thus, with increasing in the concentration of solution with addition of Pb^{2+} ionic strength increased from 0.91mM to 1.045mM. The depth of secondary minimum increased in the higher ionic strength in the solution. Deeper secondary minimum led to higher retention of OMCG colloids on the solid matrix.

The results in study I demonstrated that the depth of secondary minimum changed with changes on surface roughness of OMCG colloids. The results showed that colloids with different amount of OM coating showed different breakthrough behaviors (Study I, Fig. 1). Changes in the breakthrough behavior of OMCG colloids was attributed to different nanoscale roughness properties. A higher nanoscale roughness resulted in to higher OMCG colloids mobility in the solid matrix. DLVO theory was able to able to predict increase in the mobility of OMCG colloids through changes in the secondary minimum. A decrease in the depth of secondary minimum occurred in the colloids with higher nanoscale roughness that led to releasing of OMCG colloids in the solid matrix (Study I, Fig. 5). Changes in the depth of secondary minima in the different concentrations of OM coating on the goethite observed in the study Carstens et al (2021). Their reports showed that higher OM coating on the goethite colloids decreased the depth of secondary minima and led to release colloids into solution. Hence, it can be concluded colloid mobility not only is affected by electrostatic interaction of the solid matrix but also physico-chemical properties of solid matrix controlled colloid mobility. The results fit clearly to H6, the capability of soil to retain OMCG colloids on the surface is higher for the colloids with lower nanoscale roughness height.

Summarizing, the prediction of OMCG colloids mobility in the solid matrix controlled by, i.e. electrostatic interactions between OMCG colloids and solid matrix, changes in the ionic strength of solution and also physico-chemical properties of the surface of solid matrix had a decreasing effective on Mobility of OMCG colloids in the solid matrix. All of these changes on OMCG colloids mobility were predicted by DLVO theory.

7. Conclusions

This thesis evaluated the OM potential to form complexes with goethite colloid and provided extensive physio-chemical evidences on transport and retention of colloid in the solid matrix. Forming complexes and transport and retention of colloid in the solid matrix affect the determination of the Pb^{2+} mobility mechanism under experimental conditions.

OMCG colloid mobility depends on the microscale roughness, surface charge heterogeneity of the solid matrix, and nanoscale roughness of OMCG colloids. Mobility and retention of OMCG colloids on the solid matrix was related to fast or slow deposition under flow conditions. Fast depositions occurs on the surface with charge heterogeneity under continuous flow conditions, while slow deposition was a retention on the microscale roughness of the surface under flow interruption. The properties of nanoscale roughness of colloids determine that higher colloid retention on the solid matrix occur in the colloids with lower nanoscale roughness height. Classical DLVO theory clearly shows decreasing depth of secondary minimum in colloid with lower nanoscale roughness height, which lead to higher retention on the solid matrix.

The evaluation of DOM retention in a disturbed natural soil material was conducted under continuously water saturated condition and in drying-rewetting cycles. The results show that during the drying cycle, with increasing soil water repellency, there was a preferential retention of hydrophobic components on the solid matrix, while hydrophilic components were released in the outflow. This occurred because hydrophobic components turn toward pore space and hydrophilic components turn toward soil mineral, hence the later component can be easily released in the outflow. The mechanism of retention and release was also related to making DOM components complex with solid matrix through either inner-sphere complex or outer-sphere complex. The former complex was between hydrophobic components and the solid matrix and later complex between hydrophilic components and the solid matrix. Hence, hydrophobic components were retained more strongly than hydrophilic components. However, the second cycle of drying-rewetting likely formed multilayer OM coating structures on the surface. In the second cycle of drying-rewetting, OM retention was related to prior OM loading on the surface. At higher previous soil OM loading, hydrophilic components retained on the surface, while again there was a preferential retention of hydrophobic component on the surface with lower previous soil OM loading. However, under continuous water saturation, which rarely happens under natural conditions, the leached DOM in the outflow became enriched in hydrophilic components.

The importance of Pb^{2+} and colloidal Pb mobility in the solid matrix was inferred from the role of DOM on the mobility mechanism. The results show less Pb^{2+} mobility in the presence of highly mobile colloids in the solid matrix. The study revealed that coating of OM on the solid matrix and goethite colloid, decreased Pb^{2+} mobility through making complex with Pb^{2+}. However, comparing the Pb^{2+} mobility in the model sand (QS, GCQS) and in a disturbed natural soil show less mobility of Pb^{2+}, OMCG colloid, and colloidal Pb, in a disturbed natural soil material than model sand. This is because of increasing concentrations of sesquioxides and heterogeneities in a disturbed natural soil. The interesting findings about Pb^{2+} mobility was related to re-mobilization of Pb^{2+} from the surface of solid matrix. This depends on making complex of Pb^{2+} and surface. Strong retention of Pb^{2+} on GCQS surface with highly crystalline Fe lead to releasing very small amounts of Pb in the outflow compared to disturbed natural soil.

In conclusion, the results clearly show the important role of DOM on the mobility of OMCG colloids and Pb^{2+}. However, the mechanism of mobility became clearer when parameters like physical and chemical heterogeneity of the solid matrix and flow conditions were considered. Formation of Pb^{2+} complexes with OM decreased mobility of colloidal Pb in the presence of high mobile colloids. DLVO theory clearly predicted OMCG colloids mobility with changes in the physico-chemical conditions of solid matrix and chemical properties of solution.

8. Outlook and future work

Based on the current conducted studies, none of the stated hypotheses had to be rejected, but the future study could examine the following modifications.

In the first study, for determining the relative importance of chemical and physical heterogeneities on colloid mobility measure of size, shape and height of heterogeneities are essential parameters for prediction of OMCG colloids mobility via DLVO theory.

In the second study, in order to determine OM retention similar to natural conditions on the solid matrix. Measuring the degradation of the microbial soil community of DOM should be considered under experimental conditions. It could help to minimize the possible assumption of the effect of DOM decomposition on mobility and retention of OM on the surface of solid matrix.

In the third study, a further experimental variation for assessing mobility and retention of colloidal Pb is, conducting column experiments with measuring an equilibration time between Pb^{2+} with OMCG colloids and solid matrix. This would be a factor for determination of mobility of Pb^{2+} with OMCG colloids over a period of time.

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