COLLOID-FACILITATED TRANSPORT OF CATIONS IN AN UNSATURATED FRACTURED SOIL UNDER TRANSIENT CONDITIONS

by

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A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirement for the degree of
Doctor of Philosophy
Department of Civil, Environmental and Architectural Engineering
2011

This thesis entitled:

Colloid-facilitated transport of cations in an unsaturated fractured soil under transient condition

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Date 11/28/2011

The final copy of this thesis has been examined by the signatories, and we
Find that both the content and the form meet acceptable presentation standards
Of scholarly work in the above mentioned discipline.

ABSTRACT

Mohanty, Sanjay Kumar (Ph. D., Civil Engineering)
Colloid-facilitated transport of cations in an unsaturated fractured soil under transient condition
Thesis directed by Professor Joseph N. Ryan

Rainfall experiments were conducted using intact soil cores and an instrumented soil pedon to examine the effect of physical heterogeneity and rainfall characteristics on the mobilization of colloids, organic matter, cesium, and strontium in a fractured soil. To measure the spatial variability of infiltration of colloids and contaminants, samples were collected through a 19-port grid placed below the soil core in laboratory study and in 27 samplers at multiple depths in the soil pedon in the field study. Cesium and strontium were applied to the soil cores and the soil pedon prior to mobilization experiments. Rainwater solutions of multiple ionic strengths and organic matter concentrations were applied to the soil cores and soil pedon to mobilize in situ colloids, cesium, and strontium.

The mobilization of colloids and metal cations occurred through preferential flow paths in the soil cores. Compared to steady rainfall, greater amounts of colloids were mobilized during rainfall interrupted by pauses, which indicates that the supply of colloids to be mobilized was replenished during the pauses. A maximum in the amount of mobilized colloids were mobilized during a rainfall following a pause of 2.5 d. Pauses of shorter or longer duration resulted in less colloid mobilization. Freeze-thaw cycles, a transient condition in winter, enhanced colloid mobilization and colloid-facilitated transport of cesium and strontium in the soil cores. The exchange of solutes between the soil matrix and macropores caused a hysteretic mobilization of colloids, cesium, and strontium during changes in ionic strength. Colloid-facilitated mobilization of cesium and strontium was important at low ionic strength in fractures where slow flow allowed greater exchange of flow between the fractures and the surrounding matrix. The release of cesium and strontium by cation exchange occurred at high ionic strength in fractures where there is a little exchange of pore water with the surrounding matrix. The results of the field experiment suggested that ion exchange, and not organic matter- or colloid-facilitated transport, was the dominant mechanism for mobilization of cesium and strontium through the macropores of the fractured soil.

This work is dedicated to my wife

Jharana

for standing by me when things are not perfect.

ACKNOWLEDGEMENTS

> "By three methods we may learn wisdom: first, by reflection, which is noblest; second, by imitation, which is easiest; and third by experience, which is the bitterest."
>
> -- Confucius

I was fortunate to learn through all these three methods by just being around my advisor, Prof. Joe Ryan. He has made my learning experience very enjoyable and motivational. I will always remember Joe for his unique ability to ask insightful questions that bring the best out of me. Discussions and meeting with Joe helped me reflect on my approach that led to develop my research hypotheses. His patience and comments on my writing were vital for successful completion of my dissertation. In addition to professional development, I am indebted to Joe for inspiring in me, a positive approach to my academic and personal life. He is the mentor I have ever longed for.

The journey to get my doctoral degree would not have been this incredible without the insightful comments and guidance from the other four committee members. The enthusiasm that Prof. Alexis Templeton showed in "Geomicrobiology" class helped me look beyond my research and learn more about microbial process related to the scope of my doctoral study. Prof. Harihar Rararam was instrumental in teaching me the flow of water through porous media - a key component in developing most hypotheses in my dissertation. I was able to broaden the scope of my research work due to the thoughtful comments from Prof. Diane McKnight. My understanding on the transport of organic matter would have been incomplete without the guidance from Dr. George Aiken from the United State Geological Survey (USGS), Boulder, CO.

Soil core sampling and field experiment was completed because of arduous efforts from many personnel at the University of Colorado and the Oak Ridge National Laboratory (ORNL), Tennessee. I am grateful for the generous help from Prof. Joseph Ryan, Timothy Dittrich, Marc Serravezza, Tonia Mehlhorn (ORNL), and Dr. Phillip Jardine (ORNL) to collect soil cores. Field experiments were feasible due to the timely help from Prof. Joseph Ryan, Audrey Norvell, Brett Poulin, David Metge (USGS), Prof. James Saiers (Yale University), Jana Philips (ORNL), Dr. Scott Brooks (ORNL).

I am thankful to Vivy Mei Mei Dong and Kenna Butler (USGS) for analyzing samples for dissolved organic carbon. I deeply appreciate Dr. Dennis Eberl's help the X-ray diffraction analysis of colloids and soil samples. An incomplete list of the important people to whom I owe debts of gratitude include Alison Craven, Jeffrey Writer, Chase Gerbig, Jack Webster, Tesfayohanes Yacob, Aditya Kausik, Arvind Mohanram, Suraj Thiagarajan, Gopi Krishnan, Shriram Santhanagopalan, Himansu Sahoo, Yanling Li, Atiim Senthill, and Nicole Scheman. Their support at different times in graduate school was valuable.

With no further promises but with some guilty feelings, I would like to thank my parents, Saraswati Mohanty and Sudarsan Mohanty, for their patience, understanding, and encouragement. Despite being thousands of miles away, they never overlooked a single opportunity to provide me with the tools necessary to succeed in every aspect of my life. Finally, I would have taken decade to finish my doctoral degree without the sacrifices, support, and love from my wife, Jharana Dhal. I am grateful for each contribution she made to my life, with and without my knowledge.

This research was supported by the Department of Energy through grant DOE-FG02-08ER64639

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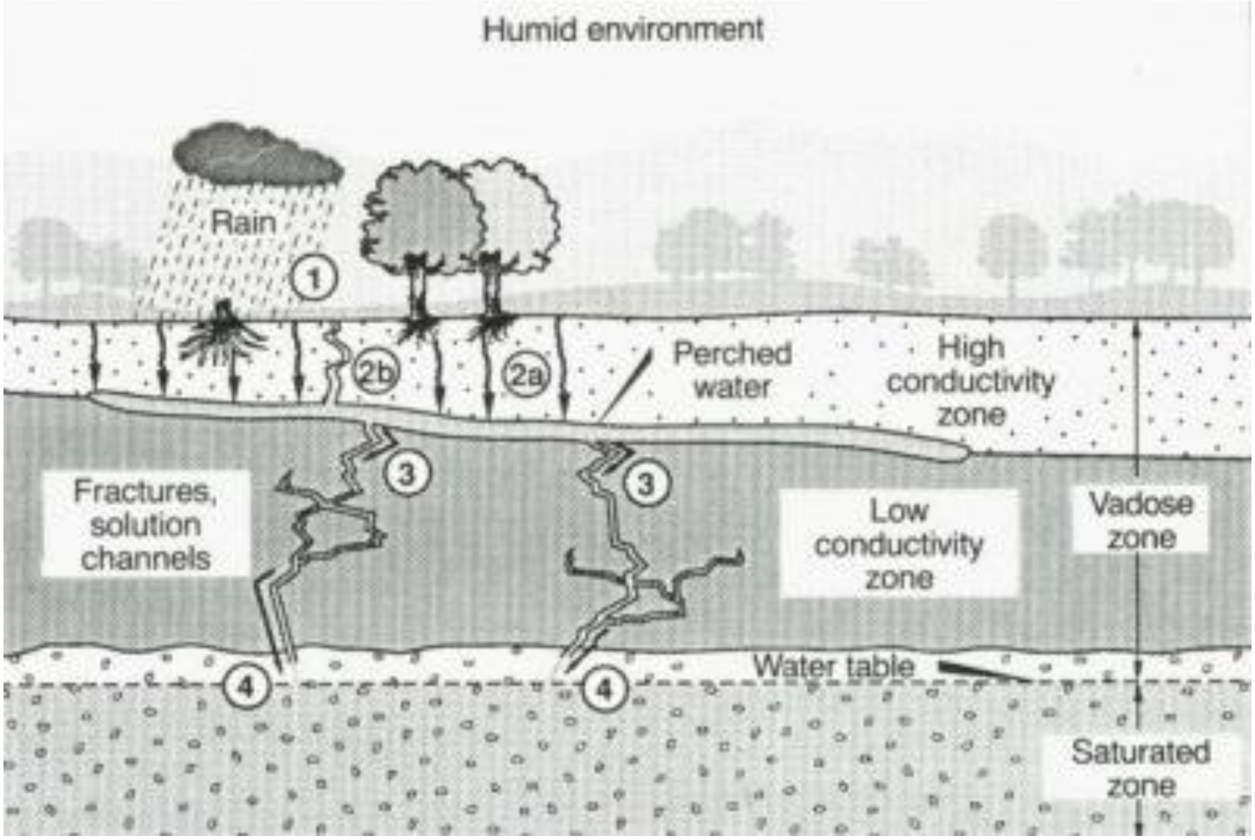
CHAPTER 1

UNDERSTANDING THE TRANSPORT OF COLLOIDS AND CONTAMINANTS IN HETEROGENEOUS SOILS UNDER TRANSIENT CONDITIONS



An illustration of contaminant transport process in vadose zone

Subsurface contaminant transport: An historical perspective

Industrial waste containing heavy metals and radionuclides poses a serious threat to the terrestrial ecosystem as well as the subsurface environment. More than six billion cubic meters of soils are contaminated with radionuclides, metals, and organic solvents at facilities of the U.S. Department of Energy (DOE, 2006). Loosely-bound contaminants infiltrate through soil by rainwater and contaminate the groundwater sources. Contaminated groundwater can pose serious risks to public health through drinking water exposure. Protection of groundwater requires us to improve our understanding of the processes that mobilize contaminants in the vadose zone. This chapter is focused on the transport processes of radioactive cations that are commonly found at waste disposal sites.

Contaminant transport in vadose zone: Infiltrating rain transports contaminants from waste disposal sites into unsaturated soil layers through fractures and soil matrix (Figure 1.1). The transport processes responsible for the migration of radioactive cations through soils are advection and dispersion. Hydraulic conductivity, grain-size distribution, and moisture content of soils can affect these transport processes. At lower moisture content, most pores are disconnected and water can by-pass a larger portion of soil matrix through preferential channels (Pace *et al.*, 2003; Allaire *et al.*, 2009). During high flow or intense rainfall, radioactive cations can move faster within these preferential channels (Cey *et al.*, 2009). Therefore, soil heterogeneity plays an important role in dictating the flow path of rain water as well as fate of contaminants dissolved in rain water (Simunek *et al.*, 2003; Jarvis, 2007).

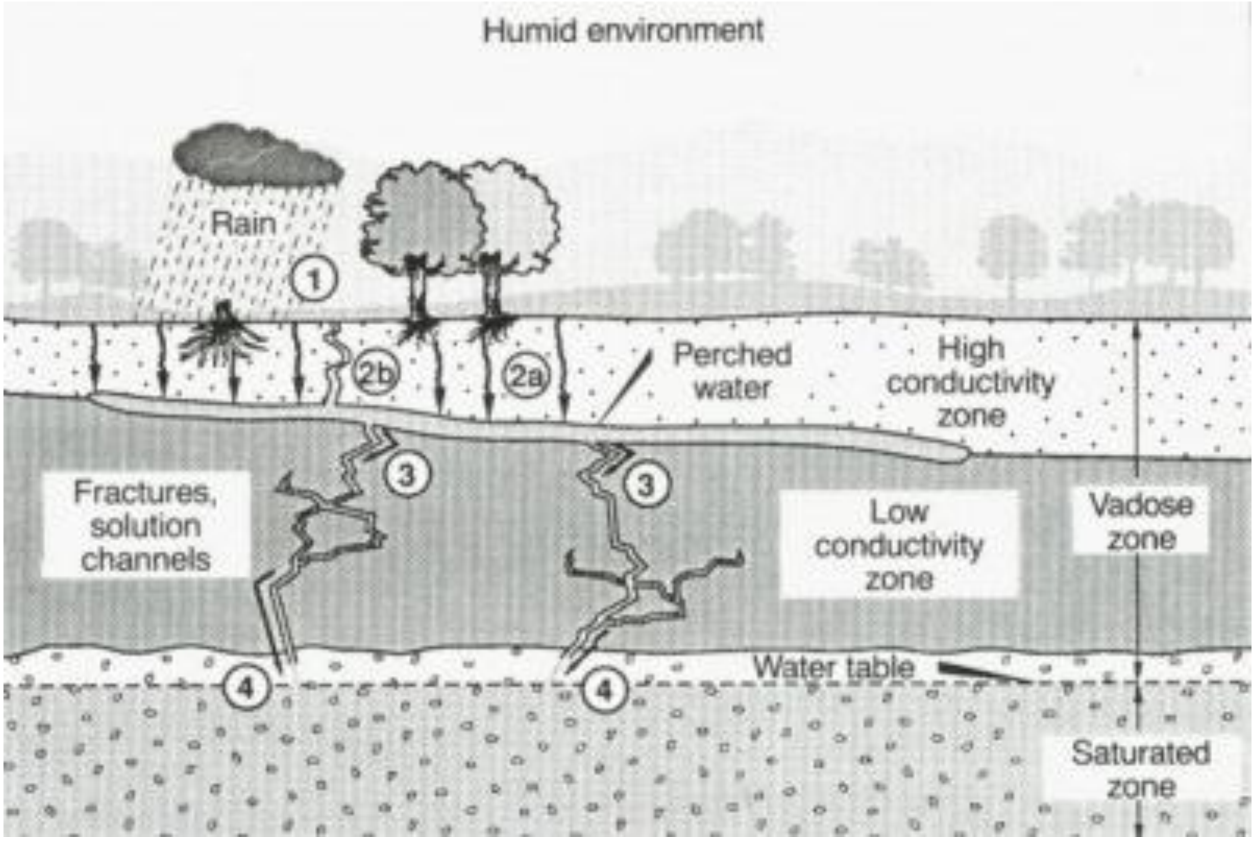


Figure 1.1. Transport of contaminant through vadose zone (McCarthy and Zachara, 1989). The pathways of contaminants in water were depicted according to regions: (1) rainwater on surface, (2) advection in fracture (a) or matrix (b) in high conductive zone, (3) flow through fractures in low conductivity zone connecting perched water and ground water, and (4) groundwater.

Contaminants are removed from solution by adsorption on soil – particularly, on soil components with high surface area, like clays, metal oxides, and soil organic matter. Adsorption, or sorption, occurs through multiple mechanisms that include phase partitioning to nonspecific sites and complexation to specific sites. For non-specific sorption, van der Waals attraction and hydrophobic bonding are major driving forces. Hydrogen bonding, charge transfer, ion exchange, and ligand exchange are the major driving forces for specific adsorption. For some contaminants and soils, adsorption occurs by combinations of these mechanisms. The strength of adsorption depends on characteristic of contaminants, properties of the adsorption sites, and geochemical conditions of the water. Chemical parameters, including organic matter concentration, cation exchange capacity, pH, ionic strength, and redox potential, affect the adsorption of contaminants on soil.

Distribution coefficients measured in laboratory experiments have been traditionally used to estimate the absorption capacity of soils at equilibrium. The distribution coefficient K_d is a ratio of the concentration of a contaminant in the soil (q) and the concentration of a contaminant in water (C_{aq}) (Equation 1).

$$K_d = \frac{q}{C_{aq}} \qquad (1)$$

Contaminants move slowly compared to the water by a factor (R_f) known as retardation factor (Equation 2). The retardation factor for a specific contaminant is estimated by using the distribution coefficient of the contaminant and the bulk density (ρ_b) and porosity (θ) of the soil.

$$R_f = 1 + \frac{\rho_b}{\theta} K_d \qquad (2)$$

Using this traditional approach, the migration of contaminants has been underestimated due to inaccurate estimation of distribution coefficients of contaminants with soils (Means *et al.*, 1978; Coles and Ramspott, 1982; Kersting *et al.*, 1999; Novikov *et al.*, 2006). Failure of the distribution coefficient and retardation to accurately estimate the migration of contaminants led to recognition of a third phase of contaminants – a mobile phase bound to colloids or organic matter.

Contaminant transport by colloids and organic matter: Colloids are fine particles that stay suspended in water. The typical size range of colloids is from 10 nm, where the distinction between colloids, clusters, and polymers becomes indistinct, to about 10 µm, where colloids are readily removed from suspension by settling. Colloids are generally composed of metal oxides, clay minerals, and organic matter (McCarthy and Zachara, 1989; Ryan and Elimelech, 1996; DeNovio *et al.*, 2004). Contaminants move in water in association with colloids and organic matter (Gabrieli, 1953; Buddemeier and Hunt, 1988). The fate and transport of contaminants is governed by complex interactions among competing cations, soil minerals, colloids, and organic matter (Figure 1.2). In order to understand how colloids and organic matter enhance the transport of contaminants, transport mechanism of colloids and organic matter in soil must also be understood.

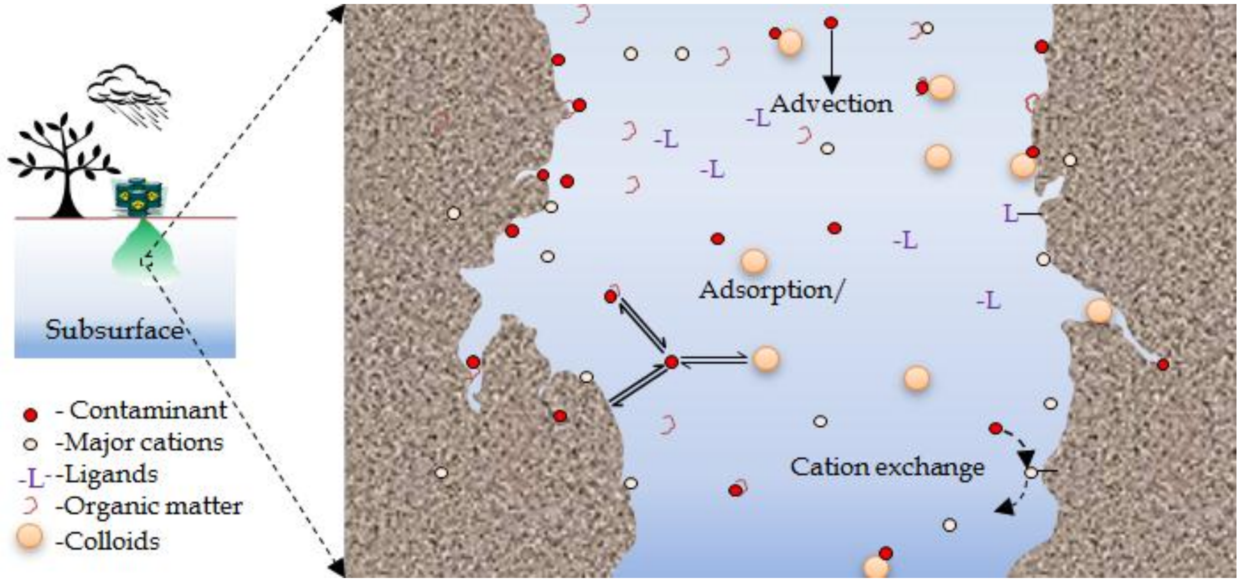


Figure 1.2. Schematic of coupled processes during transport of cations in the subsurface environment. Cation exchange and colloid- and organic matter-facilitated transport may occur to mobilize the contaminants from soil.

Transport of contaminants with colloids and organic matter

Colloid- or organic matter-facilitated transport is important when three conditions are met (McCarthy and Zachara, 1989; Ryan and Elimelech, 1996; DeNovio *et al.*, 2004):

(1) Colloids or organic matter must be present in abundance.

(2) Colloids or organic matter must be move faster than the contaminants.

(3) Contaminants must absorb strongly to and desorb slowly from the colloids or organic matter.

Mobilization and transport of colloids in soil: The first condition for colloid-facilitated transport to be important is that colloids are abundant. For colloids to be abundant, they must be mobilized from the soil into the pore water. There are physical (erosion, shear force from flow) and chemical (decreasing ionic strength, increasing pH, increasing organic matter) processes that contribute to the mobilization of colloids in soils. Erosion caused by the impact of rain drops and runoff with the soil surface generates colloids (Tinnacher and Honeyman, 2010). Colloids are also generated due to drying of soil pores. Increasing capillary pressure during drying of soil can crumble the pore wall to produce colloids (Majdalani *et al.*, 2008; Michel *et al.*, 2010). A decrease in ionic strength occurs concomitantly with flow transients, where the repulsive forces between colloids and mineral grains increase (Gamerdinger and Kaplan, 2001; Gao *et al.*, 2004). Under this condition, colloids are released from the soil surface (Ryan and Gschwend, 1994; Gao *et al.*, 2004; Zhuang *et al.*, 2010).

Several recent investigations in the laboratory have shown that transient flow mobilizes more colloids compared to steady flow (Saiers and Lenhart, 2003; Zhuang *et al.*, 2007; Majdalani *et al.*, 2008). The steady-state condition is not always adequate to represent field scenarios. The transient nature of a rainfall event is reflected by fluctuations of the infiltration rate and soil moisture profile during and after a rainfall event. Increasing rainfall frequency (Zhuang *et al.*, 2007) and pauses between rainfalls (Majdalani *et al.*, 2008) mobilize more colloids compared to steady-state rainfall conditions. Transients in flow promote the mobilization of colloids through multiple mechanisms: shear, viscous drag, and changes in the air-water configuration. Colloids are released by shear forces that arise from flow rate increases during imbibition (Laegdsmand *et al.*, 1999; Saiers *et al.*, 2003). Expanding water films and a decrease in the capillary forces during imbibition release colloids attached to the solid-water interface (Saiers *et al.*, 2003; Gao *et al.*, 2006).

The second condition for colloid-facilitated transport to be important is that colloids must be transported through soil faster than the contaminants whose transport they may be facilitating. Advection and dispersion are considered to be the primary transport mechanisms of colloids in unsaturated soils under steady-state conditions in the laboratory (Zhuang *et al.*, 2004; Torkzaban *et al.*, 2008) as well as in the field (Vilks *et al.*, 1997; Möri *et al.*, 2003; Goeppert and Goldscheider, 2008). The pore-scale physical heterogeneity of soil influences the flow and transport of colloids by moving colloids through preferential flow paths in heterogeneous soils (Kjaergaard *et al.*, 2004).

The transport of colloids in soils is limited by their removal from pore waters through multiple mechanisms: (1) deposition at solid-water or air-water interfaces, (2) straining at narrow pore throats, and (3) capture in water films of decreasing thickness during soil drying. Attachment of colloids from solution on soil surfaces as well as on the interfaces between soil, water and air is governed by electrostatic, hydrophobic, and capillary forces (Wan and Wilson, 1994; Wan and Tokunaga, 1997; Schafer *et al.*, 1998). These forces are influenced by moisture content, pH, ionic strength and surface roughness (DeNovio *et al.*, 2004). For example, a decrease in moisture content results in a higher rate of colloid removal (Wan and Wilson, 1994; Lenhart and Saiers, 2002). Increases in ionic strength suppress the electrostatic repulsion between charged surfaces and increase the colloid deposition rate (Saiers and Lenhart, 2003; Torkzaban *et al.*, 2010). Straining involves the retention of colloids in a region where the width of flow path is smaller than the diameter of colloids. Colloids are deposited in the narrow pore throats near grain to grain contact point (Bradford *et al.*, 2003). Colloids are also deposited at the air-water-solid contact within pendular rings of unsaturated pores (Crist *et al.*, 2004). Capillary force holds colloids at air-water interfaces where the thickness of water film is less than colloid size (Wan and Tokunaga, 1997). Therefore, the removal of colloids from pore waters depends on rainfall characteristic and soil heterogeneity that control moisture content in soil.

Mobilization and transport of organic matter in soil: The first condition for organic matter-facilitated transport to be important is that organic matter must be present at sufficiently high concentrations to bind the contaminants that they will facilitate. This condition requires that the organic matter be mobilized from soil to pore water. Both physical (high flow, increasing temperature) and chemical processes (pH, ionic strength, redox potential) contribute to the mobilization of organic matter in the subsurface environment. Xu and Saiers (2010) demonstrated that changes in the intensity and frequency of rainfall affected the mass of organic matter mobilized, while changes in temperature and drought period affected the mass and structure of organic matter mobilized. Transients in temperature, such as freeze-thaw cycles, also liberate greater quantity of soil organic matter compared to a heavy rainfall event (Dudal *et al.*, 2005). Adsorbed organic matter is displaced by hydroxide and released into solution at high pH (Kaiser and Zech, 1999; Zhao *et al.*, 2011). Organic matter attached to the air-water interface can be released in response to pH perturbations (Lenhart and Saiers, 2004). Ionic strength has no effect on the mobilization of organic matter as long as the solution does not contain any ions that can either compete or form complexes with organic matter (Kaiser and Zech, 1999; Reemtsma *et al.*, 1999; Artiola and Walworth, 2009). Organic matter is also mobilized under reducing conditions due to reductive dissolution of ferric iron- or manganese (III, IV)-containing minerals (Hagedorn *et al.*, 2000).

The second criterion for organic matter-facilitated transport to be important is that the organic matter must move faster and farther than contaminants in the subsurface environment. Organic matter moves though soil pores through advection and dispersion. Unlike colloids, organic matter passes through soil matrices where colloids are filtered owing to their larger size (Kaiser and Zech, 1998).

The transport of organic matter is reduced due to electrostatic interaction, anion exchange, or surface complexation, and hydrophobic interaction of organic matter with minerals in soil (Jardine *et al.*, 1992; Kothawala *et al.*, 2008). Surface functional groups of organic matter are electrostatically attracted towards positively-charged mineral surfaces (Kaiser *et al.*, 1997; Evanko and Dzombak, 1998). The adsorption of organic matter to mineral surface occurs through ligand exchange reactions between carboxylic acid groups on organic matter and hydroxylated surface sites on the minerals (Gu *et al.*, 1995; Joo *et al.*, 2008; Vreysen and Maes, 2008; Schneider *et al.*, 2010). The same sites on organic matter could bind metals (Davis, 1984; Nelson *et al.*, 1985; Helal *et al.*, 1998). Organic matter, such as humic acids and fulvic acids, is preferentially adsorbed onto Mg/Al layered double hydroxides because these fractions can access small pores and form ligand exchange reactions with surface hydroxide groups (Vreysen and Maes, 2008). Ligand exchange by carboxylic acid is not favorable in soils that are typically negatively charged. In this case, soils preferentially bind organic matter with higher molecular weight, possibly due to increase in hydrophobic interaction (Guo and Chorover, 2003). The surface charges of soil or minerals are sensitive to pH of pore water. Adsorption of organic matter on mineral surfaces decreases as pH increases (Oste *et al.*, 2002; Illes and Tombacz, 2003). Organic matter also adsorbs at air-water interface when the pH of pore waters decreases (Lenhart and Saiers, 2004). At an ionic strength of 0.1 M or above, the structure of organic matter changes to a more compact form due to the suppression of the surface charges by steric hindrance. In this more compact configuration, more organic matter adsorbs onto a given area of soil surface (Murphy *et al.*, 1992; Drotz *et al.*, 2010).

Association of contaminants with colloids and organic matter: The third condition for colloid- or organic matter-facilitated transport is that contaminants must desorb slowly from colloids or organic matter relative to travel time. Weak and readily reversible adsorption of cations to colloids will decrease the importance of colloid-facilitated transport because cations will desorb from colloids and adsorb to immobile soil surfaces as the cations are carried away from their source (Vilks *et al.*, 1993; Roy and Dzombak, 1998). The Damkohler number (*Da*), a ratio of transport time to reaction time, is used to elucidate the effect of desorption kinetics on the facilitated transport of radioactive cations (Bold *et al.*, 2003; Turner *et al.*, 2006):

$$Da = \frac{t_{travel}}{t_{reaction}} = \frac{t_{travel}}{t_{desorption}} = \frac{L}{U} \cdot k_{desorption} \qquad (3)$$

where t_{travel} is the time of travel, $t_{reaction}$ is the characteristic time associated with reaction, $t_{desorption}$ is the time associated with a desorption reaction, L is the transport length, U is the velocity at which the contaminant is moving, and $k_{desorption}$ is the rate coefficient for the desorption reaction. A Damkohler number larger than 1 corresponds to longer transport time or residence time compared to the reaction time. Cations with low Da (< 0.01) with respect to colloid-cation interactions are suitable for facilitated transport. Slow desorption of cations from colloids makes facilitated transport more effective in saturated column experiments (Vilks and Baik, 2001; Liu *et al.*, 2003; Turner *et al.*, 2006) and a field study (Missana *et al.*, 2004). In a saturated experiment using organic matter, a slowly desorbing cation (Pb) was observed to travel faster through a column compared to a readily desorbing cation (Zn) (Schmitt *et al.*, 2003). Research evaluating the importance of desorption kinetics on the facilitated transport of cations in unsaturated media remain scant.

The strength of adsorption of cations to colloids or organic matter depends on whether adsorption occurs through the formation of either inner-sphere or outer-sphere surface complexes or the simple accumulation of an ion swarm near the colloid surface without complex formation (Xu and Saiers, 2010). For example, Cs^{+} forms stronger surface complexes with illite by ion exchange and inner-sphere complexation to frayed-edge (surface hydroxyl) sites, whereas Sr^{2+} binds with illite by ion exchange only. The transport of readily desorbing Sr^{2+} is not effectively facilitated by colloids compared to slowly desorbing Cs^{+} (Turner *et al.*, 2006). Colloid-facilitated transport of Cs^{+} was also observed due to transient in flow condition, where the cesium peak was found to coincide with colloids mobilized after consecutive rainfall events (Sigurgeirsson *et al.*, 2005).

Knowledge gaps in the previous studies

Previous studies have improved our understanding of colloid- and organic matter-facilitated transport of radioactive cations. Due to the inherent complexities faced under field conditions, the results obtained from laboratory studies may not accurately describe the actual processes that occur during the transport of radioactive cations (Pace *et al.*, 2007; Mitsunobu *et al.*, 2008). The complexities of natural systems arise due to the increase in scale, the heterogeneity of the medium, and the transient conditions pertaining to rainfall events. Continued advances in our understanding of colloid- and organic matter-facilitated transport research require a shift in focus from ideal homogeneous systems to non-ideal heterogeneous systems and a corresponding transition from laboratory-scale to field-scale under transient flow conditions. The shortcomings of previous studies are described elaborately below.

Role of transient conditions: Recent studies in the laboratory have demonstrated the importance of transient conditions on the mobilization of colloids from soils (Zhuang *et al.*, 2007; Majdalani *et al.*, 2008). Under transient conditions, colloids are mobilized due to scouring by moving air-water interfaces (El-Farhan *et al.*, 2000), release by thin-film expansion (Gao *et al.*, 2006), reconnection of stagnant-water zones with bulk-water flow (Schelde *et al.*, 2002), and increases in shear forces (Kaplan *et al.*, 1993). The importance of any mechanism is sensitive to physical and chemical heterogeneity of soil (Jacobsen *et al.*, 1997; Vilks and Baik, 2001; Kjaergaard *et al.*, 2004; Rousseau *et al.*, 2004; Levin *et al.*, 2006; Mishurov *et al.*, 2008; Cey *et al.*, 2009). Few studies have been conducted to understand the mechanism of colloid mobilization through heterogeneous soil under transient conditions (Schelde *et al.*, 2002; Majdalani *et al.*, 2007; Majdalani *et al.*, 2008). Michel *et al.* (2010) suggested that differential capillary pressure across wall separating macropores and micropores could break pore walls and generate colloids (Figure 1.3). The differential capillary pressure depends on pore size as well as moisture content of soil after a pause. However, the role of moisture content and heterogeneity is not addressed in the previous research. It is not clear why colloids are mobilized in higher amount after a pause between rainfalls. Colloids were replenished due to pause in rainfalls. The effect of pause on total amount of colloids released was varied in previous studies (Schelde *et al.*, 2002; Majdalani *et al.*, 2008). Schelde *et al.* (2002) observed higher mobilization of colloids with increases in pause duration, whereas Majdalani *et al.* (2008) found a decrease in colloids after 8.1 d of pause. Schelde *et al.* (2002) found the supply of colloids not limiting due to time-dependent and diffusion-limited mobilization colloids from stagnant water. Majdalani *et al.* (2008) found the supply of colloids limiting when pause was more than 8 d. A decrease in the mobilization of colloids with longer pause was attributed to increase in cohesion of colloids to soil minerals by inter-particle bridging and capillary trap at thin water film. More experiments are needed to examine the mechanism of colloid mobilization during pauses. Results of laboratory studies under transient conditions have not been verified at the field scale.

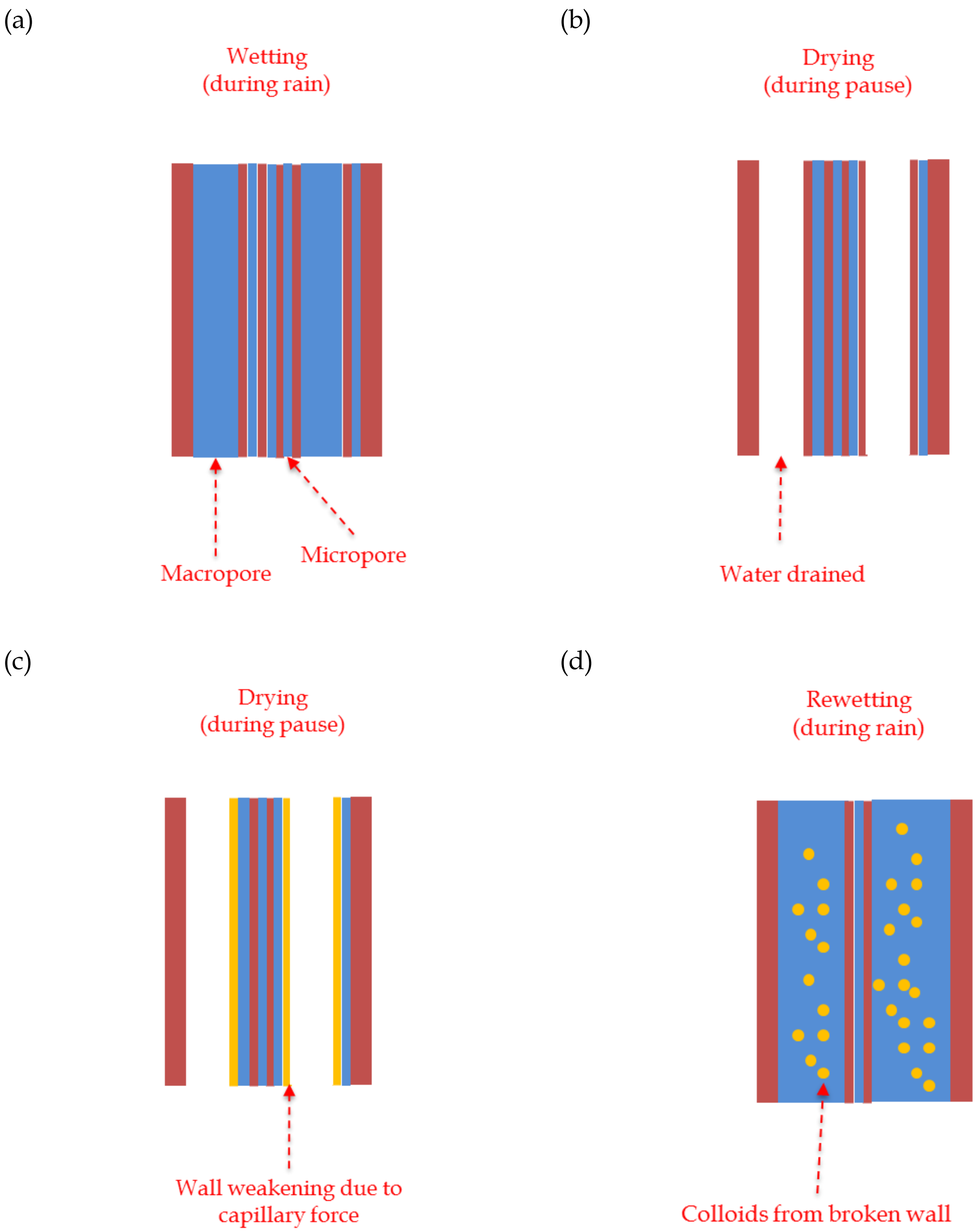


Figure 1.3. A conceptual model showing the mobilization of colloids due to differential capillary pressure generated during wetting and drying of pores: (a) macropores and micropores are filled with water during rain, (b) water in macropores drains due to low capillary tension, (c) differential capillary pressure weakens the walls separating macropores and micropores, and (d) weakened wall breaks and colloids are mobilized during wetting cycle [modified from Michel *et al.* (2010)].

Previous studies have not addressed the mobilization of colloids during snowmelt, which can be considered another type of transient condition. In winter, flow transients occur during cycles of freezing and thawing. Analogous to evaporation in dry seasons, the liquid water content decreases in soils during winter due to the formation of ice. During freezing, water expands to form ice, and the expansion creates cracks in the soil pores. Water in large pores freezes before the water in matrix due to the absence of capillary tension. This causes the water to move from the soil matrix to macropores, which causes capillary stress in the pores of matrix (Hohmann, 1997) – the same kind of capillary stress considered to mobilize colloids during drying cycles in soils (Michel *et al.*, 2010). Few studies have demonstrated a decrease in stability of aggregates due to freezing (Lehrsch *et al.*, 1991; Oztas and Fayetorbay, 2003). Destabilization of soil aggregates could generate colloids that can be mobilized during infiltration events that follow soil thawing. These processes could expose contaminants in the soil matrix that are otherwise immobile (Niven and Singh, 2008). To date, the effect of freeze-thaw cycles on the mobilization of colloids and colloid-associated contaminants is not quantified.

Heterogeneity of soil: The role of heterogeneity on colloid transport has not been properly investigated even though most soils are naturally heterogeneous with respect to mineral components (geochemical heterogeneity) and pore sizes (physical heterogeneity) (Ryan and Elimelech, 1996). Preferential flow paths exist in natural soils due to the differences in grain-size distribution, cracks, fissures, biopores (earthworm burrows, root channels) and wetting front instabilities (Flury *et al.*, 1994; Bundt *et al.*, 2001). Knowledge of chemical and physical heterogeneity is required for accurate simulation of the transport of colloids in the vadose zone (Bradford and Torkzaban, 2008). The effects of chemical heterogeneity have been studied in previous studies (Elimelech *et al.*, 2000; Chen *et al.*, 2001; Schumacher *et al.*, 2005).

The effects of physical heterogeneity on colloid transport have been studied in saturated sand (Saiers *et al.*, 1994; Bradford *et al.*, 2002), unsaturated sand (Mishurov *et al.*, 2008), and soils in laboratory (Jacobsen *et al.*, 1997; Kjaergaard *et al.*, 2004) as well as field studies (Mailloux *et al.*, 2003; Cey *et al.*, 2009). Multiples peaks have been observed in the breakthrough of colloids due to combined contribution of macropore and matrix of soil. These studies did not investigate the effect of exchange between macropore and matrix on colloid transport. In order to quantify the exchange between macropore and matrix, water samples must be collected from different regions of soil (Aggelopoulos and Tsakiroglou, 2008). An exchange of solutes among pores of different sizes will occur due to hydraulic gradient (physical non-equilibrium) and concentration gradient between both regions (chemical non-equilibrium). A difference in bromide peaks between macropores and the matrix in heterogeneous soil provided further evidence of physical and chemical non-equilibrium in heterogeneous soil (Jardine *et al.*, 1990). The infiltration of rainfall introduces pore water of low ionic strength to macropores (Figure 1.4). It takes a longer time for the rainwater to enter into soil matrix compared to the macropores due to the low hydraulic conductivity of the soil matrix. The chemistry of pore waters in the soil matrix may remain unaffected by rainwater during a short rainfall event. A difference in ionic strength due to the slow exchange of ions between macropores and the soil matrix may affect the mobility and rate of mass transfer of colloids, metal cations between macropores and the matrix. Further experiments are required to evaluate the role of exchange of water between macropores and the soil matrix on the transport of colloids and organic matter.

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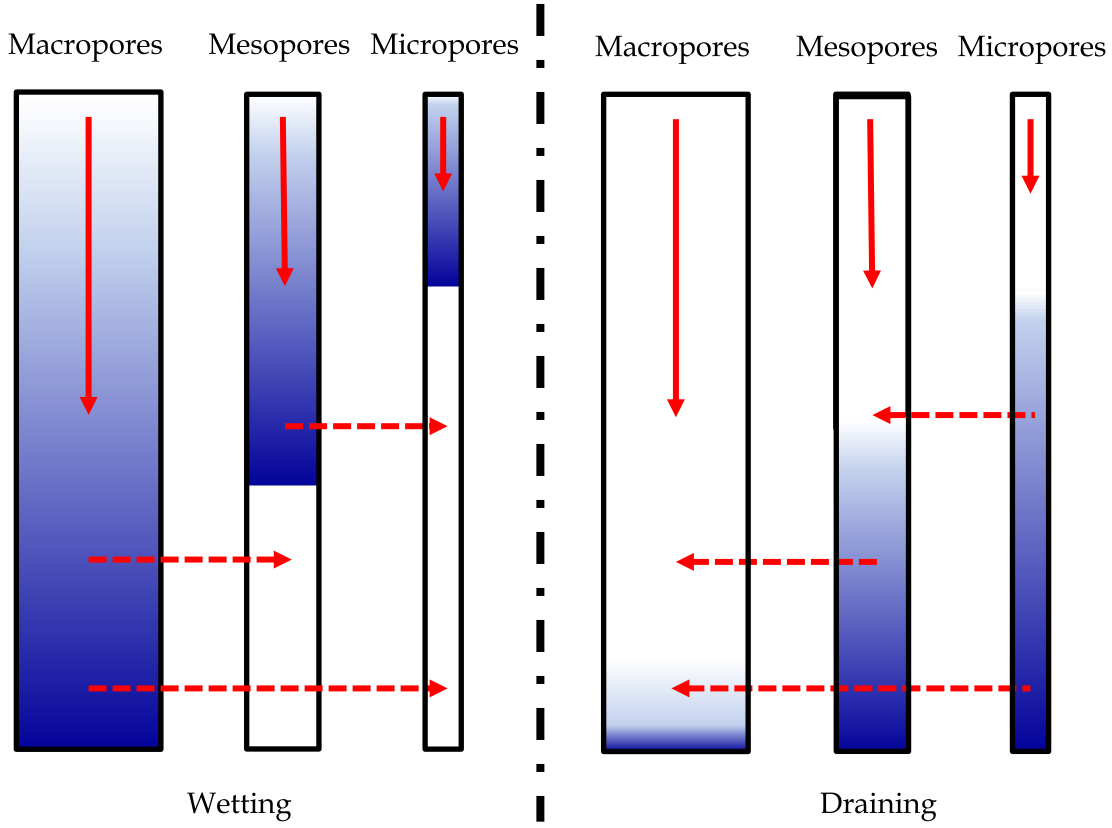

Figure 1.4. A difference in hydraulic conductivity among macropores, mesopores, and matrix causes a different rate of advection (solid arrow). Variation in advection rates causes a concentration gradient of solute in pores and solutes diffuse (dashed arrow) between macropores and the matrix during wetting and draining of water [modified from Clothier *et al.* (1998)].

The relative importance of colloids, organic matter, and ion exchange to the mobilization of colloids: Studies have not been conducted to estimate the relative importance of colloids, organic matter, and ion exchange in the release of adsorbed metal cations from soil. The release of metal cations may occur simultaneously by all three processes under natural conditions. However, conditions may exist for which each process could dominate. For example, colloids are removed from pore waters due to straining in pore throats and interfaces between water, air, and solids, but organic matter does not have the constraint of size to pass through smaller pores. The role of organic matter on transport of colloids in soil has not been investigated in detail even though organic matter and colloids are ubiquitous in the vadose zone.

The effects of colloids-facilitated transport and cation exchange on mobilization of metal cations are sensitive to ionic strengths. Low ionic strength is a favorable condition for colloid-facilitated transport of cations (Ryan and Gschwend, 1994). The transport of metal cations by colloids is not favorable at high ionic strength when colloids are removed from water by deposition on sand (Bridge *et al.*, 2009). High ionic strength is favorable for the release of metal cations from colloids by cation exchange (McKinley *et al.*, 2007). A prerequisite for colloid-facilitated transport to be important is that metal cations should bind strongly with colloids (McCarthy and Zachara, 1989). Metal cations with different sizes may release at a different rates from colloids in response to changes in ionic strengths. For example, colloid-facilitated transport of cesium was higher than strontium due to formation of stronger inner-sphere complexes by cesium with illite colloids (Turner *et al.*, 2006). In this case, illite colloids pre-equilibrated with cesium and strontium were injected in uncontaminated sand. However, different results were found when transport of cesium and strontium was examined by mobilization of in situ colloids from a contaminated soil (Chang *et al.*, 2011). In this study, ion exchange was found to be the dominant mechanism for release of cesium and mineral dissolution was suggested as the major releasing pathway of strontium in contaminated Hanford sediment. It appeared that the transport mechanisms of metal cations by colloids or ion exchange were sensitive to experimental conditions. More work is needed to examine the importance of ion exchange and colloid-facilitated transport under natural conditions.

Appropriate experimental techniques: Clay minerals, metal oxides, and polystyrene latex microspheres with homogeneous surface properties have been used as model colloids to evaluate the colloid-facilitated transport of cations. These inorganic minerals are not representative of natural colloids, where chemical heterogeneity is prevalent on the surface of colloids. Under natural conditions, the surfaces of most inorganic colloids are coated by organic matter, which changes the interaction of cations with the surfaces of mobile colloids (Laegdsmand *et al.*, 2005; Bellenger and Staunton, 2008). The use of natural colloids can further improve our understanding of colloid transport in the vadose zone.

Previous studies predominantly used columns packed with sand or soil to examine the transport of colloids. Packing destroys the physical heterogeneity of natural soil. Accurate description of contaminant transport in natural soil requires experiments with soil column where physical heterogeneity of soil is preserved. Previous studies using intact cores usually employed one outlet to collect water samples containing colloids, organic matter, and contaminants. One outlet is not adequate to capture and differentiate the contribution of macropores and matrices on contaminant transport (Aggelopoulos and Tsakiroglou, 2008). Water samples need to be collected from multiple regions to understand the effect of physical heterogeneity on the release of colloids (Figure 1.5).

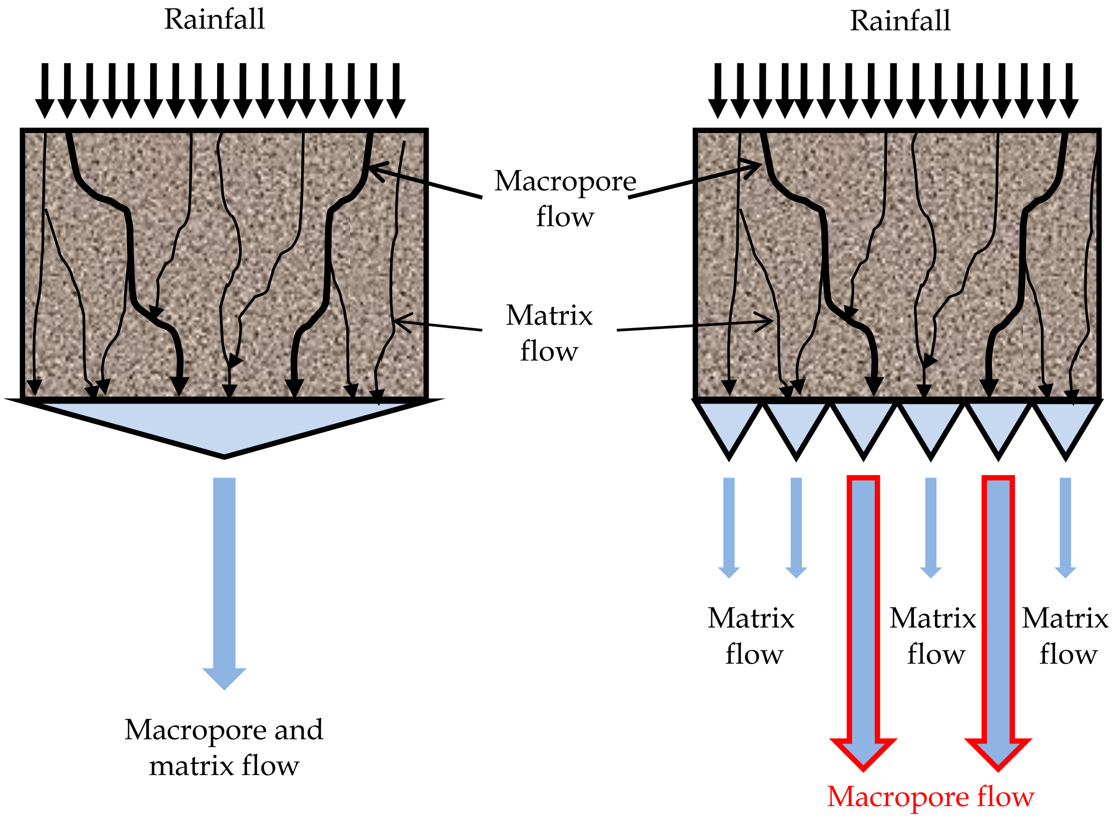

Figure 1.5. Single port and multi-port sample collection system. Multi-port sample collection allows capture of water samples from macropores and matrix.

Organization of the thesis

The objective of the current study is to examine the effect of rainfall characteristics and soil physical heterogeneity on release of cesium and strontium from a fractured soil by cation exchange, colloids- and organic matter-facilitated release processes. Laboratory and field experiments were conducted to examine the processes governing the mobilization of cesium and strontium under natural conditions. The results of laboratory experiments are presented in Chapters 2, 3, 4, and 5. The results of a field study are presented in Chapter 6.

The effect of pauses between rainfalls on the mobilization of colloids is presented in Chapter 2. In the Chapter 2, it is shown that the mobilization of colloids is sensitive to residual moisture content of soil after varying the duration pause between rainfalls. Chapter 3 describes a study that demonstrates significant mobilization of colloids and metals cations by freeze-thaw cycles, which is a transient condition during winter. Chapter 4 is focused on evaluating the effect of pore water exchange between macropores and the soil matrix on the mobilization of colloids and metal cations. In the Chapter 4, it is demonstrated that colloid mobilization from soil depends on the water quality of preceding rainfall and residual ionic strength of pore water before a rainfall. Geochemical conditions where ion exchange dominates over colloids in releasing metal cations from soil are presented in Chapter 5.   This chapter also reports results that demonstrate the effect of physical heterogeneity of soil on cation exchange and colloid-facilitated transport of metal cations.

Chapter 6 reports a field study evaluating the relative importance of cation exchange, organic matter-facilitated transport, and colloid-facilitated transport of cesium and strontium under transient in flow condition.

Chapter 7 is a summary of the major findings of current study with recommendations to advance the scope of the reported work across multiple disciplines that include geology, microbiology and atmospheric science.

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CHAPTER 2

MOBILIZATION OF COLLOIDS FROM INTACT CORES OF A FRACTURED SOIL: EFFECT OF TRANSIENT CONDITIONS AND PHYSICAL HETEROGENEITY

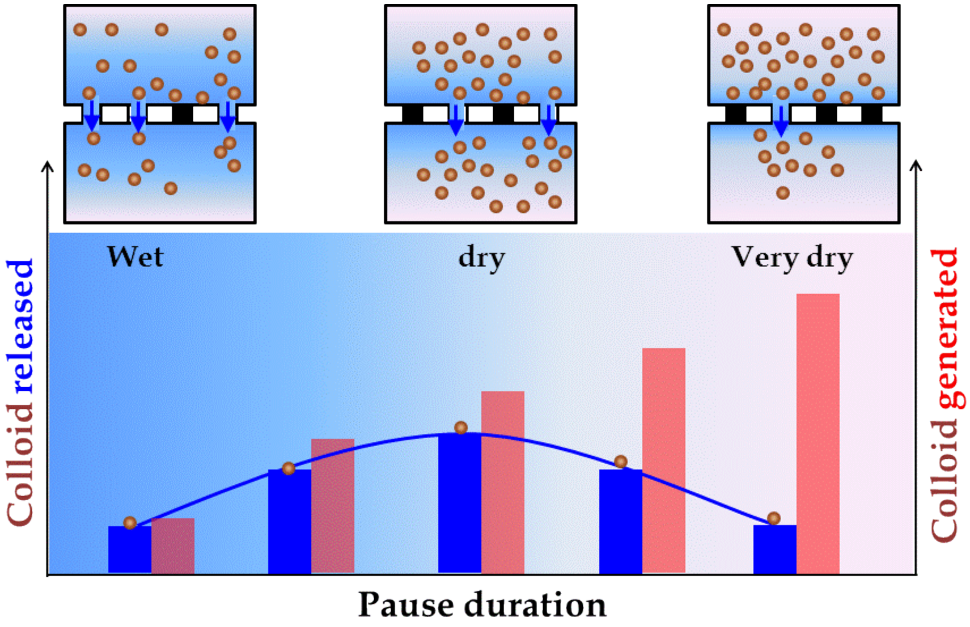

Illustration of colloid mobilization due to flow interruptions between rainfalls

Abstract

Understanding the transport process of colloids under natural conditions is essential for evaluating colloid-facilitated transport of contaminants in the vadose zone. The coupled effect of physical heterogeneity and rainfall characteristics on the mobilization of colloids is not clearly understood. Rainfall experiments were conducted on intact cores of a fractured soil by varying the duration of pauses between rainfalls. Colloids mobilized from the cores were collected through a 19-port sampling grid to evaluate the effect of preferential flow on colloid release. Active ports were characterized by flow rate and pore volume of the regions contributing to the flow through port. Different amounts of colloids were mobilized through multiple sampling ports. The amount of colloids mobilized through a port was correlated to either the flux of water or the breakthrough time of bromide through the port. Compared to steady rainfall, greater cumulative amounts of colloids were mobilized during rainfall punctuated by pauses, which indicates that the supply of colloids to be mobilized was replenished during the pauses. A maximum amount of colloids was mobilized during a rainfall when duration of preceding pause was 2.5 d. Pauses of shorter or longer duration resulted in less colloid mobilization. We attribute the effect of pause on colloid mobilization to changes in the moisture content of the soil during pause between rainfalls.

Introduction

Understanding the mobilization of colloids under natural condition is essential to estimate the potential for colloid-facilitated transport of contaminants, including radionuclides, metal ions, and organic contaminants in the vadose zone (McCarthy and Zachara, 1989; Ryan and Elimelech, 1996; DeNovio *et al.*, 2004). Under natural conditions, infiltration of rainfall and snowmelt cause temporal and spatial variations in moisture content of the soil and velocity of pore water. These changes in moisture content and flow promote the release of colloids by multiple mechanisms that includes scouring of colloids by moving air-water interfaces, release by thin-film expansion, reconnection of stagnant-water zones with bulk-water flow, and increases in shear forces (DeNovio *et al.*, 2004).

During a single rainfall, the mobilization of colloids from soil follows a general pattern with a characteristic peak in colloid concentration at the start of the rainfall followed by an exponential decrease of the colloid concentration to a constant level (Jacobsen *et al.*, 1997; Ryan *et al.*, 1998; El-Farhan *et al.*, 2000; Schelde *et al.*, 2002; de Jonge *et al.*, 2004; Kjaergaard *et al.*, 2004; Zhuang *et al.*, 2007; Majdalani *et al.*, 2008). The peak in colloid concentration was attributed to colloids mobilized from soil grains during the pause preceding the rain (Schelde *et al.*, 2002; Majdalani *et al.*, 2008). Zhuang *et al.* (2007) found that rainfall interrupted by pauses mobilized greater amounts of colloids than steady rainfall of the same volume. The extra amount of colloids mobilized was attributed to mobilization of colloids due to transient conditions associated with the pause. The peak concentration of colloids decreased with an increase in the number of pauses of constant duration, which indicated that successive application of rainfall depleted the supply of colloids that could be mobilized (Kaplan *et al.*, 1993; Zhuang *et al.*, 2007). However, others found no changes in the peak colloid concentration after pauses, which indicates an unlimited supply of colloids in soil for mobilization during successive rainfalls (El-Farhan *et al.*, 2000; Schelde *et al.*, 2002). With few exceptions (*Schelde et al., 2002; Majdalani et al., 2008*), the duration of pauses in rainfall application as a variable for colloid mobilization was not considered.

The effect of the duration of pauses between rainfalls on the mobilization of colloids was reported in two studies (Schelde *et al.*, 2002; Majdalani *et al.*, 2008). Schelde *et al.* (2002) reported an increase in the mobilization of colloids with increases in the duration of preceding pause between 0.5 and 168 h. They stated that the supply of colloids was not limited, but that the kinetics of their release was limited by diffusion through the stagnant water (i.e., pore water in the soil matrix). Majdalani *et al.* (2008) investigated the mobilization of colloids from an intact soil core with increasing pause durations from 1 h to 70 d. They observed that the amount of mobilized colloids increased as the duration of pause was increased from 1 h to 8.1 d and decreased as the pause duration exceeded 8.1 d. The optimal duration of pause was 13 d for a different soil with saturated conductivity lower by one order magnitude. Majdalani *et al.* (2008) suggested that the supply of colloids available for mobilization was enhanced by shorter pauses because the drying of soil during the pause resulted in the breaking of pore walls due to the differential capillary stress. During longer pauses, they surmised that drying of soil matrix decreased the mobilization of colloids due to their attachment to thin water film and precipitation of salts that bind colloids with soil. Mechanisms suggested by both studies were not comparable because Schelde *et al.* (2002) did not investigate pauses sufficiently long to see a decrease in colloid mobilization. The flow interruption by Schelde *et al.* (2002) involved storing of the soil core at 2 °C after 20 min of rainfall to prevent drying of the soil. There, the diffusion process was found to be important for the replenishment of colloids because most pores remained filled with water during the pauses. The relative importance of diffusion or capillary pressure depends on the size of the pores and the degree of physical heterogeneity, of the soil. Previous studies did not consider the effect of physical heterogeneity on the mobilization of colloids during flow pauses.

The physical heterogeneity of soil must be taken into account in order to improve our understanding of colloid mobilization during pauses in rainfall. The aim of this study was to evaluate the coupled effect of heterogeneity and pauses in rainfall application on the mobilization of colloids in soil. The study was conducted using intact cores of a fractured saprolite soil that were sampled using a multi-port grid to identify spatial variations in the flow.

Experimental Details

Intact soil core sampling: Intact soil cores were collected from the bottom of a hill slope in the Melton Branch watershed on the grounds of the Oak Ridge Reservation, Tennessee (Luxmoore and Abner, 1987). The field site and soils are described in detail by Jardine et al. (1993). The soil consists of fractured shale saprolite that has been weathered by 130 cm y^{-1} of rainfall. Infiltrating water predominantly passes through the bedding planes and fractures, which dip at an angle of 30° (Jardine *et al.*, 1993). The bedding planes and fractures are coated with iron(III) and manganese oxyhydroxides and translocated clay minerals.

Intact soil cores were collected using a hand-sculpting method (Jardine *et al.*, 1993). Vegetation and the O-layer of the soil were removed from the sample sites. Cylinders of soil in the A-horizon were excavated and trimmed to fit inside polyvinylchloride (PVC) pipes of 30.5 cm height and 25.4 cm width. In some cases, the top and sides of the soil cylinders were coated with melted paraffin wax to prevent the fractured soil from falling apart. The gap between the PVC pipe and the soil cylinder (approximately 1.2 cm) was filled with polyurethane expandable foam (US Composites). The soil collection method preserved the structural integrity of soil.

Preliminary experiments confirmed no leaching of dissolved organic carbon from the paraffin wax and foam.

Experimental setup: Colloid mobilization experiments were conducted using a rainfall simulator consisting of a reservoir, a peristaltic pump, a rainfall distributor, the soil core, a sampling grid, and sample collection tubes (Figure 2.1). The peristaltic pump transferred rainfall solutions (0.01 mM NaCl) from the reservoir to the rainfall distributor. Rainfall was simulated by dripping water through 85 needles (25 gauge) at the bottom of the rainfall reservoir. The intact core was placed under the rainfall reservoir on a sampling grid with 19 ports to resolve spatially the flow of water through macropore (fractures) and matrix. The arrangement and the numbering of ports in the grid and arrangement of needles below the rainfall reservoir are described in Figure 2.1. The ports delivered samples of infiltrating water to 19 sample collection tubes (glass, 2.5 cm diameter × 25 cm length). Each port captured water flowing through an area of 11.4 cm^2; the total collected area was 340 cm^2. Water flowing near the perimeter of the soil cores was collected in a channel (1.3 cm width) around the sample ports to be discarded. The water flows to each port from the bottom surface of soil under zero tension.

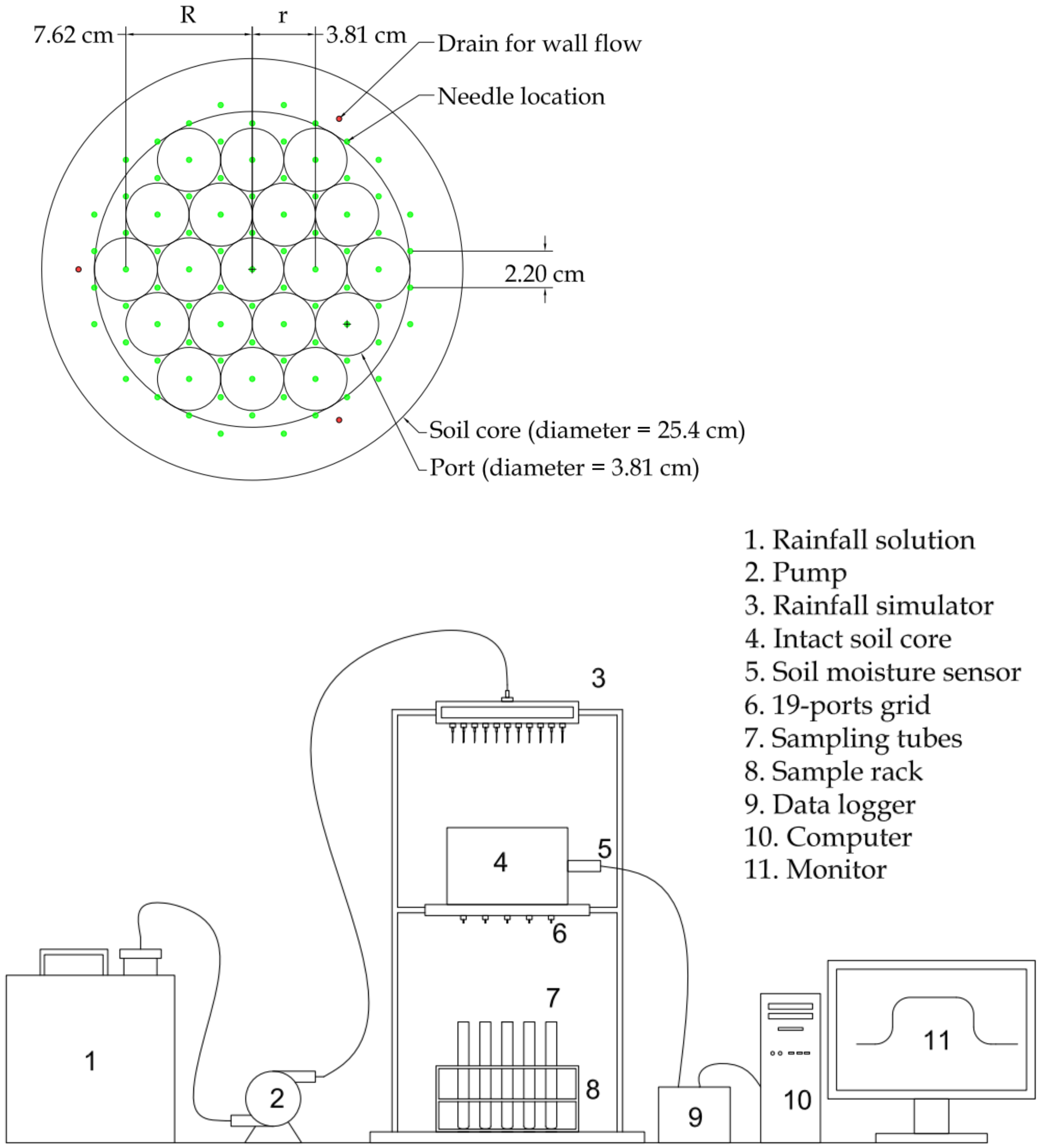

Figure 2.1. Column setup to examine the mobilization of colloid from an intact core of a fractured soil. The 19 ports were arranged in a hexagonal pattern. The ports (diameter of 3.81 cm) were arranged in two concentric hexagons around a center port. The center port is designated as “00”. The inner hexagon contains six ports at a center-to-center distance of maximum 3.81 cm from port 00 and is designated as “r” followed by an angle. The outer hexagon contains 12 ports at center-to-center distance of maximum 7.62 cm and is designated as “R” followed by an angle. The 85 needles of the rainfall reservoir were arranged in hexagonal pattern with closest distance between two needles as 2.2 cm.

In the preliminary rainfall experiments soil cores with the full-height (30.5 cm), we observed that the bedding plane fractures carried most of the infiltrating water to the walls because the fractures intersected the core walls. To avoid this problem, the soil cores were cut to a height of 15 cm. A soil moisture probe (Delta-T Devices, Theta Probe MLX2) was inserted in the side of the soil core to monitor moisture content. The probe was located 7.5 cm below the soil surface and extended 6 cm into the soil. The probe was interfaced with a computer through a data logger (DATAQ Instruments, DI 710) to record and store moisture content at 1 min intervals.

Three cores were used in this study to examine the mobilization of colloids by rainfalls interrupted by pauses of either equal or increasing durations. Rainfall pauses of equal duration were used in the first core. Rainfall pauses of increasing durations were used in second and third cores. Other experimental conditions are summarized in Table 2.1.

Table 2.1. Rainfall characteristics used in the three soil cores.

Core number	Pause and Durations	Rainfall intensity (cm h^{-1})	Number of rainfalls
1	Constant , 0.9 d	2.5	3
2	Varying, 0.7 to 34 d	0.5	5
3	Varying , 0.7 to 13 d	2.5	7

Identification of physical heterogeneity: We investigated the effect of physical heterogeneity on the mobilization of colloids. Based on previous experiments (Jardine *et al.*, 1993), we expected rapid infiltration through the bedding plane fractures and slow infiltration through the shale saprolite under heavy rainfall. We refer to these flow paths as macropore and matrix. We used the bromide breakthrough times as an indicator of the flow paths of the infiltrating water – increases in breakthrough time were assumed to represent increased residence time in the soil matrix. Bromide breakthroughs were obtained for each flowing port by applying a rainwater solution of 1 mM NaBr at 2.5 cm h^{-1} on the first and third core, and at 0.5 cm h^{-1} on the second core. At these rainfall application rates, water did not pool on top of the soil cores. A rainfall application at 2.5 cm h^{-1} represents a typical heavy rainfall at Oak Ridge, Tennessee (Wilson *et al.*, 1990). The breakthrough time of bromide was estimated as the time at which the bromide concentration in a port reached 50% of bromide concentration in the rainfall solution.

Mobilization of colloids: We investigated the mobilization of colloids by infiltrating rainfall by conducting a series of rainfall applications with multiple flow interruptions of equal duration and increasing duration. The rainfall solution was prepared from 0.01 mM NaCl. In order to examine the effect of flow interruptions on the mobilization of colloids, we compared the amount of colloids mobilized by an 8.1 h rainfall with and without three flow interruptions for 21.3 h each in the first core. The effect of duration of flow interruption on colloid mobilization was examined by stopping the flow for a minimum of 0.6 d to a maximum of 35 d in the second and third core. The total amount of colloids mobilized during a rainfall was calculated by integrating the mass of colloid mobilized over the volume flowing through each port.

Analysis of water samples: The infiltrating water samples collected in all of the active ports were analyzed for pH, conductivity, turbidity, and bromide. The pH was measured using a pH/ion-selective electrode meter (Orion 720A) and a combination electrode (Orion 8102BNU). Conductivity was measured using a conductivity meter (Orion 105) and cell (Orion 011050). Bromide concentration was measured using the pH/ion-selective electrode meter and a combination bromide-selective electrode (Accumet 13-620-524). Turbidity was measured using a turbidity meter (Hach 2100N). The measured turbidities were converted to colloid concentrations (mg L^{-1}) using a calibration curve of total suspended sediment concentration versus turbidity (Appendix B). The suspended sediment concentration was measured by drying colloid suspensions (20 mL) of increasing turbidity in pre-weighed aluminum cups in an oven at 104 °C and weighing the mass of the dried colloids. The contribution of total dissolved solids to the suspended sediments concentration was estimated to be less than 1% based on a conversion of the maximum conductivity (25 μS cm^{-1}) to total dissolved solids.

Results

Characterization of physical heterogeneity of the soil: The relative saturation of soil cores was affected by rainfall application rates and heterogeneity of soil cores (Figure 2.2). A rainfall application rate of 2.5 cm h^{-1} resulted in higher saturation of the third soil core compared to the second core where the rainfall application rate was 0.5 cm h^{-1}. However, a rainfall application rate of 2.5 cm h^{-1} partially saturated the first and third core to different extents.

The flux of infiltrating water in three cores varied with rainfall intensity and heterogeneity of the soil cores (Figure 2.3). In the first core, five ports conducted 72 % of the total rainwater applied. In the second core, three ports conducted 98 % of the total rainwater applied. In the third core, five ports conducted 31% of the total rainwater applied. The remainder was discarded as wall flow in all the three cores. The flux through each port was greater than rainfall application rates in each core. The bromide breakthrough curves for active ports in three cores are shown in Figure 2.3. The bromide breakthrough times varied in active ports in the three cores, which indicated that flow paths, with different contributions from macropores and matrix, carried water sample to ports.

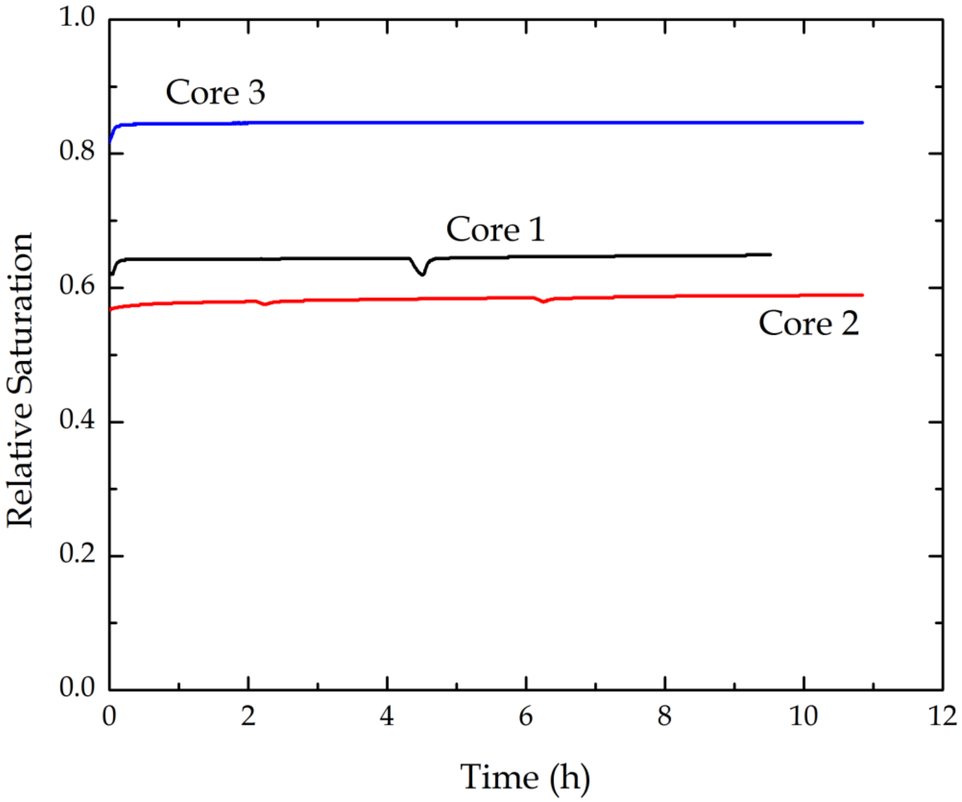

Figure 2.2. Relative saturation of soil cores during rainfall application. The rainfall application rate on core 1 and 3 was 2.5 cm h^{-1} and the rainfall application rate on core 2 was 0.5 cm h^{-1}.

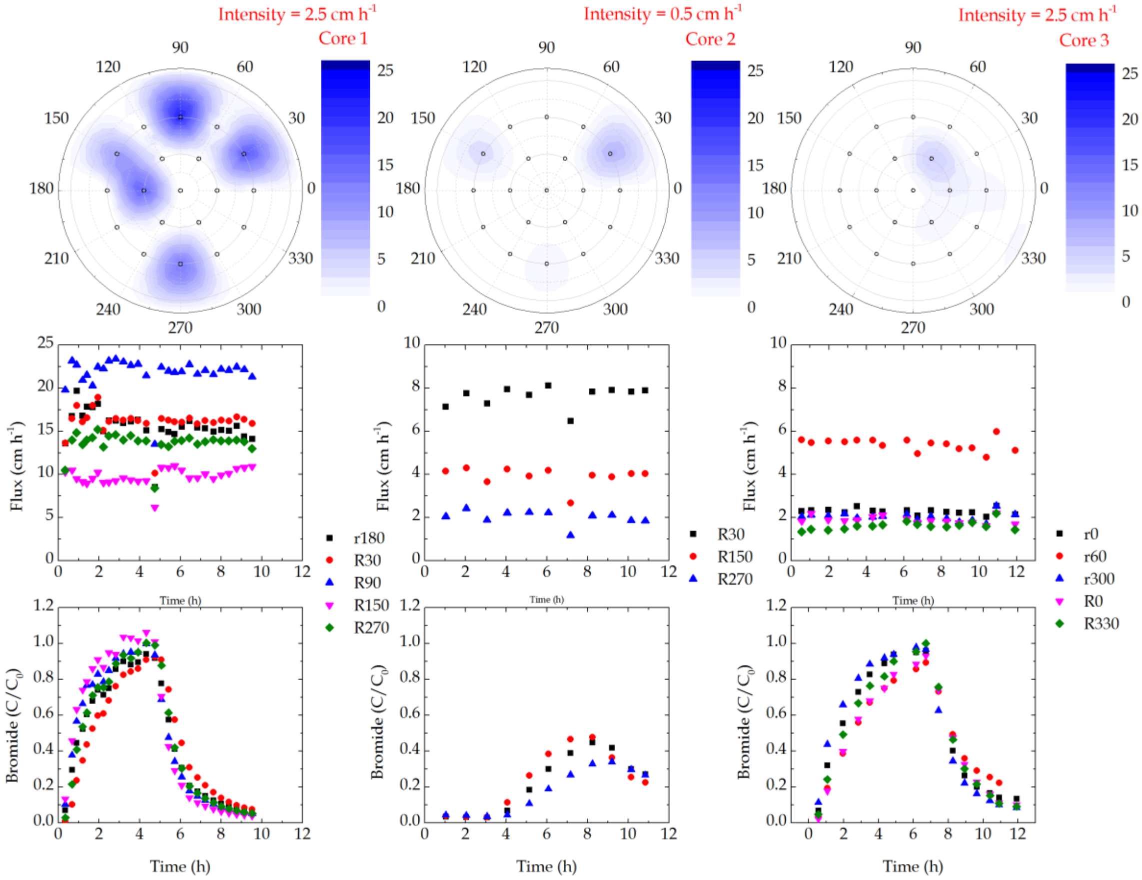

Figure 2.3.The flux distribution at bottom surface of cores (top row), flux (center row) and bromide breakthrough curves (bottom row) through active ports in core 1 (left column), core 2 (center column) and core 3 (right column).

***Colloid mobilization without flow interruption*:** Infiltration of the 0.01 mM NaCl rainfall at a rate of 2.5 cm h^{-1} for 8.1 h resulted in colloid mobilization through the five active ports. The colloid concentration peaked shortly after the start of the rainfall and decreased rapidly with time (Figure 2.4). The cumulative colloid mass increased linearly with the square root of time (Figure 2.4). The total amount of colloids mobilized from five ports of the first core during a 5 h rainfall is presented in Table 2.2 together with the fluxes and bromide breakthrough times in the corresponding ports.

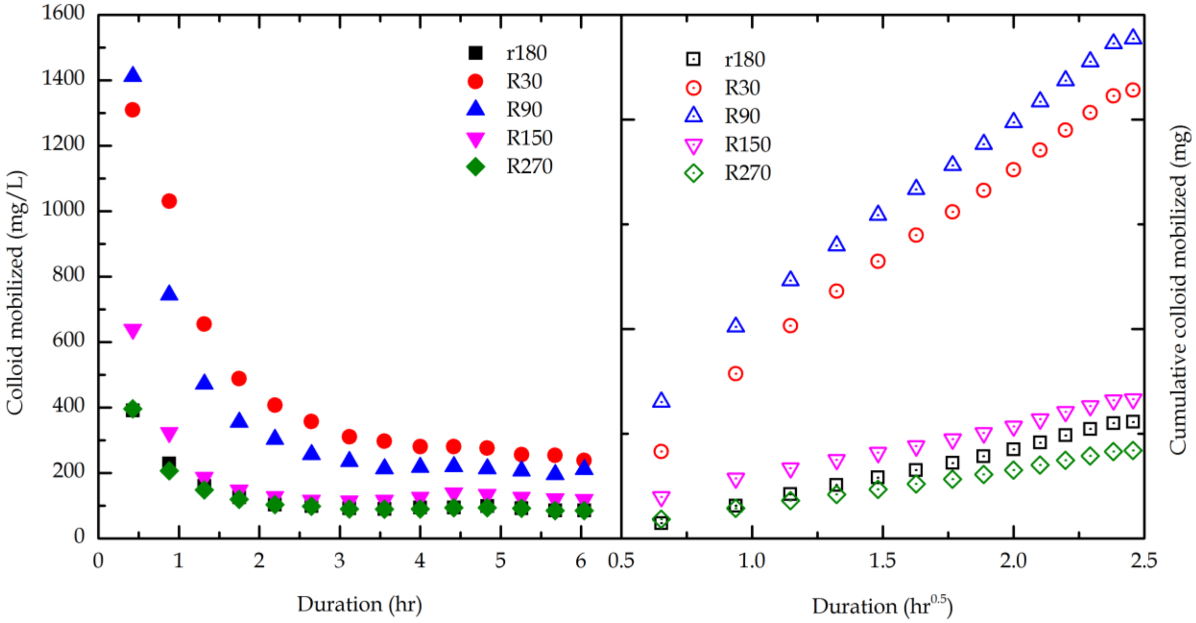

Figure 2.4. Mobilization of colloids though different ports from the first core subjected to rainfall at 2.5 cm h^{-1}. Left: Colloid concentrations at different ports during different time of rainfall. Right: Cumulative mass of colloids mobilized with respect to the square root of time.

Table 2.2. Flux, bromide breakthrough time, volume of water for 50% breakthrough of bromide, and total amount of colloids mobilized from the first core during a 5 h rainfall.

Port	Infiltrating water Flux (cm h^{-1})	Bromide breakthrough time (h)	[a] Volume of water for 50% bromide breakthrough (mL)	[b] Colloids (mg)
R150	9.8	0.7	80.8	17.6
R270	13.6	1.1	172.1	5.2
r180	15.6	1.1	196.0	10.7
R30	16.1	1.6	294.4	34.4
R90	21.8	0.8	203.2	37.1

[a] The volume was calculated multiplying flux with breakthrough time and the area of the port

[b] Amount of colloids mobilized during rainfall was calculated based on concentration and the volume of rainwater

Colloid mobilization with flow interruption of constant duration: In the first core, the total amount of colloids mobilized by rainfall applied with three interruptions of 21.7 h each was greater than the amount of colloids mobilized by the same amount of rainfall without flow interruption (Figure 2.5). After each flow interruption, the colloid concentration peaked rapidly and decreased slowly. The amount of colloids mobilized due to flow interruptions varied among the five ports.

***Colloid mobilization with flow interruption of increasing duration*:** In the second core, the total amount of colloids mobilized during rainfall applications increased as the duration of the preceding pause increased from 0.6 d to 2.5 d and decreased as the pause duration increased from 2.5 to 34 d (Figure 2.6). In the third core, the total amount of colloids mobilized during rainfall applications increased as the duration of the preceding pause increased from 0.6 d to 2.5 d and decreased as the pause duration increased from 2.5 to 13 d. The amounts of colloids mobilized from each port varied during the successive rainfall applications. The relative saturation of column decreased steadily with increases in the duration of pauses. The third core had higher water content than the second core for same duration of pauses.

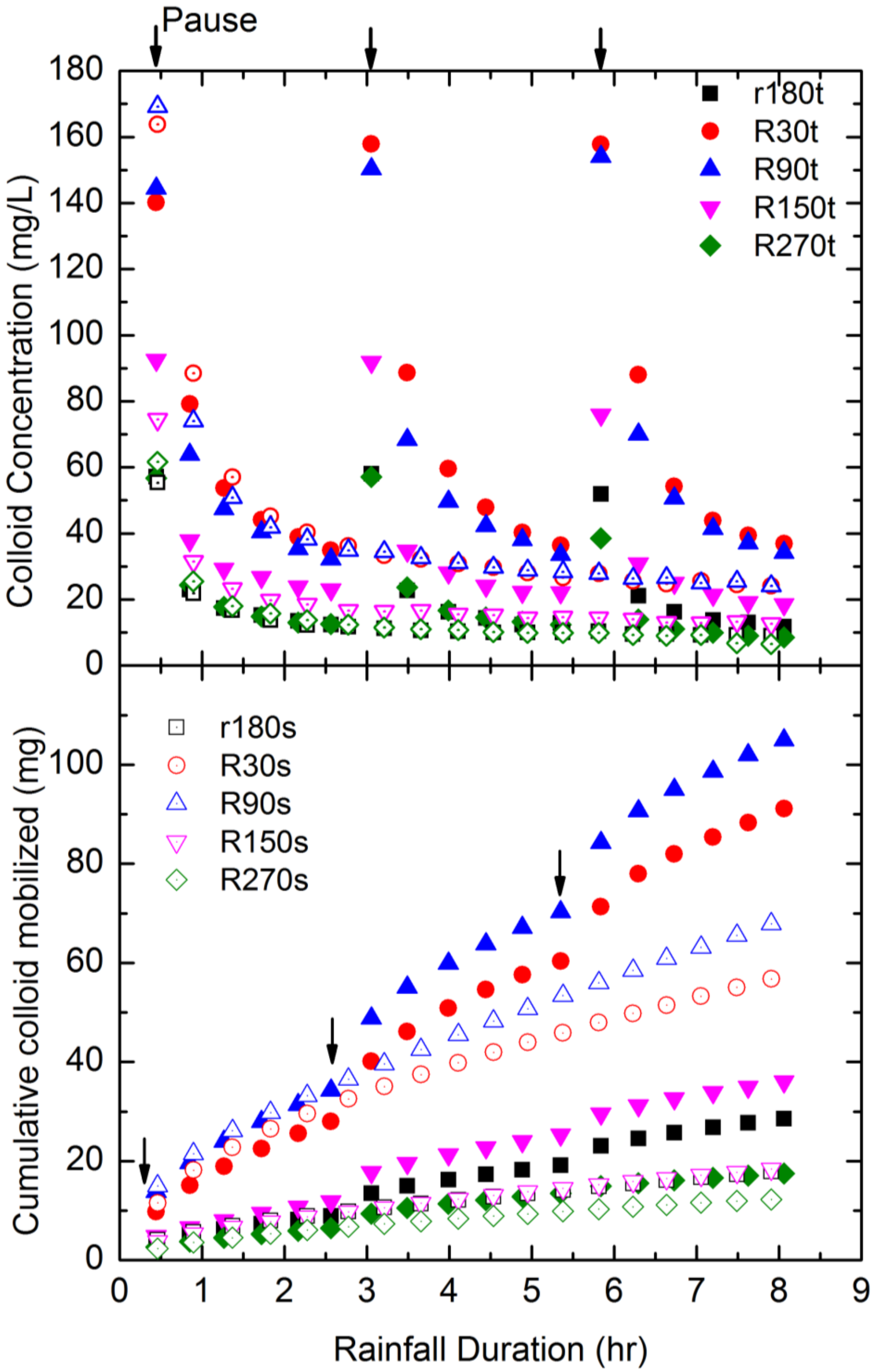

Figure 2.5. Concentration (upper) and cumulative mass (lower) of colloids mobilized through different ports of the first core during a continuous rainfall at 2.5 cm h^{-1} without pauses(open symbols) and rainfall at 2.5 cm h^{-1} interrupted by pauses (closed symbols). The three arrows indicate the timing of the 21.3 h pauses between rainfalls.

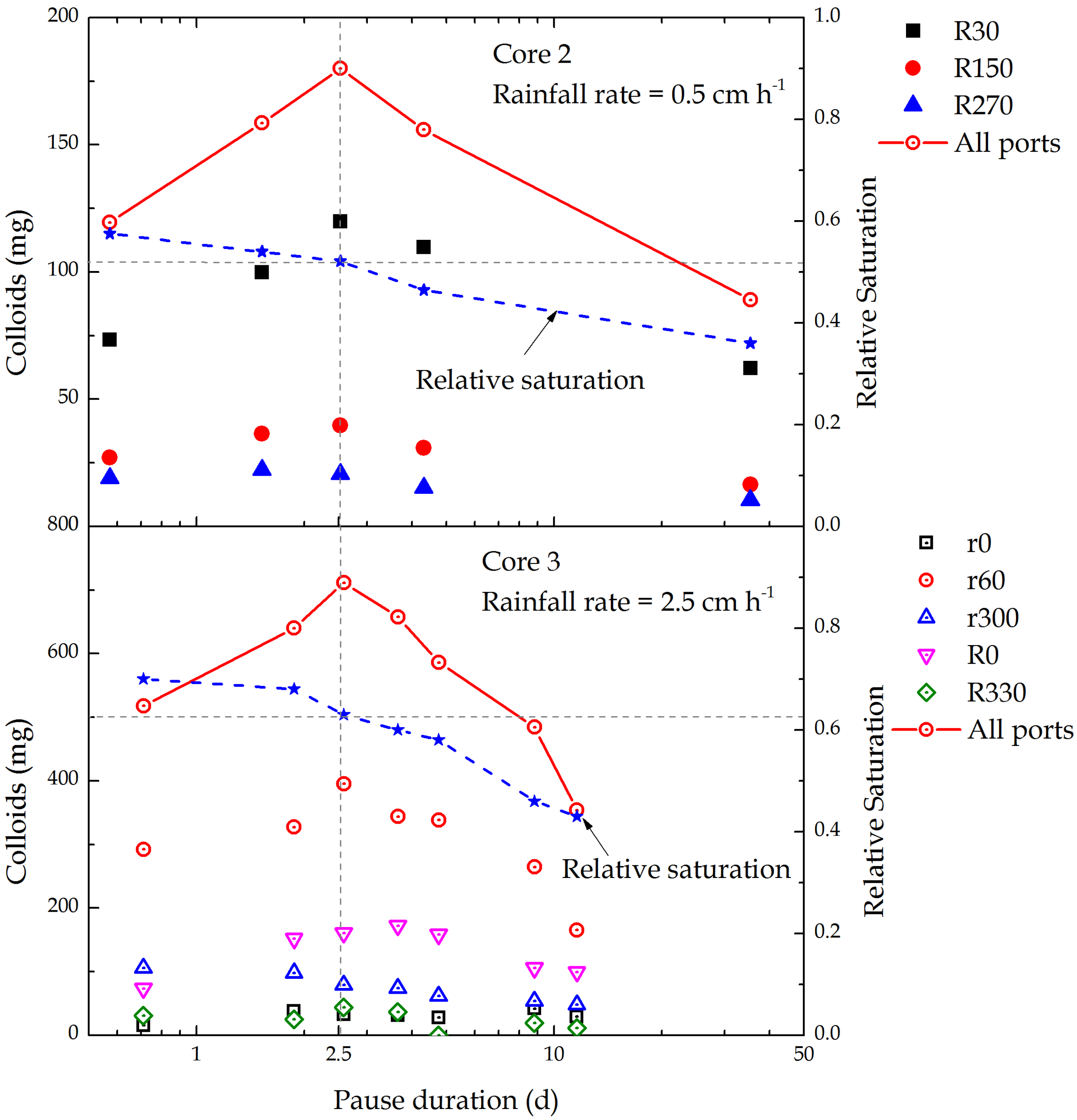

Figure 2.6. Total amount of colloids mobilized and moisture content as a function of the duration of pauses between rainfall applications in specific ports in the second and third soil cores.

Discussion

***Effect of physical heterogeneity on the movement of water*:** The distribution of the flux of infiltrating water among the sample ports indicates that water flowed through a mixture of macropore and matrix flow paths (bedding plane fractures and shale saprolite) in all three cores (Figure 2.3). The fluxes at all ports were greater than the rainfall application rates due to preferential flow through the bedding plane fractures. The variation of the bromide breakthrough times between ports indicates different extents of bromide diffusion into matrix. Long tailing of bromide indicates that an exchange of bromide among regions of different permeability may occur during the transport through preferential flow paths. Water is expected to move by advection through macropores in the fractured soil. A field study indicated that water infiltrated through macropores and mesopores under extreme wet and dry conditions and water infiltrated through small pores in the matrix under intermediate wet conditions (Wilson *et al.*, 1990). Gwo *et al.* (1996) classified the soils used in our study into three regions: macropore (> 0.1 cm), mesopore (0.001 to 0.1 cm) and micropore (< 0.001 cm). Differences in hydraulic and concentration gradients between regions of different permeability are known to cause the advection and diffusion of water, solutes and colloids (Luxmoore *et al.*, 1990). The occurrence of preferential flow under unsaturated conditions depends on rainfall intensity, moisture content, and the distribution of pore sizes of the medium (Jarvis, 2007). Increases in rainfall intensity caused infiltration of water through preferential channels because matrix diffusion was not sufficient to disperse the water through soil (Pot *et al.*, 2005).

***Effect of physical heterogeneity on colloid mobilization*:** In order to examine the effect of physical heterogeneity on the mobilization of colloids, we correlated the total amounts of colloids mobilized from all ports in the first core with flow rates and bromide breakthrough times (Figure 2.7). If shear were the driving force in mobilizing the colloids, increases in the flux would have mobilized larger amounts of colloids in all ports. However, water samples from port R150 with low flow rate contained more colloids than samples from ports R270 and r180 with higher flow rates. Diffusion was suggested as another mechanism for colloid mobilization (Schelde *et al.*, 2002). A linear increase of the cumulative amount of colloids mobilized with an increase in the square root of time (Figure 2.4) suggests that diffusion was the dominant mechanism for colloid mobilization (Jacobsen *et al.*, 1997). The initial peak in the colloid concentrations may be due to mobilization of colloids by mechanisms that includes scour at the air-water interface and expansion of the water film (DeNovio *et al.*, 2004). In a recent study, colloid mobilization was also attributed to increases in capillary stress as a result of drying that occurs during pauses between rainfalls (Majdalani *et al.*, 2008). A decrease in moisture content occurred during pause and increases in colloid concentration were observed during succeeding rainfalls. Based on this result, we suggest that colloids were generated on the macropore walls due to capillary stress during pause, mobilized from wall by moving air-water interface during the start of rainfall and later mobilized by diffusion. The mobilization of colloids at each port depends on physical heterogeneity of soil.

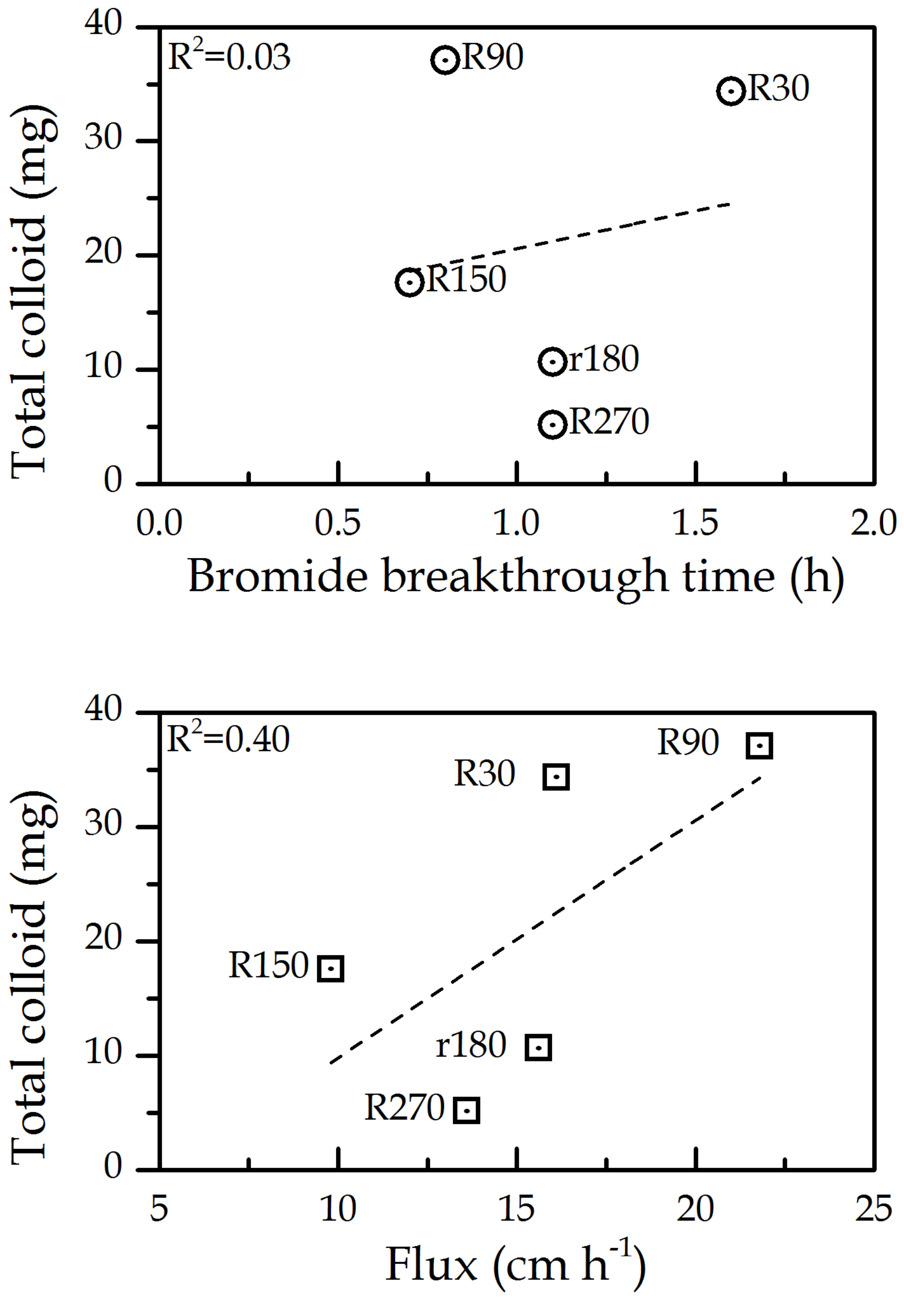

Figure 2.7. Total amount of colloids mobilized from the first core during a 5 h rainfall event correlated to bromide breakthrough time (top) and flux (bottom) through all sampled ports.

***Effect of flow interruptions on colloid mobilization*:** The interruptions in rainfall application resulted in an increase in the mobilization of colloids (Figure 2.6). These results are similar to those of previous studies (Schelde *et al.*, 2002; Zhuang *et al.*, 2007; Majdalani *et al.*, 2008). An increase in the duration of pauses increased the capillary pressure in pore wall. The capillary pressure could mobilize larger amounts of colloids by breaking the weak pore walls (Majdalani *et al.*, 2008). Longer pauses may induce higher capillary stress to generate more colloids.

The decrease in the amount of colloids mobilized with the increase in the duration of the pause beyond 2.5 d indicates that the generation of colloids might be limiting the amount of colloids mobilized. The continued decrease in moisture content and drying of pores that occurs over longer pauses may disconnect the pore water and block the colloids from distributing into nearby pores. For example, a decrease in moisture content limited the release of colloids from pore water (Shang *et al.*, 2008). The release of colloids during a period of drying depends on the relative saturation of soil. In our study, the relative saturation of the soil cores decreased with an increase in the duration of pause. The moisture contents at which the greatest amount of colloid mobilization occurred were 0.52 for core 2 and 0.63 for core 3 (Figure 2.6). Decreasing the moisture content further decreased the mobility of colloids. Majdalani *et al.* (2008) suggested that an increase in cohesion between colloids by thin water film and salt precipitated during a longer pause could immobilize colloids. Schelde *et al.* (2002) argued that time dependent diffusion of colloids could have contributed to an increase in the amount of colloid mobilization during longer pauses. Neither Schelde *et al.* (2002) nor Majdalani *et al.* (2008) provided any direct evidence (e.g., soil moisture content) to support their proposed mechanisms of the effect of pause duration on colloid mobilization.

A drying duration of 2.5 days was found to be optimum for mobilization of colloids from the soil cores. The optimum duration found in this study was shorter than the optimum durations found by Majdalani *et al.* (2008). Majdalani *et al.* (2008) used two soils with different hydraulic conductivities and found that the soil with higher conductivity had shorter optimum pause durations. Soil with higher conductivity drains water quickly to attain the critical moisture content for colloid mobilization. The soil used in our study has relatively higher conductivity due to preferential flow through fractures. Preferential flow paths drain water faster than matrix and dry quickly to attain the critical moisture content for colloid mobilization. Therefore, it is expected that a relatively shorter duration of pause maximizes the mobilization of colloids. We suggest that infiltrating water mobilizes colloids from stagnant pore water near the macropore wall if an exchange of colloids between the macropore and matrix occurs. For example, increases in duration of pauses decreased the mobilization of colloids in port r300 in the third core where bromide dispersion was the least. Longer tailing or breakthrough times of bromide are indications of diffusion of bromide out of the macropore flow and into the stagnant matrix pore water. Colloids may diffuse similar to bromide across the concentration gradient, but in a slower flow rate. Increasing the duration of pause decreased the colloid concentration when diffusion of colloids through the macropore-matrix interface was less. The lack of exchange of colloids prevented replenishment of colloids near the macropore-matrix interface along the flow path to port r300. Port R0, with higher dispersion of bromide, mobilized more colloids than r300 when the duration of pause was increased.

The mechanism of the mobilization of colloids under transient conditions could be explained based on the moisture content of soil (Figure 2.8). When pause is short, moisture content in soil is high. High moisture content may not cause enough capillary stress within pores to generate colloids. On the other hand, moisture content is low when the pause is long. Low moisture content could increase the capillary stress within pores and generate more colloids in matrix due to the presence of disconnected pore water. We suggest a four-step process to explain the colloid mobilization due to pause between rainfalls: (1) colloids are generated due to increase in capillary stress, (2) colloids are released into pore water, (3) colloids are distributed through connected pores by diffusion, and (4) transport of colloids from the macropore wall during a following rainfall. The mobilization of colloids during interrupted rainfall is sensitive to physical heterogeneity of soil because the pore size distribution affects the moisture content of pores (generation of colloids by capillary) and the diffusion of colloids between macropore and matrix (supply of colloids).

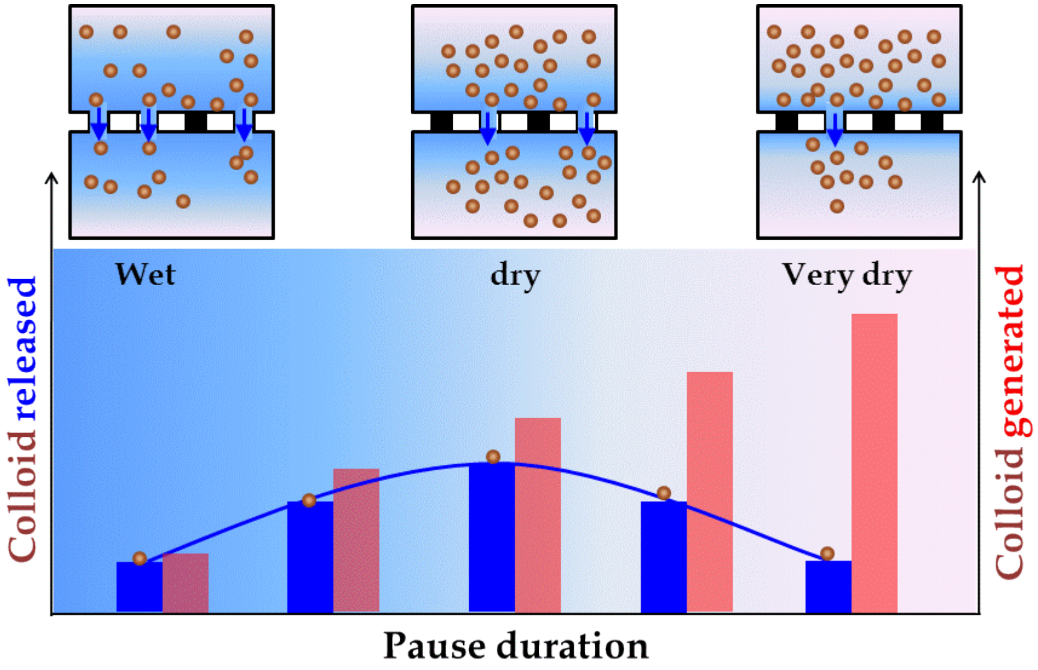

Figure 2.8. Illustration of colloid mobilization due to flow interruptions during rainfall.

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CHAPTER 3

EFFECT OF FREEZE-THAW CYCLES ON THE COLLOID-FACILITATED TRANSPORT OF METAL CATIONS IN AN UNSATURATED FRACTURED SOIL

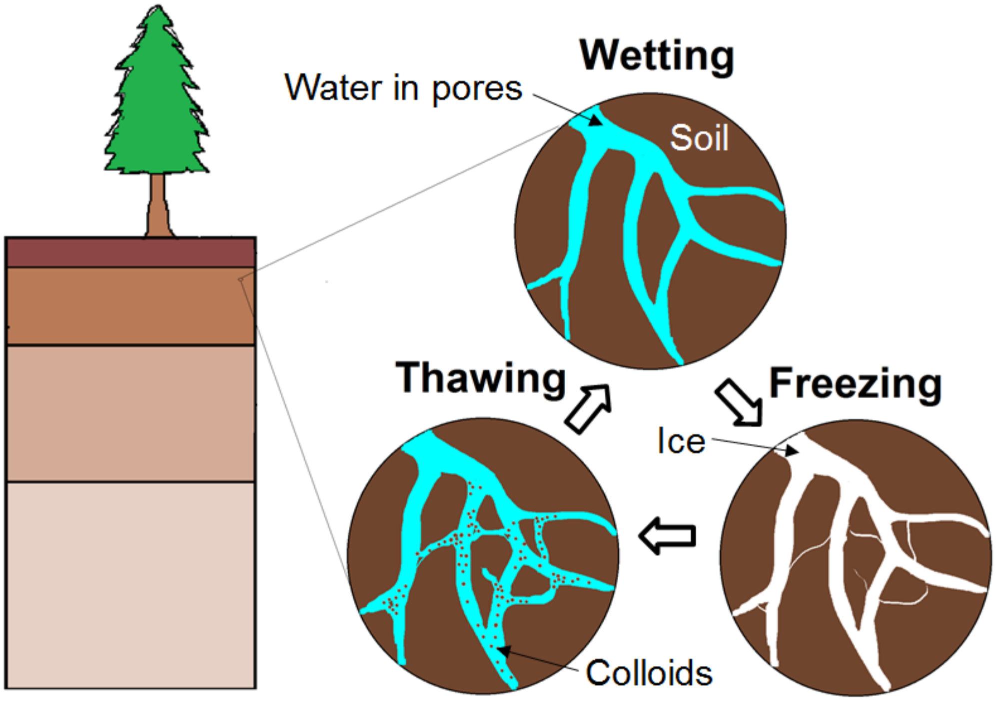

Illustration of the effect of freeze-thaw cycle on the mobilization of colloids

Abstract

This study was conducted to evaluate the effect of freeze-thaw cycles on the mobilization of colloids and colloid-facilitated transport of cesium and strontium in intact cores of fractured shale saprolite soil in a laboratory rainfall simulator. The intact cores were contaminated with cesium and strontium before being subjected to several freeze-thaw cycles and rainfall events. The amounts of colloids and cations mobilized from cores subjected to freeze-thaw cycles between rainfalls events were compared to the amount of colloids mobilized from a control core kept at room temperature between rainfall events. Significantly greater amounts of colloids were mobilized from the cores subjected to freeze-thaw cycles than from the cores kept at room temperature. Each freeze-thaw cycle resulted in greater mobilization of colloids compared to the previous freeze-thaw cycle, whereas the mobilization of colloids did not increase in the control core. Freeze-thaw cycles appeared to create new preferential flow paths for the breakthrough of cesium and strontium. Colloid-facilitated transport of cesium and strontium was greater in the cores subjected to the freeze-thaw cycles than in the control core due to the mobilization of a greater amount of colloids during the freeze-thaw cycles. The freeze-thaw cycles mobilized more cesium than strontium. These findings suggest that greater colloid and colloid-associated contaminant mobilization will occur in the vadose zone when temperature varies near the freezing point of water.

Introduction

Understanding the processes governing the mobilization of colloids and colloid-associated contaminants in subsurface environments is essential for protection of groundwater (McCarthy and Zachara, 1989; McCarthy and McKay, 2004). Colloids and contaminants are mobilized by water due to rain or snow melt. Recent studies have highlighted the importance of pauses in rainfall in mobilizing greater amount of colloids and colloid-associated contaminants compared to rainfall without pause (Zhuang *et al.*, 2007; Majdalani *et al.*, 2008). Pauses between rainfalls cause soil pores to dry and consequently break due to increases in capillary pressure (Majdalani *et al.*, 2008; Michel *et al.*, 2010). Colloids generated from broken pores are mobilized during re-wetting by expanding residual water films and moving air-water interfaces (DeNovio *et al.*, 2004). These findings are useful for predicting the extent of mobilization of colloids and colloid-associated contaminants due to pauses between rainfalls.

The liquid water content of the topsoil also decreases due to freezing – a pause in flow that occurs during winter before infiltration due to snowmelt. During cold weather, flow transients occur during cycles of freezing and thawing. Analogous to evaporation in dry seasons, the liquid water content decreases in soils during winter due to the formation of ice. During freezing, water expands to form ice, and the expansion creates cracks in the soil pores. Water in large pores freezes before the water in matrix due to the absence of capillary tension. This causes the water to move from the soil matrix to macropores, which causes capillary stress in the pores of matrix (Hohmann, 1997) – the same kind of capillary stress considered to mobilize colloids during drying cycles in soils (Majdalani *et al.*, 2008). These processes could mobilize contaminants from soil matrix that are otherwise immobile (Niven and Singh, 2008;

Singh *et al.*, 2011). To date, the effect of freeze-thaw cycles on the mobilization of colloids and colloid-associated contaminants has not been quantified.

The objective of this work is to evaluate the effect of freeze-thaw cycles on the mobilization of colloids and colloid-associated metal cations from soil. Intact cores of a fractured shale saprolite soil were subjected to sequences of freezing, thawing, and rainfall infiltration. Each soil core was monitored for releases of colloids and colloid-associated metal cations. The releases from the cores subjected to freeze-thaw cycles were compared to releases from cores kept at room temperature between rainfall infiltration events. We hypothesized that the formation of ice and the resulting increase in stress in the soil pores would generate colloids that could be mobilized during infiltration events that follow soil thawing.

Experimental details

Intact soil core sampling: Intact soil cores were collected from the bottom of a hill slope in the Melton Branch watershed on the grounds of the Oak Ridge Reservation, Tennessee (Luxmoore and Abner, 1987). The field site and soils are described in detail by Jardine *et al.* (1993). The soil consists of fractured shale saprolite that has been weathered by 130 cm y^{-1} of rainfall. Infiltrating water predominantly passes through the bedding planes and fractures, which dip at an angle of 30° (Jardine *et al.*, 1993). The bedding planes and fractures are coated with iron(III) and manganese oxyhydroxides and translocated clay minerals.

Intact soil cores were collected using a hand-sculpting method (Jardine *et al.*, 1993). Vegetation and the O-layer of the soil were removed from the sample sites. Cylinders of soil in the A-horizon were excavated and trimmed to fit inside polyvinylchloride (PVC) pipes of 30.5 cm height and 25.4 cm width. In some cases, the top and sides of the soil cylinders were coated with melted paraffin wax to prevent the fractured soil from falling apart. The gap between the

PVC pipe and the soil cylinder (approximately 1.2 cm) was filled with polyurethane expandable foam (US Composites). The soil collection method preserved the structural integrity of soil. Preliminary experiments confirmed no leaching of dissolved organic carbon from the paraffin wax and foam.

Experimental setup: Colloid mobilization experiments were conducted using a rainfall simulator consisting of a reservoir, a peristaltic pump, a rainfall distributor, the soil core, a sampling grid, and sample collection tubes (Figure 3.1). The peristaltic pump transferred rainfall solutions (0.01 mM $NaNO_3$) from the reservoir to the rainfall distributor. Rainfall was simulated by dripping water through 85 needles (25 gauge) at the bottom of the rainfall reservoir. The intact core was placed under the rainfall reservoir on a sampling grid with 19 ports to resolve spatially the flow of water through macropore (fractures) and matrix. The arrangement and the numbering of ports in the grid and arrangement of needles below the rainfall reservoir are described in Figure 3.1. The ports delivered samples of infiltrating water to 19 sample collection tubes (glass, 2.5 cm diameter × 25 cm length). Each port captured water flowing through an area of 11.4 cm^2; the total collected area was 340 cm^2. Water flowing near the perimeter of the soil cores was collected in a channel (1.3 cm width) around the sample ports to be discarded. The water flows to each port from the bottom surface of soil under zero tension.

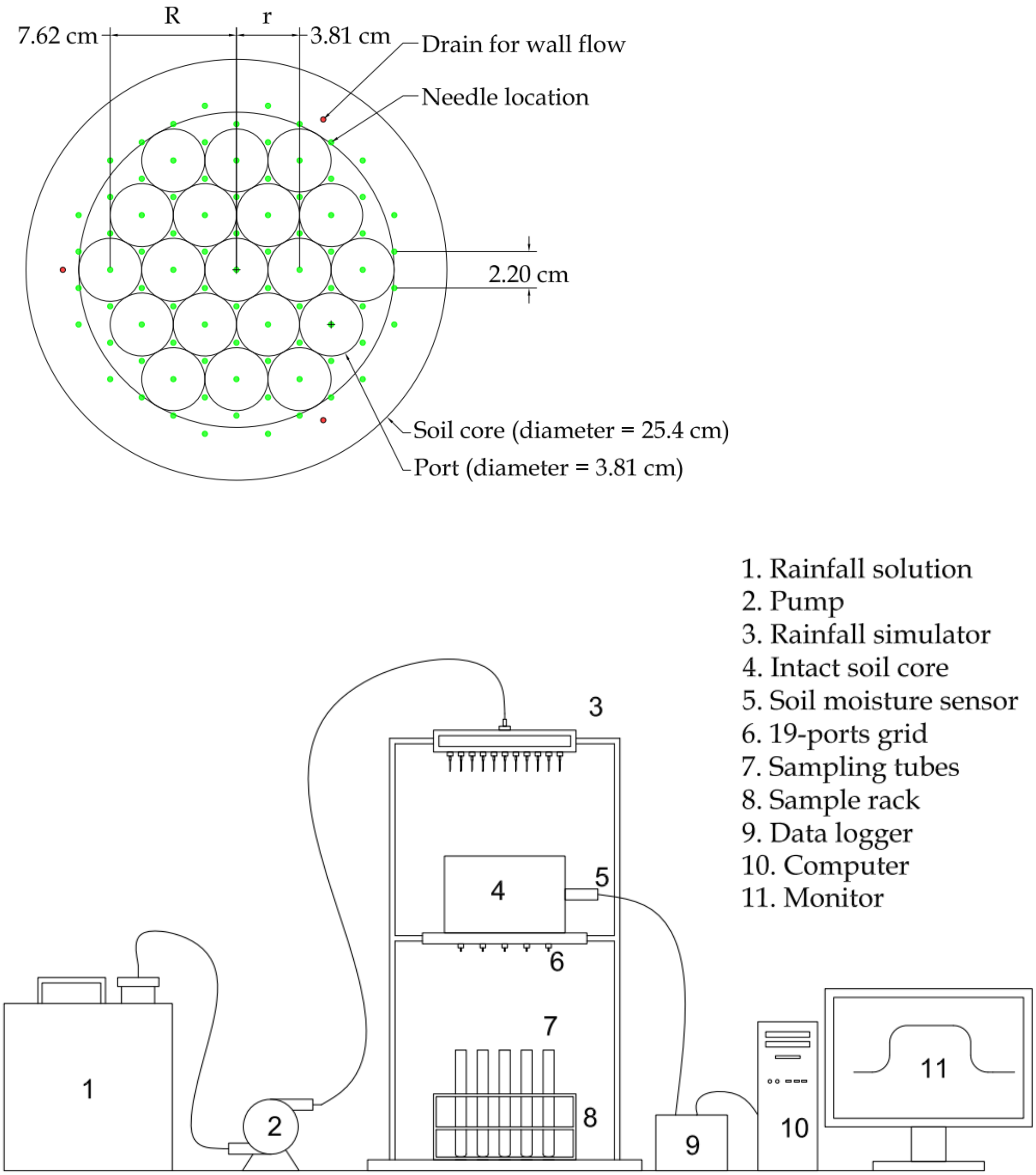

Figure 3.1. Column setup to examine the mobilization of colloid from intact core of a fractured soil. The 19 ports were arranged in a hexagonal pattern. The ports (diameter of 3.81 cm) were arranged in two concentric hexagons around a center port. The center port is designated as "00". The inner hexagon contains six ports at a center-to-center distance of maximum 3.81 cm from port 00 and is designated as "r" followed by an angle. The outer hexagon contains 12 ports at center-to-center distance of maximum 7.62 cm and is designated as "R" followed by an angle. The 85 needles of the rainfall reservoir were arranged in hexagonal pattern with closest distance between two needles as 2.2 cm.

In the preliminary rainfall experiments with soil cores of the full-height (30.5 cm), we observed that the bedding plane fractures carried most of the infiltrating water to the walls because the fractures intersected the core walls. To avoid this problem, the soil cores were cut to a height of 15 cm. A soil moisture probe (Delta-T Devices, Theta Probe MLX2) was inserted in the side of the soil core to monitor moisture content. The probe was located 7.5 cm below the soil surface and extended 6 cm into the soil. The probe was interfaced with a computer through a data logger (DATAQ Instruments, DI 710) to record and store moisture content at 1 min intervals.

***Application of rainfall containing cesium and strontium*:** A rainfall solution of 1 mM CsBr (99.99%, Argo Chemical) and 1 mM $SrBr_2$ (99.9%, MP Biochemicals) was applied at a rate of 2.5 cm h^{-1} for 51 h in soil cores prior to freeze-thaw cycles. At this rainfall application rate, the maximum amount of rainwater infiltrated through cores without occurrence of water pool on top of the soil cores. A rainfall application at 2.5 cm h^{-1} represents a typical heavy rainfall at Oak Ridge (Wilson *et al.*, 1990). After adding cesium and strontium, a rainfall solution of 4 mM $NaNO_3$ (same ionic strength as the solution with cesium and strontium) was applied to the soil cores for 17 h to decrease the concentrations of cesium and strontium to a steady level in the effluent. Rainwater of lower ionic strength (0.01 mM $NaNO_3$) was injected for another 24 h until the effluent concentration of cesium and strontium decreased below 0.1% of the injected concentration.

***Freeze-thaw cycles*:** A freeze-thaw cycle involved an application of rainwater (0.01 mM $NaNO_3$) for 6-7 h at 2.5 cm h^{-1} and a 66 h-pause in the rainfall during which the soil core was frozen at -15 °C for 42 h and thawed at 25 °C for 24 h. Control experiments were conducted in which the soil core was not frozen after the rainfall; instead, the soil core was dried at 25 ^{o}C during the 66 h-pause in rainfall. Two cores (core 1 and core 2) were used as control. The control experiment was repeated five times in cores 1 and 2. Both cores were subjected to five freeze-thaw cycles after the control experiments on the same cores.

Analysis of water samples: The infiltrating water samples collected in all active ports were analyzed for pH, conductivity, turbidity, and bromide. The pH was measured using a pH/ion-selective electrode meter (Orion 720A) and a combination electrode (Orion 8102BNU). Conductivity was measured using a conductivity meter (Orion 105) and a cell (Orion 011050). Bromide was measured using the pH/ion-selective electrode meter and a combination bromide-selective electrode (Accumet 13-620-524). Turbidity was measured using a turbidity meter (Hach 2100N). The measured turbidities were converted to colloid concentrations (mg L^{-1}) by using a calibration curve of total suspended sediment concentration versus turbidity. The suspended sediment concentration was measured by drying colloid suspensions (20 mL) of increasing turbidity in pre-weighed aluminum cups in an oven at 104 °C and weighing the mass of the dried colloids. The contribution of total dissolved solids to the suspended sediments concentration was estimated to be less than 1% based on a conversion of the maximum conductivity (25 $\mu S\ cm^{-1}$) to total dissolved solids.

Concentrations of the major cations (Na^+, K^+, Mg^{2+}, Ca^{2+}), iron, aluminum, and silicon were measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES; ARL model 3410+) in samples collected only at the start, middle, and end of each rainfall. For ICP-AES, a blank and three standards made by accurately diluting certified standards were used for calibration. Cesium and strontium concentrations were measured using inductively coupled plasma-mass spectrometry (ICP-MS; Perkin Elmer SCIEX Elan DRC-e). Cesium and strontium were measured as total and dissolved concentrations, with dissolved defined as passing through a 0.2 μm nylon filter (VWR, 25 mm diameter). The concentration of cesium and strontium associated with colloids was calculated as the difference between the total and dissolved concentrations. For ICP-MS, indium was used as an internal standard and a blank and three standards (100, 500, and 1000 ppb) made by accurately diluting certified standards were used for calibration. The detection limits for cesium and strontium were 2.0 and 1.0 μg L^{-1}, respectively.

Characterization of soil and colloids**:** Soil (< 75 um) and colloids mobilized from the control and freeze-thaw cores were characterized by X-ray diffraction analysis (XRD; Siemens D5000). The colloids were isolated from column effluent samples by centrifugation at 1617 *g* for 25 min. After decanting the supernatant, the settled colloids were air-dried and grounded with mortar and pestle. The prepared colloid samples and the soil samples were exposed to Cu K_α radiation over a range of 5-65° 2θ at 2 s per 0.02° step. The XRD data were analyzed quantitatively for minerals present using the RockJock computer program (Eberl, 2003).

The elemental composition of the colloids was measured by acid digestion and ICP-MS. The acid digestion was done using a modified version of the technique reported by Farrell *et al.* (1980). About 0.1 g of colloids was mixed with 5 mL of a 7:3 mixture of hydrochloric acid and hydrofluoric acid and 2 ml of nitric acid in a 50 mL digestion tube. The mixture was heated to 95°C in a digestion block for 2 h. The digested solution was cooled and diluted to 50 mL with a 1.5%(wt/wt) boric acid solution. The solution was reheated to 95°C for 15 min and cooled for analysis by ICP-MS. The analyzed elements were aluminum, calcium, iron, potassium, magnesium, manganese, silicon, titanium, and zinc.

Results

Flow of water through soil due to freeze-thaw: The flux through cores 1 and 2 during control and freeze-thaw experiments varied (Figure 3.2). The average flux in core 1 during the freeze-thaw experiment was 2.0 ± 0.3 cm h^{-1}, similar to the flux of 2.0 ± 0.4 cm h^{-1} during the control experiment. The average flux rate in core 2 during the freeze-thaw experiments was 1.5 ± 0.5 cm h^{-1}, similar to 1.42 ± 0.60 cm h^{-1} during the control experiments. The flux of water fluctuated in core 2 in both control and freeze-thaw experiments. The flux through the core 2 decreased with the number of wet-dry cycles. The number of active ports conducting water increased with the number of freeze-thaw cycles in both cores. There was no change (core 1) or a decrease in the number of active ports in the control experiments. The number of ports conducting water was 8 to 10 during the freeze-thaw experiments in contrast to 5 ports in the control experiments. The number of ports conducting water in core 2 was 4 to 7 during the freeze-thaw experiments in contrast to 3 to 4 ports in the control experiments (Figure 3.2).

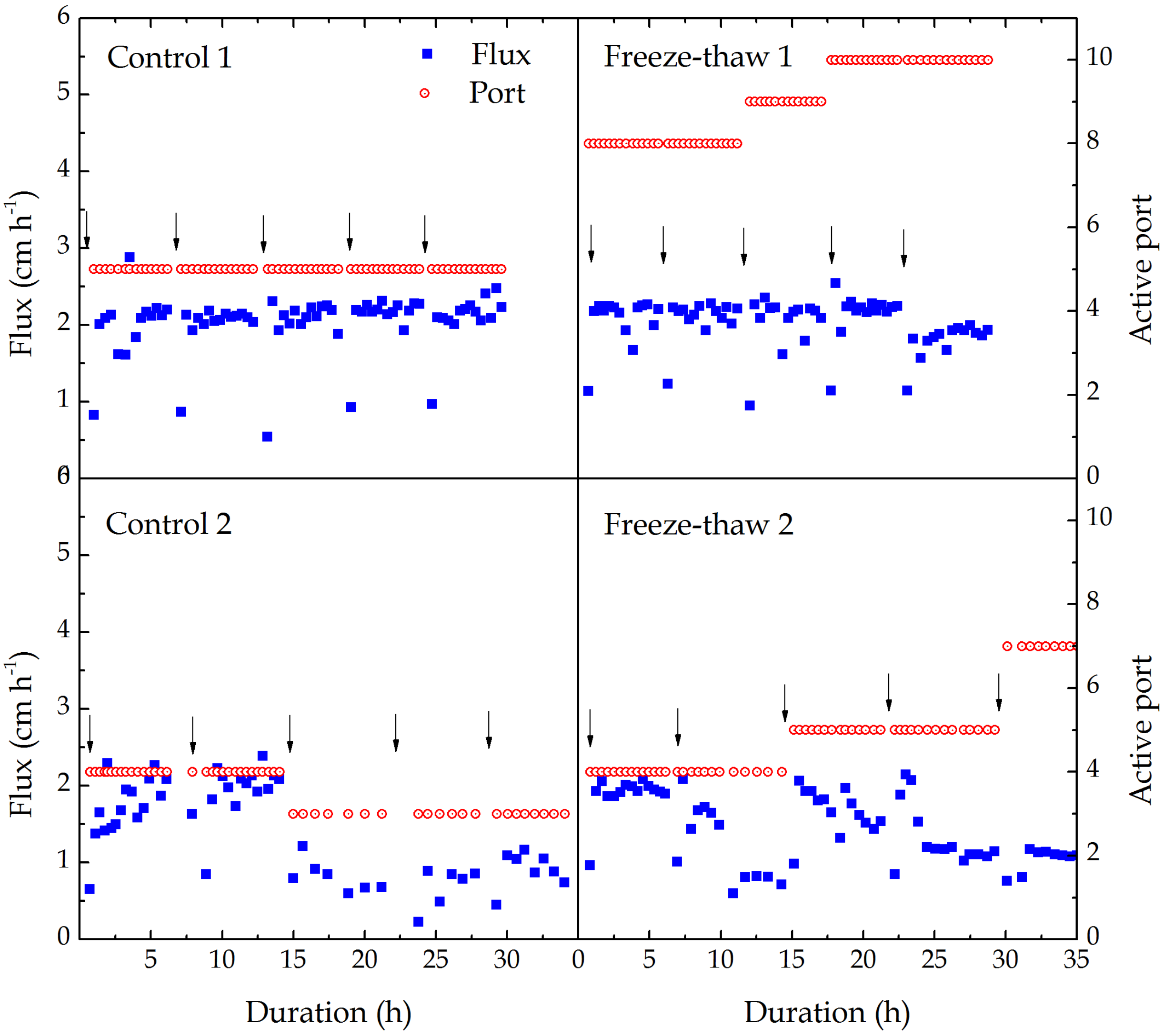

Figure 3.2. Flux and the number of active ports in the freeze-thaw and control experiments. The arrows mark the start of rainfall after a freeze-thaw cycle or drying in control experiments.

***Colloid mobilization*:** After the freeze-thaw cycles, the infiltrating water mobilized larger amounts of colloids (a cumulative mass of 4.3 g) than the control experiments (a cumulative mass of 2.0 g) in core 1 (Figure 3.3). The amount of colloids mobilized increased with successive freeze-thaw cycles between rainfall events. Successive wet-dry cycles in the control experiments did not increase the amount of colloids mobilized. The results were consistent in core 2 in which 4.2 g of colloids were mobilized during the freeze-thaw cycles compared to 2.1 g during the control experiments.

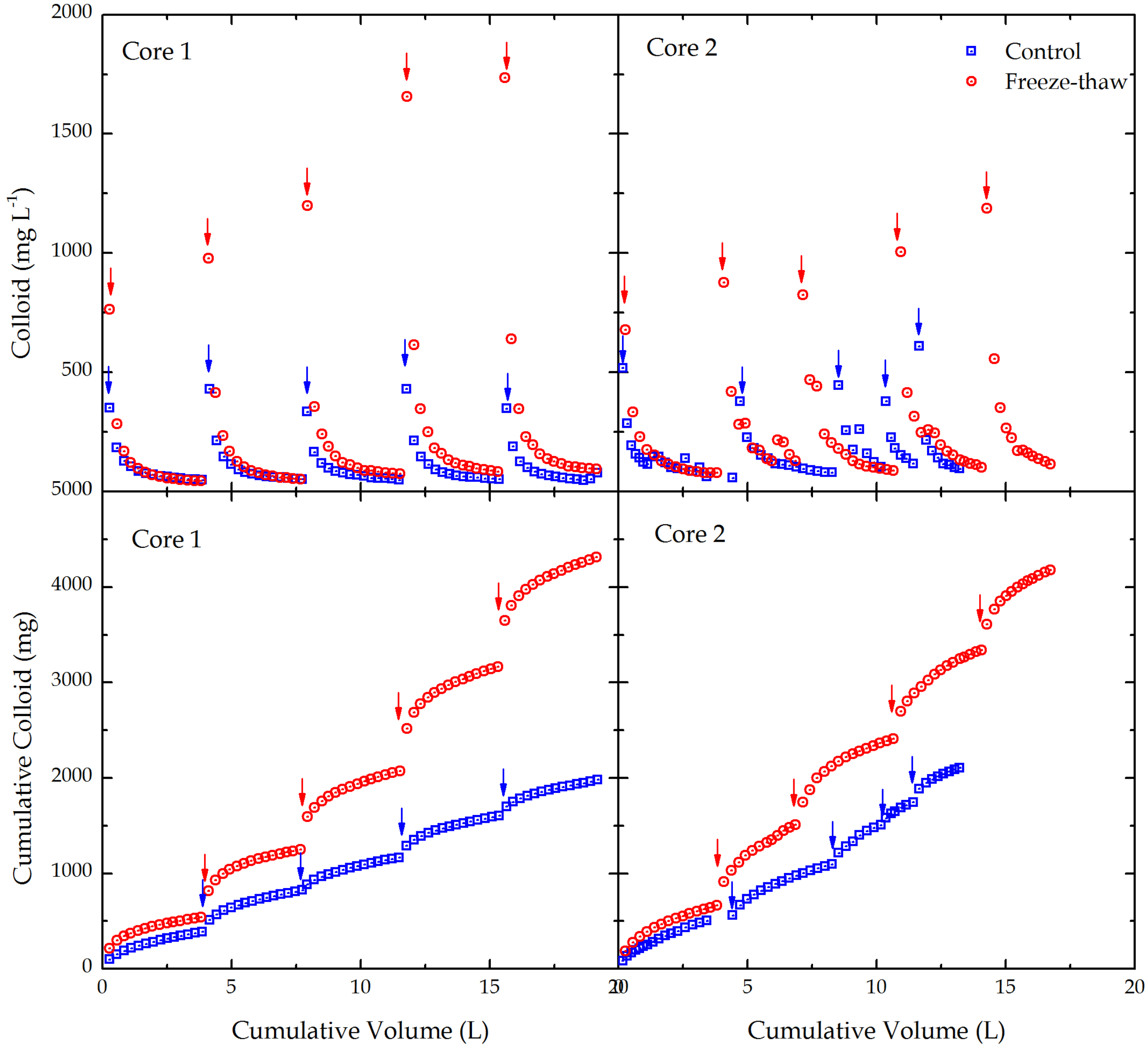

Figure 3.3. The mobilized colloid concentration (upper row) and cumulative mass of colloids mobilized (lower row) as a function of the cumulative volume of infiltrated water during control and freeze-thaw experiments. The arrows mark the start of rainfall after a freeze-thaw cycle or drying in the control experiments.

***Mineral composition of colloids*:** Results of XRD analysis indicated an increase in clay minerals and iron-containing minerals and a decrease in quartz fractions in the mobilized colloids compared to the soil from which colloids were mobilized (Table 3.1). The soil consisted of 35.7% clay minerals, 43.3% quartz, and 1.5% iron-containing minerals including ferruginous smectite, goethite, and amphibole. In contrast, colloids mobilized from the freeze-thaw cores had 64.3% clay minerals, 21.7% quartz, and 5.5% of iron-containing minerals. The colloids mobilized in control soil had 73.7% clay minerals, 3.5% quartz, and 4.6% iron-containing minerals. The clay minerals mobilized due to freeze-thaw cycles were identified as 2:1 clays. The acid digestion test showed the major elements (> 1 wt%) of the soil and mobilized colloids were silicon, aluminum, iron, potassium, and calcium (Table 3.2). Silicon was present in higher amounts in the colloids mobilized from the freeze-thaw cores than the colloids mobilized from the control cores.

Table 3.1. Minerals in weight percentage present in soils and mobilized colloids as determined by X-ray diffraction.

Minerals	Soil (< 75 um) (wt %)	Colloids (Control) (wt %)	Colloids (Freeze-thaw) (wt %)
Quartz	43.3	3.5	21.7
K-feldspar (microcline, orthoclase)	17.2	38.2	29.1
Plagioclase (albite)	11.3	8.6	4.4
Calcite	9.7	22.6	21.4
Amphibole (ferrotschermakite)	8.8	0.6	0.5
Goethite	7.5	8.6	11.6
Fluorapatite	1.3	3.5	1.4
Diaspore	0.8	2.4	3.0
Halloysite	0.0	0.7	0.7
Kaolinite (disordered)	0.0	4.8	0.1
Smectites	0.0	2.2	2.5
Illite	0.0	3.0	2.1
Muscovite (2M1)	0.0	1.4	1.4

Table 3.2. Elements present in soil minerals and colloids measured by acid digestion.

Sample	Al (wt %)	Ca (wt %)	Fe (wt %)	K (wt %)	Mg (wt %)	Mn (wt %)	Si (wt %)	Ti (wt %)	Zn (wt %)
Soil (<75um)	5.99 ± 0.37	1.24 ± 0.01	3.61 ± 0.42	2.77 ± 0.40	0.68 ± 0.04	0.06 ± 0.01	24.24 ± 1.10	0.45 ± 0.04	0.01 ± 0.01
Colloids (Control)	10.29± 0.86	1.63 ± 0.16	6.69 ± 0.88	2.93 ± 0.38	1.25 ± 0.12	0.02 ± 0.00	16.21 ± 1.35	0.46 ± 0.04	0.01 ± 0.01
Colloids (freeze-thaw)	9.50 ± 1.02	1.87 ± 0.14	7.45 ± 0.97	3.21 ± 0.41	1.42 ± 0.18	0.05 ± 0.01	21.06 ± 1.98	0.71 ± 0.08	0.01 ± 0.01

Colloid-facilitated transport of cesium and strontium: Figures 3.4 and 3.5 show the mobilization of total, dissolved, and colloidal cesium and strontium during the control and freeze-thaw experiments. During each of the five rainfall events, the total concentrations of cesium and strontium decreased over time following an initial spike caused by the wetting of the soil cores. Over the five rainfalls, the total amount of cesium and strontium mobilized during control and freeze-thaw experiments gradually decreased. The total and dissolved concentration of cesium was higher than the concentration of strontium. The difference in concentration between cesium and strontium decreased with increases in the number of freeze-thaw cycles. The dissolved fractions of cesium and strontium decreased after each freeze-thaw cycle, but increased during the control experiments. The colloidal concentration of cesium and strontium increased after each rainfall pause and the concentration of colloidal cesium and strontium mobilized was greater in the freeze-thaw experiment than in the control experiment. The amount of cesium associated with colloids was higher than amount of strontium associated with colloids.

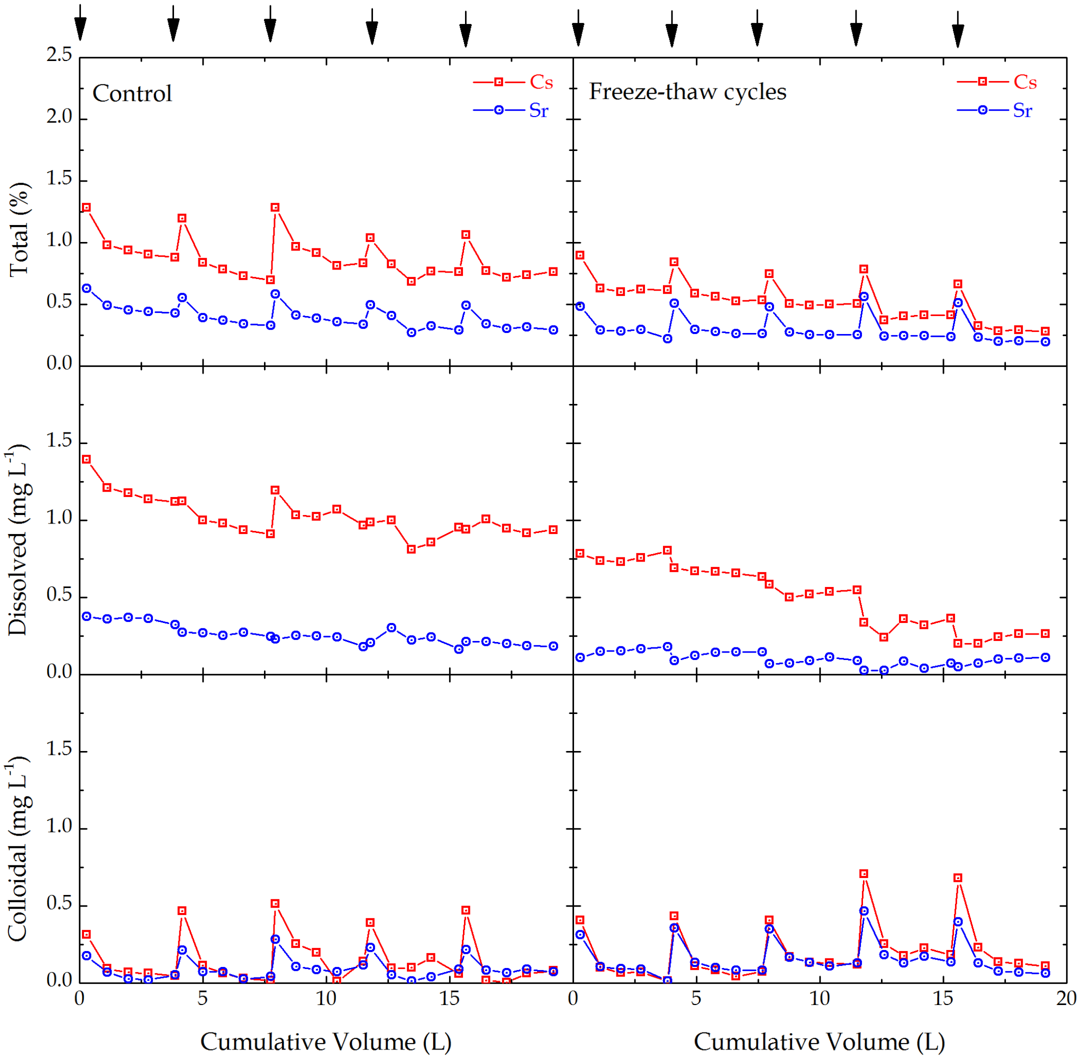

Figure 3.4. The total, dissolved, and colloidal concentrations of cesium and strontium mobilized from core 1 as a function of the cumulative volume of infiltrating water during the control experiments (left column) and the freeze-thaw experiments (right column). The arrows mark the start of rainfall after a freeze-thaw cycle or drying the control experiments.

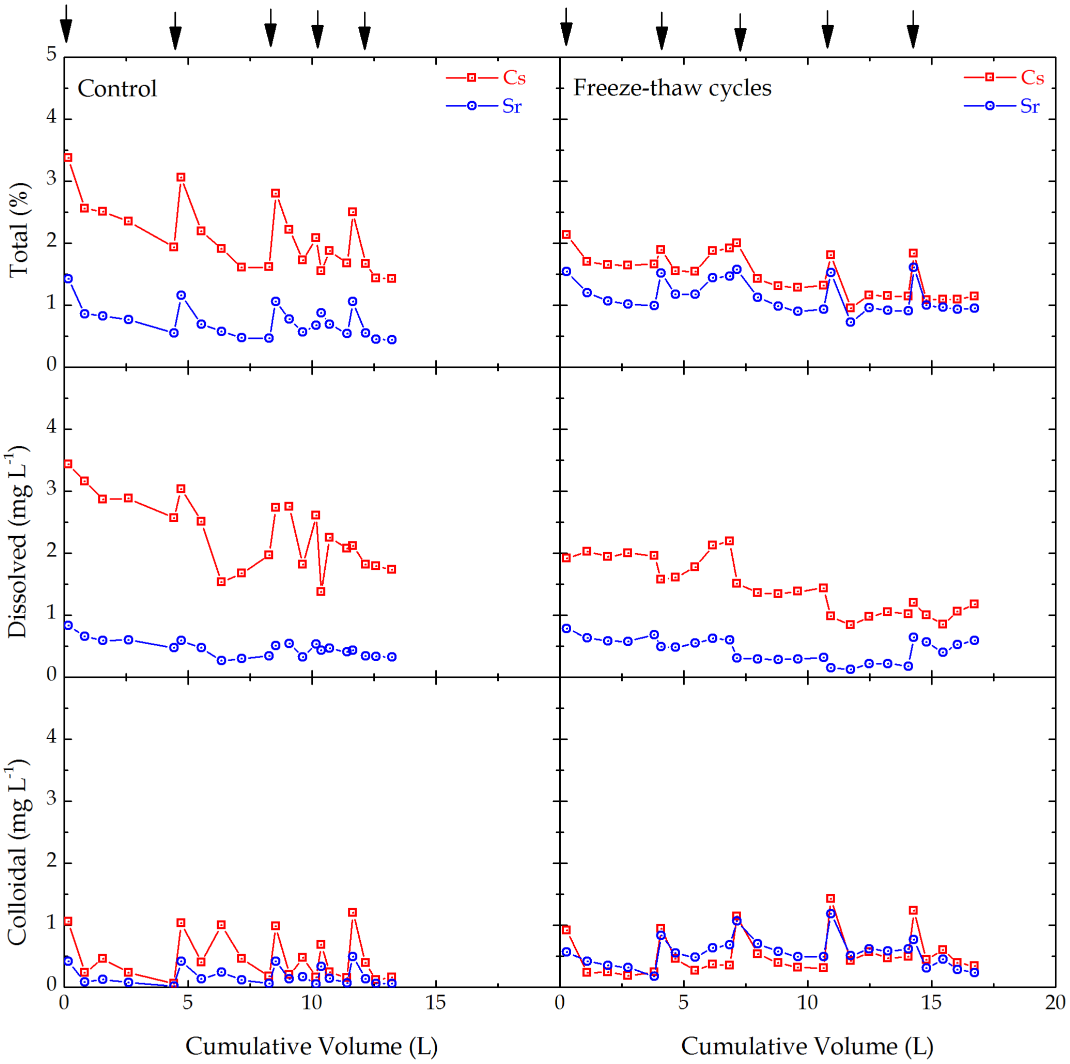

Figure 3.5. The total, dissolved, and colloidal concentrations of cesium and strontium mobilized from core 2 as a function of the cumulative volume of infiltrating water during the control experiments (left) and the freeze-thaw experiments (right). The arrows mark the start of rainfall after a freeze-thaw cycle or drying in the control experiments.

Discussion

***Role of freeze-thaw cycles on flow of water*:** There were more active ports in the freeze-thaw experiments than in the control experiments indicating an increase in preferential flow due to freeze-thaw cycles (Figure 3.2). A decrease in the number of active ports in core 2 during the control experiments suggests that preferential flow paths were clogged by mobilized colloids. In contrast to the control experiment, the number of active ports increased in core 2 during the freeze-thaw experiments, which indicates an increase in preferential flow through core 2. Increase in the number of active ports during the freeze-thaw experiments did not increase the average flux of water through all ports. The average flux through the soil core did not increase during the freeze-thaw experiments compared to control experiments because the rainfall intensity was lower than the conducting capacity of soil. Therefore, flux rate could not be used as an indicator to estimate the changes hydraulic conductivity due to freeze-thaw.

The soil used in this study was primarily composed of fractured saprolite with higher fraction of clays. The fractures in this soil could be widened due to expansion and contraction of water during freeze-thaw. The colloids generated during this process may further facilitate the transport of colloids and associated contaminants through newly created preferential flow paths. A previous study reported increases in preferential flow or the hydraulic conductivity of soil due to freeze-thaw cycles (Taumer *et al.*, 2006). Increases in hydraulic conductivity could be attributed to increases in soil fractures caused by disintegration of soil aggregates. Oztas and Fayetorbay (2003) reported a decrease in the stability of aggregates with an increase in the number of freeze-thaw cycles and the decrease in aggregate stability was dependent on soil types. Results of another study suggested that soil texture and organic matter, not mineralogy affects aggregate stability (Lehrsch *et al.*, 1991). Kvaerno and Oygarden (2006) found that a silty soil was more heavily eroded than two soils with higher clay contents. This result verified the mechanism suggested by Taber (1930) – that clays conduct water too slowly to supply water to the freezing front and silts, owing to their moderate grain size, can sustain a steady supply of water to growing ice fronts. In addition, water is held in clays at strong capillary pressure that lowers the freezing point of water. Therefore, ice is formed in larger pores of the silt.

Role of freeze-thaw cycles on the mobilization of colloids: More colloids were released from the soil cores subjected to freeze-thaw cycles than from the control soil cores (Figure 3.3). We attribute the effect of freeze-thaw cycles on colloid mobilization to destabilization of soil aggregates (Figure 3.6). Expansion of water during ice formation would widen soil cracks and generate colloids. The formation of fracture would allow water to fill the pores that are not previously accessible during the previous freeze. Previous studies have shown a decrease in the stability of soil aggregates during freeze-thaw cycles (Lehrsch *et al.*, 1991; Oztas and Fayetorbay, 2003; Kvaerno and Oygarden, 2006). The generation and release of colloids from soil pores could be a direct result of the formation of ice in pores and the movement of water during freezing. This process is known as frost heaving (Taber, 1929). During frost heaving, the water on surface of the soil freezes in contact with air at sub-freezing temperatures. The nucleated ice is surrounded by a film of supercooled water that is gradually frozen. The water from nearby pores flows towards the freezing front because (1) water move towards colder regions due to the temperature gradient in the soil (Dash, 1989), (2) higher vapor pressure in warmer water pushes the water toward colder water, and (3) water driven by osmosis moves towards a freezing front where salt content of water is higher after the formation of ice. The extent of ice formation depends on the supply of water at the freezing front. In the unsaturated zone, the water flows through the water films attached to soil grains. With the formation of ice and the depletion of available liquid water, the thickness of water film decreases. The thinning of water film during freezing may result in the release of colloids in the same way as soil drying results in the release of colloids (Gao *et al.*, 2006). The freezing of soil water also causes expansion of soil pores, and the expansion may break up soil aggregates, and is likely to generate colloids available for mobilization during ensuing infiltration events (Figure 3.6). The freezing front may also move colloids downward because suspended colloids are excluded from the freezing water in the same way solutes are excluded (Jackson and Uhlmann, 1966). These colloids may also be washed away during subsequent rainfall events.

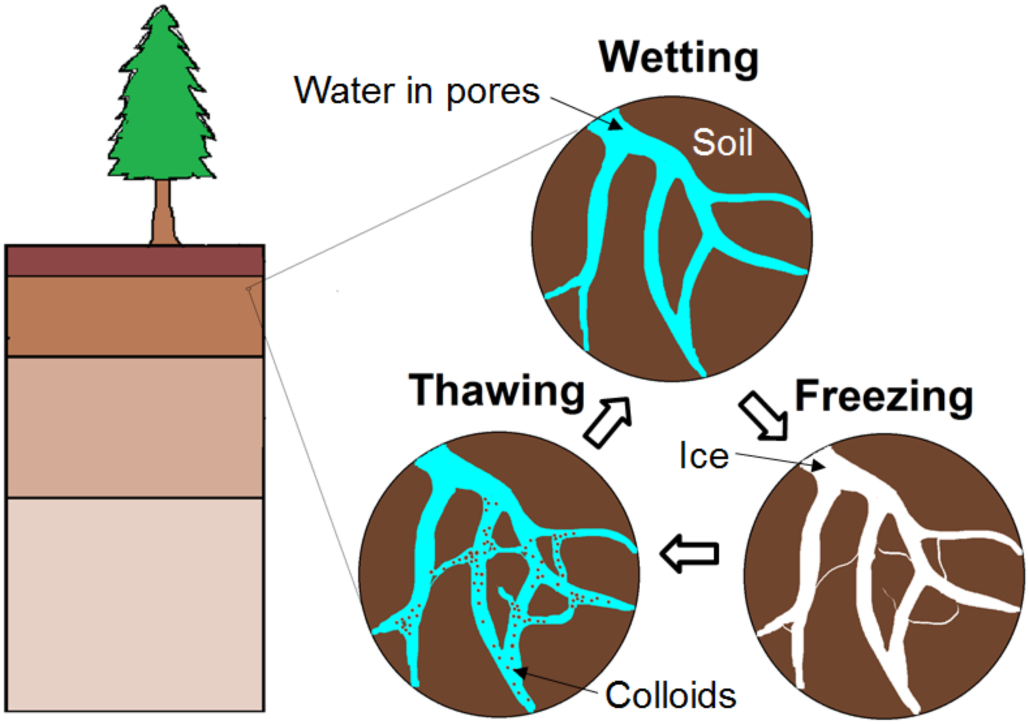

Figure 3.6. Illustration of the effect of freeze-thaw cycling on the mobilization of colloids.

***Effect of freeze-thaw on mobilization of minerals from soil*:** X-ray diffraction analysis shows that the proportion of quartz and iron containing minerals are higher in colloids mobilized during freeze-thaw than colloids mobilized during the control experiments (Table 3.1). The pressure generated due to successive expansion and contraction of water and ice could break a fraction of the soil minerals dominated by quartz fragments. On the other hand, capillary pressure, which is the dominant force for generation of colloids in the control cores, may not be enough to mobilize quartz colloids. Freeze-thaw cycles could mobilize colloids from matrix filled with water. Drying mobilizes colloids from the interface between the macropores and matrix. The XRD result was supported by results of the acid digestion of colloids which indicated that the fraction of silicon, the primary element in quartz, was higher in colloids mobilized by freeze-thaw experiments than the control experiments (Table 3.2).

Colloid-facilitated transport of cesium and strontium: Colloid-facilitated transport of cesium and strontium was greater in the freeze-thaw cores than in the control cores due to mobilization of larger amounts of colloids by freeze-thaw. Increase in colloidal fraction of cesium and strontium after freeze-thaw experiment was larger than the colloidal fraction after control experiments (Figure 3.4 and 3.5). The dissolved concentration of cesium and strontium decreased due to freeze-thaw in contrast to the increase of dissolved fraction during the control experiment. Dissolved cations are preferentially excluded from water at freezing front. The increase in the concentration of cations in the water during freezing shifts the partition equilibrium toward the soil minerals and colloids. Increasing adsorption decreases the total amount of dissolved cations in water for mobilization during succeeding rainfall. The absorbed cations could be slow to desorb during the thawing process due to sorption hysteresis and dissolved concentrations of cations could decrease due to further dilution by infiltrating rainwater. In contrast to freeze-thaw, the dissolved fraction of cesium and strontium in the control experiment increased possibly due to chemical non-equilibrium. During the control experiment, water moves through fractures that can be designated as mobile region. The water in the matrix could be designated as the immobile region because water moves several orders of magnitude slower through matrix than through the fractures or mobile regions. A concentration gradient exists between immobile and mobile regions of the soil because of higher rate of desorption in mobile region (Brusseau *et al.*, 1997). The concentration gradient may cause the diffusion of cesium and strontium from matrix to the macropores and increase the concentration of dissolved cesium and strontium in mobile zone during control experiment.

The total concentration of cesium was greater than total concentration of strontium in the freeze-thaw experiments (Figure 3.4 and 3.5). This result could be explained by examining the residual cesium and strontium concentration in soil before the start of the control and freeze-thaw experiments. It should be noted that control experiments and freeze-thaw experiments were carried out on soil cores that were previously flushed with water to remove any cesium and strontium from the pore water. Strontium, due to its larger hydration radius than cesium, weakly binds to soil mineral by forming outer-sphere complexes and desorbs quickly into infiltrating water. A higher removal rate of strontium by uncontaminated rainwater could deplete the residual concentration of strontium below the concentration of cesium.

Greater quantities of cesium were associated with colloids compared to strontium due to a difference in their strengths of binding to colloids. The strength of adsorption of cations to colloids depends on whether adsorption occurs through the formation of either inner-sphere or outer-sphere surface complexes, or the simple accumulation of an ion swarm near the colloid surface without any complex formation. For example, Cs^+ forms stronger surface complexes with illite by ion exchange and inner-sphere complexation to frayed-edge (surface hydroxyl) sites, whereas Sr^{2+} binds with illite by ion exchange only. The transport of readily desorbing Sr^{2+} is not effectively facilitated by colloids compared to slowly desorbing Cs^+ (Turner *et al.*, 2006). X-ray diffraction confirmed the presence of illite in the mobilized colloids, which could contribute to a larger fraction of cesium in the soil compared to strontium. Colloid-facilitated transport of Cs^+ was also observed due to transient in flow, where the Cs^+ peak was found to coincide with colloids mobilized after consecutive rainfall events (Cheng and Saiers, 2010). We have reported evidence of increased mobilization of cesium and strontium by colloids due to freeze-thaw. Our findings are applicable to better understanding of the risk of contaminant transport by colloids in soils susceptible to freeze-thaw.

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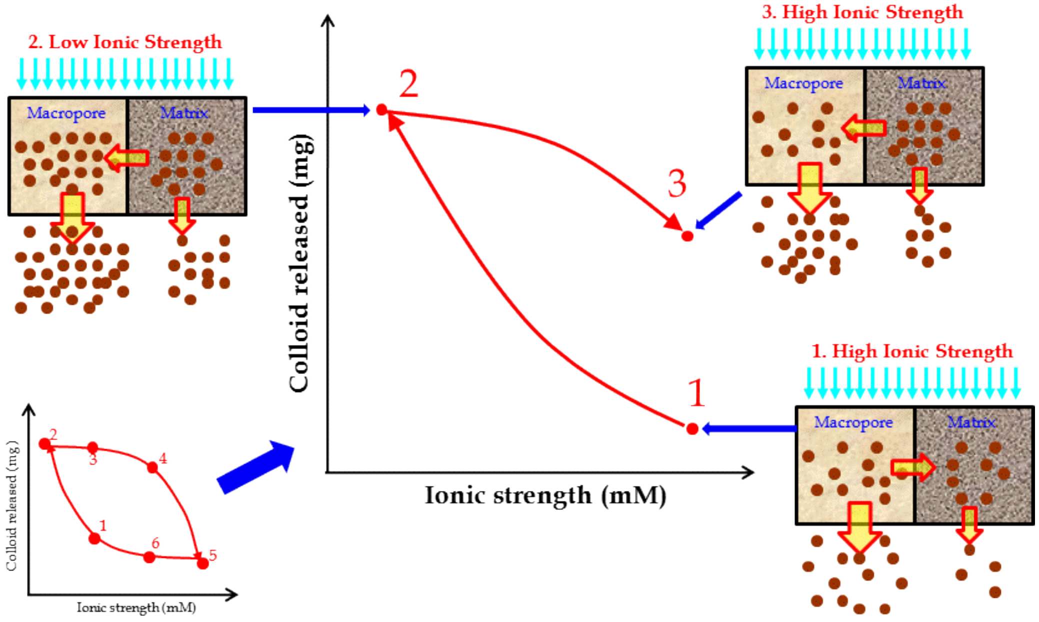
CHAPTER 4

MOBILIZATION OF COLLOIDS AND METALS CATIONS FROM INTACT CORES OF A FRACTURED SOIL: ROLE OF PORE WATER EXCHANGE BETWEEN FRACTURES AND MATRIX



An illustration of exchange of pore water with infiltrating rainwater of different ionic strengths and its effect on the mobilization of colloids

Abstract

Understanding the mechanisms of colloid mobilization is essential to predicting the importance of colloid-facilitated transport of contaminants in subsurface environment. Under natural conditions, the effect of pore water exchange between the soil matrix and macropores on the mobilization of colloids and metals is not understood. We conducted rainfall simulations in the laboratory to evaluate the effect of pore water exchange on mobilizing cesium, strontium, and colloids from intact soil cores of a fractured soil. The ionic strength of the rainfall was varied from 0.01 to 10 mM to monitor the mobilization of colloids and the exchange of solute between macropores and matrix based on a difference in the ionic strength of pore water. Samples were collected from a 19-port grid at the base of the soil core to identify the effect of physical heterogeneity on the mobilization of colloids. The mobilization of colloids decreased and the mobilization of cesium and strontium increased as the ionic strength of the infiltrating water was increased. Mobilization of both metals and colloids was hysteretic in response to changes in ionic strength – the amount of metals and colloids mobilized at a given ionic strength was not matched when the experiment was repeated following exposure to pore water of higher or lower ionic strengths. The amount of hysteresis in colloid mobilization was positively correlated with bromide breakthrough times, which was used as an indicator of the rate of exchange of solute between the macropores and the matrix. The exchange of solute between the soil matrix and the macropores was attributed as the primary reason for the hysteresis of metals and colloid mobilization during changes in ionic strength.

Introduction

The mobilization of colloids and contaminants in unsaturated soil has been extensively studied due to their implication for groundwater quality (McCarthy and Zachara, 1989; Smith and Degueldre, 1993; Sen and Khilar, 2006). Contaminants are adsorbed on soil minerals in the macropores and the matrix of a heterogeneous soil. Colloids and contaminants are mobilized from the macropores by infiltrating rainwater. The mobilization of colloids and contaminants in matrix occurs slowly relative to macropore. An exchange of pore water between macropores and soil matrix occurs due to relative differences in water potentials in pore water. Under unsaturated condition, water drains from the macropores by gravity before water drains from the matrix, which causes a difference in tension or matrix potential of the pore water. A difference in matrix potential makes the water move from the matrix to the macropores (Gerke and van Genuchten, 1993). An increase in the concentration of a solute or of the ionic strength of the pore water decreases the surface tension of water and causes a movement of water in the direction of increasing ionic strengths (Zhuang *et al.*, 2010). The driving forces for pore water exchange or solute may change the ionic strength of pore water and affect the mobilization of colloids. For example, a decrease in ionic strength is known to mobilize colloids (DeNovio *et al.*, 2004). The exchange of pore water and solute between macropores and the soil matrix has the potential to mobilize contaminants with colloids from the matrix over the long term (Jarvis, 2007).

A recent study also suggested that capillary stress in the soil matrix could break pore walls and release colloids into pore waters (Majdalani *et al.*, 2008). This recent investigation indicated that the soil matrix plays an important role in the mobilization of colloids. The potential role of the matrix in colloid mobilization has not been investigated in detail due to the presumption that the transport of colloids from the matrix to the macropores is diffusion-limited (Kjaergaard *et al.*, 2004). If colloids are mobilized from the matrix to the macropores, then assumptions about the immobilization of contaminants in the soil matrix may be invalid. However, limited studies have been carried out to identify the contribution of exchange of pore water or solute between macropore and matrix on mobilization of colloids and colloid-associated contaminants.

Colloids are mobilized in unsaturated heterogeneous soil by coupled physical and chemical processes (DeNovio *et al.*, 2004). Physical processes include transients in flow and moisture content. Chemical processes include changes in ionic strength and pH. The importance of both physical and chemical processes is sensitive to soil heterogeneity and transient flow conditions. The colloids could be mobilized where low ionic strength rainwater infiltrates. A difference in infiltration rates between the macropores and the matrix could cause a difference in the ionic strength of pore waters within the macropores and the matrix. A chemical non-equilibrium or difference in ionic strength of pore waters in the macropores and the matrix could cause a difference in the amount of colloids mobilized from the macropores and the matrix during a rainfall. Colloids are mobilized by advection through preferential flow paths during a rainfall. Advective transport of colloids ceases during a pause between rainfalls. During pauses, colloids may be mobilized due to diffusion through pores filled with water in matrix (Schelde *et al.*, 2002). These results suggest that colloids may be mobilized in the macropores during a rainfall and the matrix may contribute to colloid mobilization during pause between rainfalls. Therefore, it is important to consider the coupled effects of heterogeneity and transient conditions on the mobilization of colloids by chemical and physical processes.

A difference between the flow rates of water in the macropores and the matrix can cause a cross flow of water between the macropores and the matrix. This process is known as physical non-equilibrium. A difference in concentration of contaminants in the macropores and the matrix occurs due to physical non-equilibrium (Gwo *et al.*, 1996; Šimůnek *et al.*, 2003). In contrast to contaminant transport in heterogeneous soils, limited study has been carried out to investigate the effect of physical non-equilibrium on colloid transport (McCarthy *et al.*, 2002). Physical non-equilibrium may influence the transport of colloids in heterogeneous soil (McCarthy *et al.*, 2002). Physical non-equilibrium could explain the hysteretic nature of colloid mobilization in response to changes in the ionic strength (Torkzaban *et al.*, 2010). In a field study, the interaction between macropores and the soil matrix appeared to predict the concentration of bromide and microspheres in the macropores (Nielsen *et al.*, 2011). The results of these studies indicate that the exchange of pore water between macropores and the matrix due to physical non-equilibrium may mobilize contaminants and colloids from the matrix. However, the mechanism of colloid mobilization across the interface between macropores and the soil matrix is not clear.

The objectives of this study are to determine (1) if the exchange of pore water between the soil matrix and macropores mobilizes colloids and contaminants from the matrix, and (2) if the mobilized colloids carry contaminants from the matrix to the macropores. We hypothesized that physical non-equilibrium of water and chemical non-equilibrium of solutes could affect the mobilization of colloids in heterogeneous soil. To test this hypothesis, we applied rainfalls of multiple ionic strengths on intact cores of a fractured shale saprolite soil to mobilize colloids. We interrupted flow between rainfall of different ionic strengths to facilitate the exchange of water between the matrix and the macropores. We collected water samples multiple ports to examine the exchange of solute or pore water.

Experimental details

Intact soil core sampling: Intact soil cores were collected from the bottom of a hill slope in the Melton Branch watershed on the grounds of the Oak Ridge Reservation, Tennessee (Luxmoore and Abner, 1987). The field site and soils are described in detail by Jardine *et al.* (1993). The soil consists of fractured shale saprolite that has been weathered by 130 cm y^{-1} of rainfall. Infiltrating water predominantly passes through the bedding planes and fractures, which dip at an angle of 30° (Jardine *et al.*, 1993). The bedding planes and fractures are coated with iron(III) and manganese oxyhydroxides and translocated clay minerals.

Intact soil cores were collected using a hand-sculpting method (Jardine *et al.*, 1993). Vegetation and the O-layer of the soil were removed from the sample sites. Cylinders of soil in the A-horizon were excavated and trimmed to fit inside polyvinylchloride (PVC) pipes of 30.5 cm height and 25.4 cm width. In some cases, the top and sides of the soil cylinders were coated with melted paraffin wax to prevent the fractured soil from falling apart. The gap between the PVC pipe and the soil cylinder (approximately 1.2 cm) was filled with polyurethane expandable foam (US Composites). The soil collection method preserved the structural integrity of soil. Preliminary experiments confirmed no leaching of dissolved organic carbon from the paraffin wax and foam.

Experimental Setup: Colloid mobilization experiments were conducted using a rainfall simulator consisting of a reservoir, a peristaltic pump, a rainfall distributor, the soil core, a sampling grid, and sample collection tubes (Figure 4.1). The peristaltic pump transferred rainfall solutions (0.01 mM NaCl) from the reservoir to the rainfall distributor. Rainfall was simulated by dripping water through 85 needles (25 gauge) at the bottom of the rainfall reservoir. A stainless steel mesh (# 200) was installed at the bottom surface of the intact core.

The intact core was placed under the rainfall reservoir on a sampling grid with 19 ports to resolve spatially the flow of water through macropore (fractures) and matrix. The arrangement and the numbering of ports in the grid and arrangement of needles below the rainfall reservoir are described in Figure 4.1. The ports delivered samples of infiltrating water to 19 sample collection tubes (glass, 2.5 cm diameter × 25 cm length). Each port captured water flowing through an area of 11.4 cm^2; the total collected area was 340 cm^2. Water flowing near the perimeter of the soil cores was collected in a channel (1.3 cm width) around the sample ports to be discarded. The water flows to each port from the bottom surface of soil under zero tension.

In preliminary rainfall experiments with the full-height (30.5 cm) soil cores, we observed that the bedding plane fractures carried most of the infiltrating water to the walls because the fractures intersected the core walls. To avoid this problem, the soil cores were cut to a height of 15 cm. A soil moisture probe (Delta-T Devices, Theta Probe MLX2) was inserted in the side of the soil core to monitor relative saturation of soil. The probe was located 7.5 cm below the soil surface and extended 6 cm into the soil. The probe was interfaced with a computer through a data logger (DATAQ Instruments, DI 710) to record and store relative saturation reading at 1 min intervals.

Two cores were used in this study. Bromide was injected as a tracer in order to characterize the physical heterogeneity of soil contributing flow to each port. Cesium and strontium were injected in one of two soil cores to investigate the mobilization of cesium and strontium with rainwater of increasing or decreasing ionic strengths. The contaminated soil core in addition to another uncontaminated soil core was used to test the mobilization of colloids through fractures in the soil at multiple ionic strengths. The conditions used in both cores are summarized in Table 4.1.

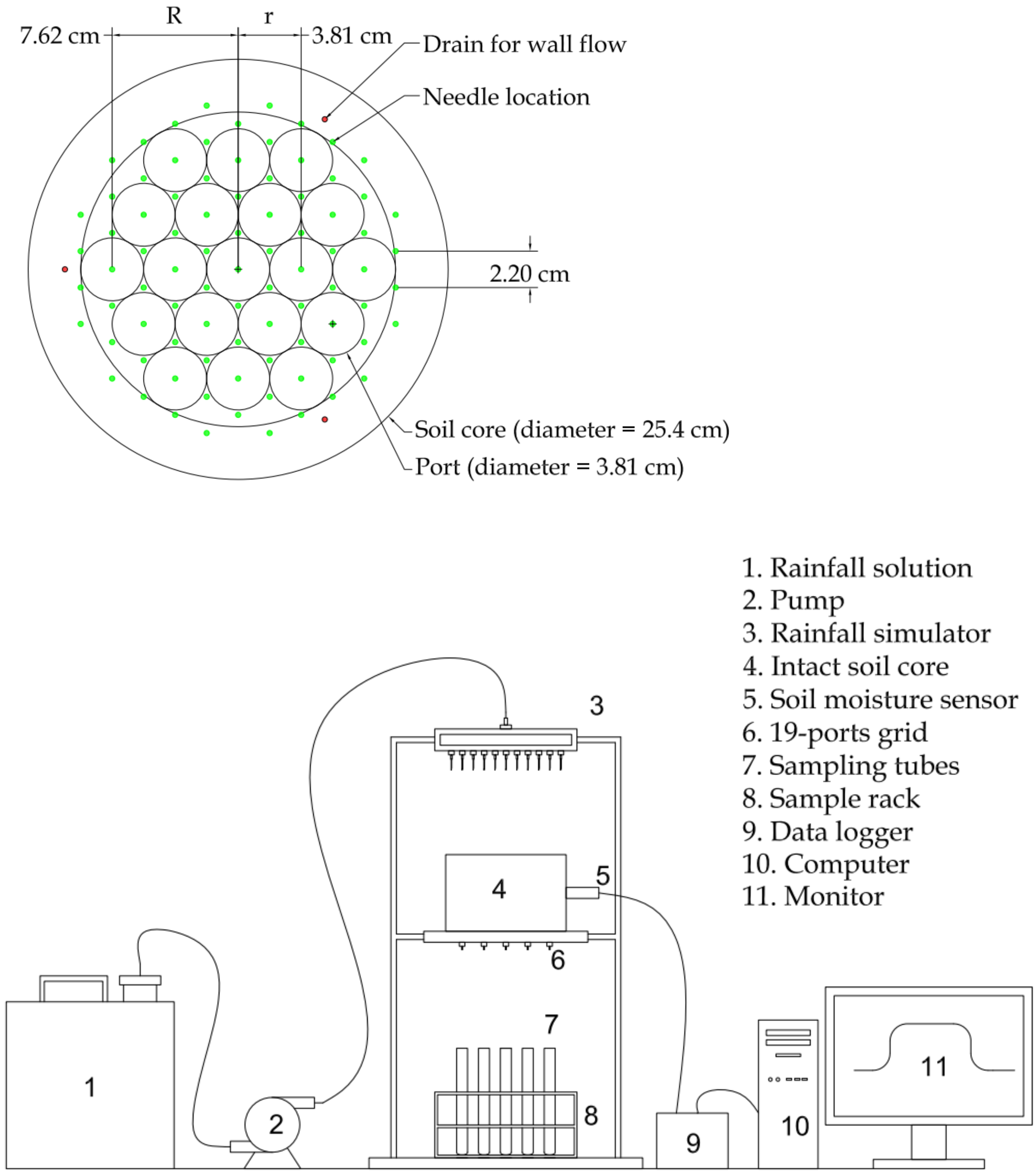


Figure 4.1. Column setup to examine the mobilization of colloid from intact core of a fractured soil. The 19 ports were arranged in a hexagonal pattern. The ports (diameter of 3.81 cm) were arranged in two concentric hexagons around a center port. The center port is designated as “00”. The inner hexagon contains six ports at a center-to-center distance of maximum 3.81 cm from port 00 and is designated as “r” followed by an angle. The outer hexagon contains 12 ports at center-to-center distance of maximum 7.62 cm and is designated as “R” followed by an angle. The 85 needles of the rainfall reservoir were arranged in hexagonal pattern with closest distance between two needles as 2.2 cm.

Table 4.1. Conditions used for rainfall applications on cores 1 and 2.

Conditions	Core 1	Core 2
Injection of cesium and strontium	No	Yes
Bromide injection	Yes	Yes
Injection (5 h) of cesium and strontium (1 mM)	No	Yes
Flow interruption (18.7 h) during bromide injection	Yes	No
Total rainfalls with varying ionic strengths	10	7
Order of ionic strengths	10, 5, 1, 0.1, 0.01, 0.01, 0.1, 1, 5, and 10	0.01, 0.1, 1, 10, 1, 0.1, and 0.01
Flux (cm h^{-1})	2.5	2.5

***Characterization of the soil physical heterogeneity*:** We investigated the effect of physical heterogeneity of soil on the mobilization of colloids and cations. Based on previous experiments (Jardine *et al.*, 1993), we expected rapid infiltration through the bedding plane fractures and slow infiltration through the shale saprolite under heavy rainfall. We refer to these flow paths as macropores and matrix, respectively. The breakthrough time of bromide in each port was used as an indicator to quantify the exchange rate of solute between the macropores and the matrix (Clothier *et al.*, 1998; Nielsen *et al.*, 2011). Greater exchange of bromide between the macropores and the soil matrix dilutes the bromide concentration in the pore water and causes later arrival of bromide at the bottom of the core. Bromide breakthroughs were obtained for each flowing port by applying a rainwater solution of 1 mM NaBr (99.9%, Fisher Chemicals) at a rate of 2.5 cm h^{-1} for 10 h in core 1 and 7 h in core 2. A rainfall application at 2.5 cm h^{-1} represents a typical heavy rainfall at Oak Ridge (Wilson *et al.*, 1990). At this rainfall rate, water did not pool on top of the soil cores used in the experiment. The breakthrough time of bromide was estimated as the time at which the bromide concentration in a port reached 50% of bromide concentration in the rainfall solution. Flow was interrupted for 18 h once on the plateau of a bromide breakthrough curve and twice on the tail of a bromide breakthrough curve of core 1 to investigate the effect of physical heterogeneity, especially matrix diffusion, on concentration of bromide (Brusseau *et al.*, 1989; Koch and Flühler, 1993).

***Application of rainfall containing cesium and strontium*:** In order to verify if colloids mobilized due to exchange of pore water could mobilize cesium and strontium adsorbed on the soil, one core was contaminated with cesium and strontium prior to the mobilization of colloids. A rainfall solution containing 1 mM CsBr (99.9% purity, Acros Organics) and 1 mM $SrBr_2$ (99.9% purity, MP Biochemicals) was prepared with high-purity water (>18.2 MΩ cm). The rainfall solution was applied to the soil core for 6 h at 2.5 cm h^{-1}. After the application of cesium and strontium, the rainfall was switched to 4 mM NaCl until the concentrations of cesium and strontium did not decrease any further in the effluent. The samples from two ports in core 2 were analyzed for total and dissolved cesium and strontium concentrations.

***Mobilization of colloids*:** We varied ionic strength between rainfalls to examine effect of the conductivity of pore water on the mobilization of colloids in heterogeneous soil. Rainwater with decreasing (10 mM to 0.01 mM) or increasing (0.1 mM to 10 mM) ionic strengths was applied at 2.5 cm h^{-1} for 5.3 h. After each ionic strength, rainfall application was paused for 18.7 h to allow for exchange of solute between the macropores and the matrix. The rainfall was resumed with the application of rainwater of different ionic strengths and the samples collected through the 19-port grid were analyzed for turbidity and conductivity.

***Colloid mobilization analysis*:** The total amounts of colloids mobilized corresponding to each ionic strength of rainwater was calculated. A hysteresis index (HI_I) was estimated for each ionic strength as the difference between the total amount of colloids mobilized during rainfall at the first ionic strength and the rainfall at the second ionic strength:

$$HI_I = \frac{\Delta C}{C_{low}}$$

where ΔC is the difference in the total amount of colloids mobilized in two rainfalls of identical ionic strength and C_{low} is the minimum value of the total amount of colloid releases between the rainfalls.

Analysis of water samples: The samples collected from all active ports were analyzed for pH, conductivity, turbidity, and bromide concentration. The pH was measured using a pH/ion-selective electrode meter (Orion 720A) and a combination electrode (Orion 8102BNU). Conductivity was measured using a conductivity meter (Orion 105) and a cell (Orion 011050). Bromide was measured using the pH/ion-selective electrode meter and a combination bromide-selective electrode (Accumet 13-620-524). Turbidity was measured using a turbidity meter (Hach 2100N). Turbidity was converted to colloid concentration (mg L^{-1}) using a calibration curve of total suspended sediment concentration versus turbidity. The total suspended sediment concentration was measured by drying colloid suspensions (20 mL) of increasing turbidity in pre-weighed aluminum cups in an oven at 104 °C and weighing the mass of the dried colloids. The contribution of total dissolved solids to the suspended sediments concentration was estimated to be less than 1% based on a conversion of the maximum conductivity (25 µS cm^{-1}) to total dissolved solids. Effluents from two ports in core 2 were analyzed for cesium and strontium using inductively coupled plasma-mass spectrometry (ICP-MS; Perkin Elmer SCIEX Elan DRC-e). Cesium and strontium were measured as total and dissolved concentrations, with dissolved defined as passing through a 0.2 µm nylon filter (VWR, 25 mm diameter). The concentration of cesium and strontium associated with colloids was calculated as the difference between the total and dissolved concentrations. The detection limits for cesium and strontium were 2.0 and 1.0 μg L^{-1}, respectively. For ICP-MS, indium was used as an internal standard. Four standards (blank, 100, 500 and 1000 ppb) made by accurately diluting certified standards were used for calibration.

Results

***Effect of physical heterogeneity on flow of water*:** A rainfall application rate at 2.5 cm h^{-1} caused a relative saturation of 65% in core 1 and 85% in core 2 (Figure 4.2). The breakthrough time of bromide varied in six active sample ports in core 1 and five active sample ports in core 2 (Figure 4.3). Other ports were not active during the rainfall applications. Changes in the concentration of bromide due to flow interruption were used as an indicator of exchange of water between macropore and matrix. The changes in concentration of bromide due to flow interruption were greater for the samples with longer breakthrough times.

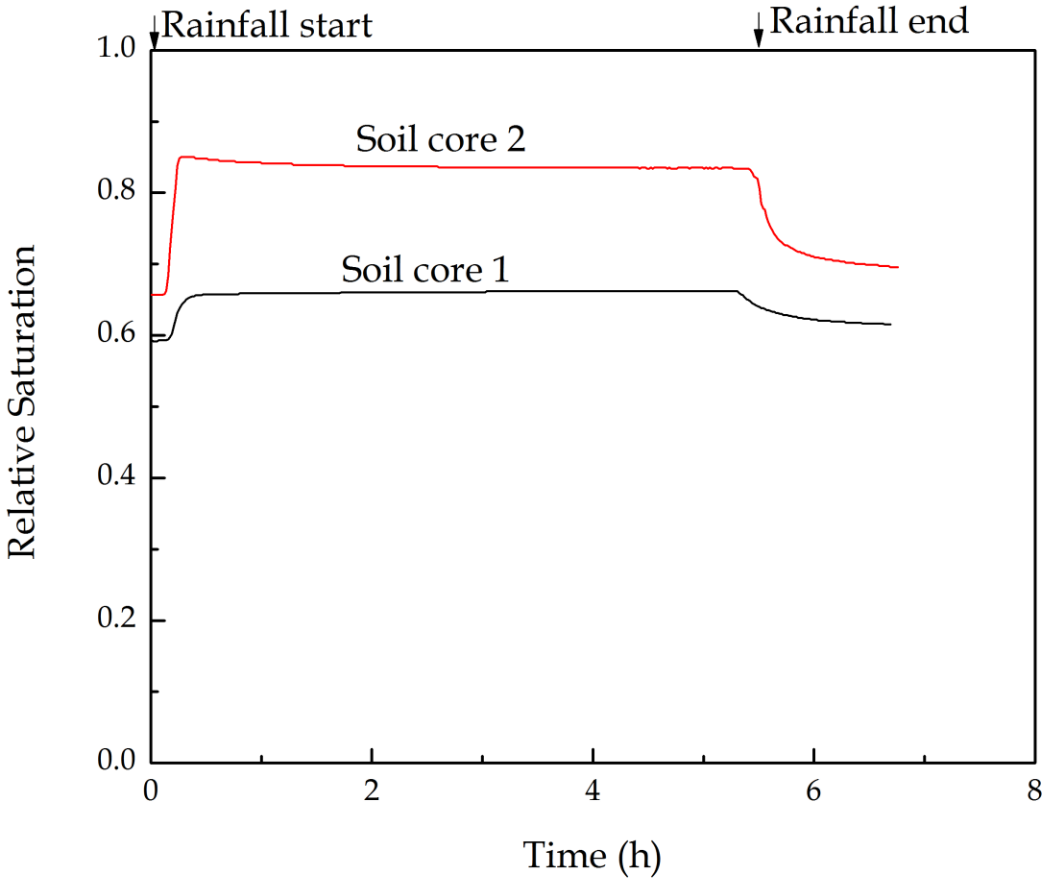


Figure 4.2. Relative saturation of soil cores during rainfall application at 2.5 cm h^{-1} for 5.3 h.

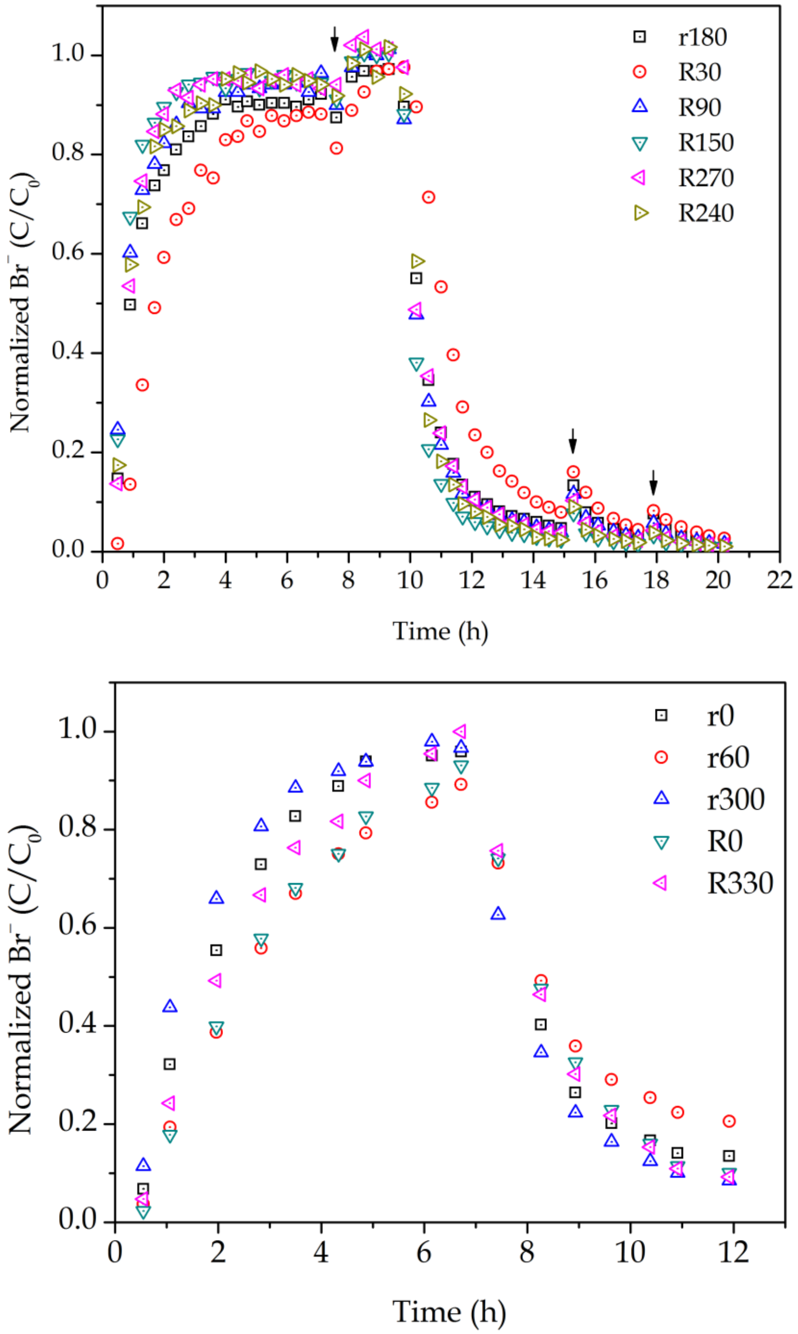


Figure 4.3. Normalized concentration of bromide as a function of time in six active sample ports in core 1 (top) and five active sample ports in core 2 (bottom). Arrows show the times at which the rainfall application was interrupted 18.7 h in core 1. Flow was not interrupted during injection of bromide in core 2.

The flow rate of the infiltrating water varied in the active ports of both cores with changes in the ionic strength of the rainfall solution (Figure 4.4). In core 1, the flow rate decreased in four of the six sampled ports (r180, R30, R90, and R270) as the ionic strength decreased. Most of the decrease in flow rate occurred during the 0.01 mM rainfall. The flow rates in the same ports increased during successive rainfalls of increasing ionic strength. Infiltrating water did not flow from one port (R240) until the 0.01 mM rainfall application. The flow rate was consistent in one port (R150). In core 2, flow rate was consistent in three of the five sampled ports (r0, R0, and R330), though no water flowed through port r0 during the first rainfall at 0.01 mM. Flow rate increased in one port (r60) when the ionic strength of rainwater was increased to 10 mM. No trend in the changes in flow rates with the ionic strength was observed in one port (r300).

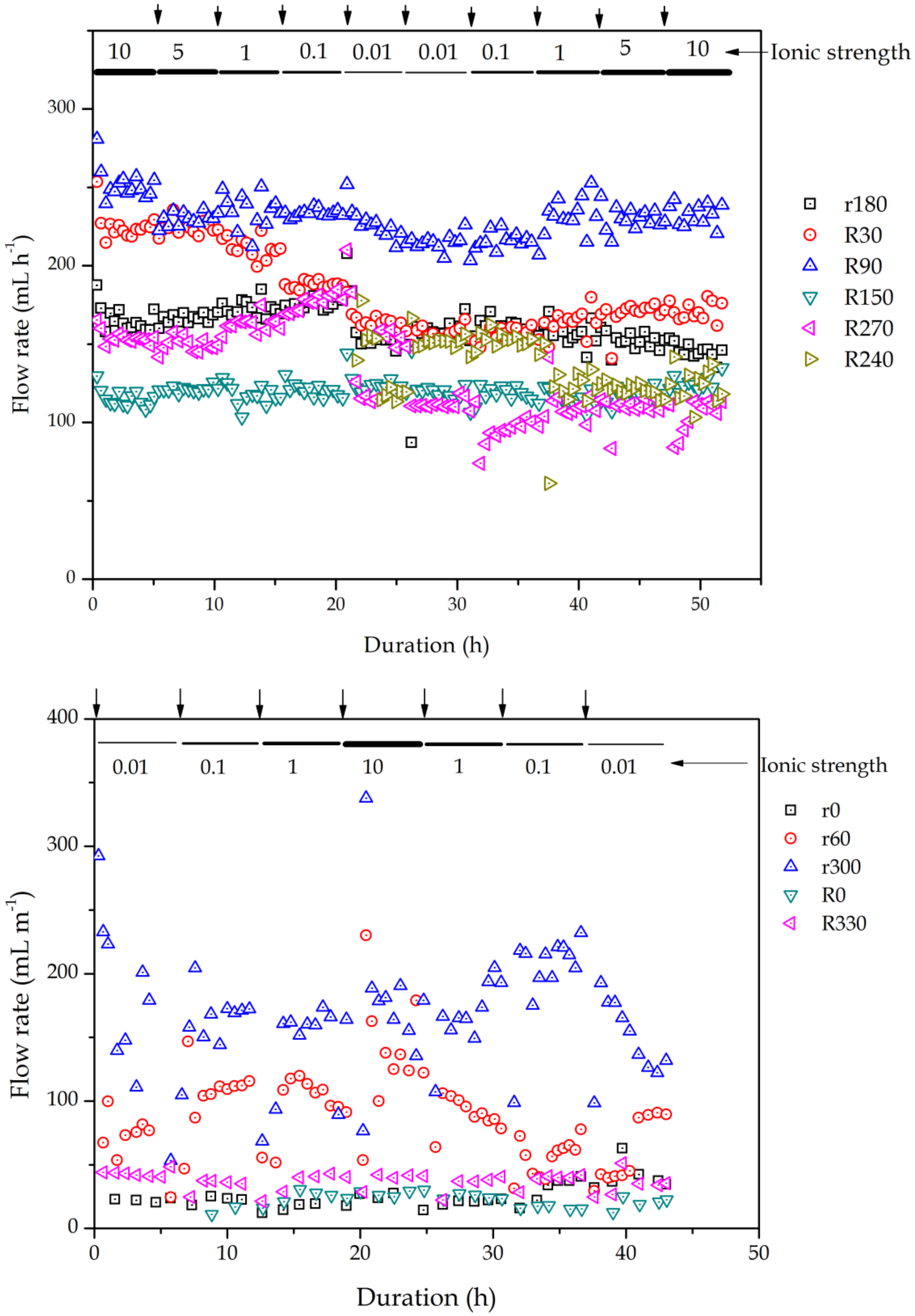


Figure 4.4. The effect of ionic strength on flow rate as a function of time in the six active ports in core 1 (top) and five active ports in core 2 (bottom). Arrows indicate flow interruptions of 18.7 h.

***Mobilization of colloids*:** A pause of 18.7 h resulted in an increase in colloid mobilization in the subsequent rainfalls (Figure 4.5). After an initial peak following the 18.7 h pause, the concentration of mobilized colloids decreased rapidly with time for each rainfall ionic strength. We used the peak concentration of mobilized colloids as an indicator of the effect of pore water exchange on colloid mobilization because colloids mobilized during the pause would be mobilized early in the rainfall application. A decrease in the ionic strength of the rainfall solution from 10 mM to 0.01 mM resulted in increases in the peak concentration of colloid mobilization in all of the six sampled ports of core 1 and all of the five sampled ports of core 2. As the ionic strength was increased from 0.01 mM to 10 mM, the peak concentration of mobilized colloids decreased. The peak concentration of mobilized colloids varied by a maximum factor of 12 in the six sampled ports of core 1 at 0.01 mM. Greater concentrations of colloids were mobilized in core 2 than core 1.

The conductivity of pore water in all active ports of both cores decreased and increased as the ionic strength of the rainfall solution was decreased and increased, respectively. The conductivity varied from one port to another by a maximum of 10%. In all sampled ports, the amount of colloid mobilization varied much more than the corresponding variations in the conductivity of the infiltrating water.

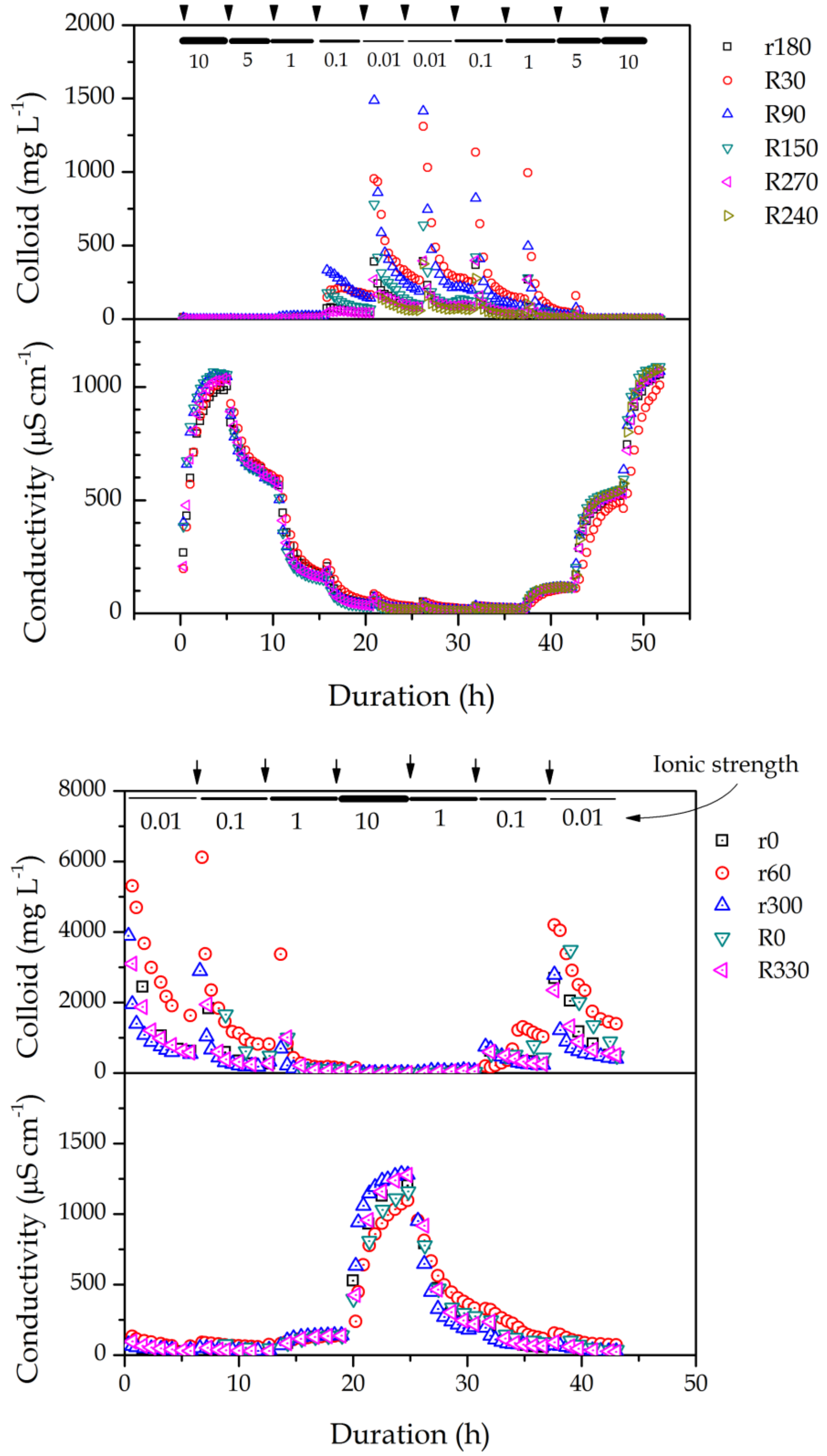


Figure 4.5. Effect of ionic strength of the rainfall solution on the mobilization of colloids and the conductivity of infiltrating water in six active ports of core 1 (top) and five active ports of core 2 (bottom). Port R240 of core 1 was not active during the first four rainfalls and port R0 of core 2 was not active during the first rainfall.

Colloid mobilization was hysteretic in response to changes in ionic strength – the peak concentration of mobilized colloids at a given ionic strength was not matched when rainfall of the same ionic strength was applied to the soil core following exposure to infiltrating water of higher or lower ionic strengths. For example, in the first core, a peak concentration of 375 mg L^{-1} of mobilized colloids was measured in port R90 at 0.1 mM ionic strength following a rainfall at 1.0 mM ionic strength. When the 0.1 mM ionic strength rainfall followed a rainfall at 0.01 mM ionic strength, a peak concentration of 800 mg L^{-1} of mobilized colloids was measured (Figure 4.6). The degree of hysteresis was different at each port. The greatest hysteresis was observed for port R30 and the least hysteresis was observed for port R150. In the second core, colloid mobilization was also hysteretic with respect to the rainfall ionic strength. The greatest hysteresis was observed for port r60 and the least hysteresis was observed for port r300 at 0.01 mM ionic strength (Figure 4.7).

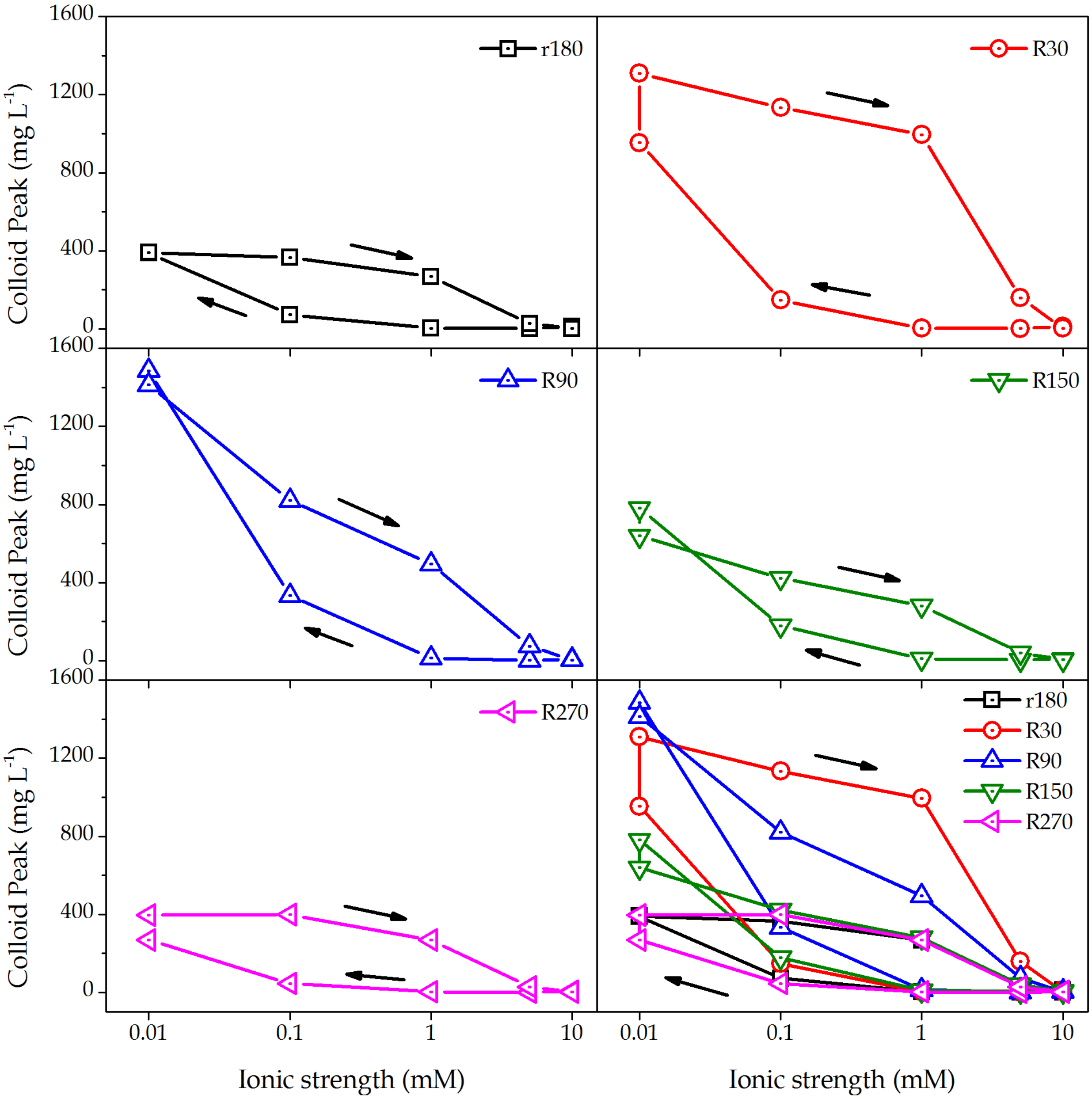


Figure 4.6. Peak concentration of colloids mobilized during the first 30 min of rainfall as a function of the ionic strength of the rainfall solution showing hysteresis in the amount of colloids mobilized in the five active ports in core 1. The sixth port (R240) is not shown because it was not active during the first 4 rainfalls. Arrows indicate the succession in which the experiments were carried out.

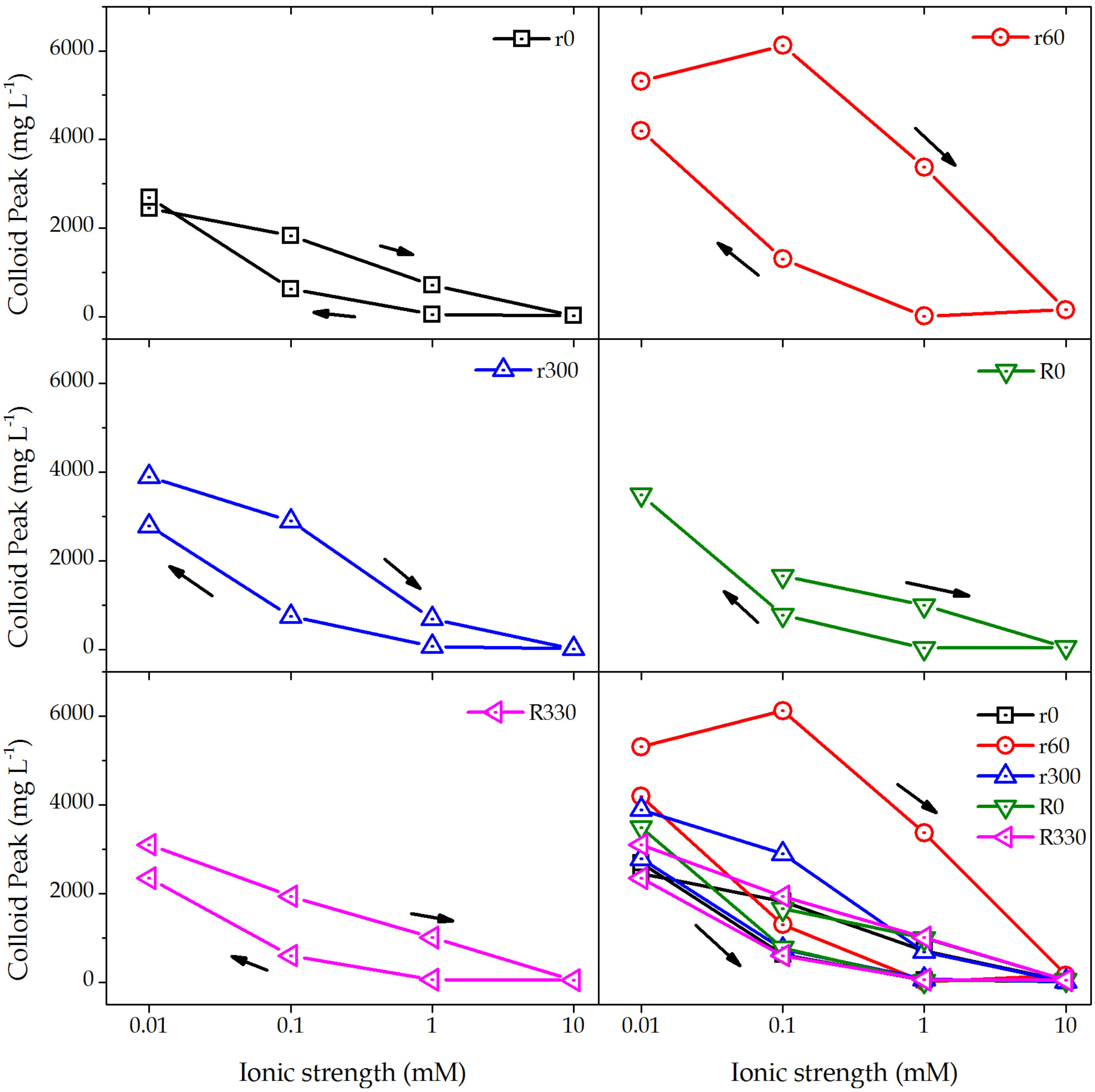


Figure 4.7. Peak concentration of colloids mobilized during the first 30 minutes of rainfall as a function of the ionic strength of the rainfall solution showing hysteresis in the amount of colloids mobilized in the five active ports in core 2. Arrows indicate the succession in which the experiments were carried out.

***Mobilization of cesium and strontium*:** Only core 2 was contaminated with cesium and strontium prior to mobilization in order to investigate if the mobilized colloids would facilitate the transport of cesium and strontium. The average concentrations of cesium and strontium (total and dissolved) mobilized during a rainfall event were also hysteretic in response to changes in the ionic strength of the rainfall solutions (Figure 4.8). The average concentration of cesium and strontium increased with an increase in the ionic strength of the rainwater. Less cesium and strontium (total and dissolved) were mobilized in rainfall with low ionic strength. Of the total amount of cesium and strontium mobilized, the colloidal fraction was higher at lower ionic strengths of rainwater. The hysteresis in colloidal cesium and strontium release was similar to that for colloid mobilization.

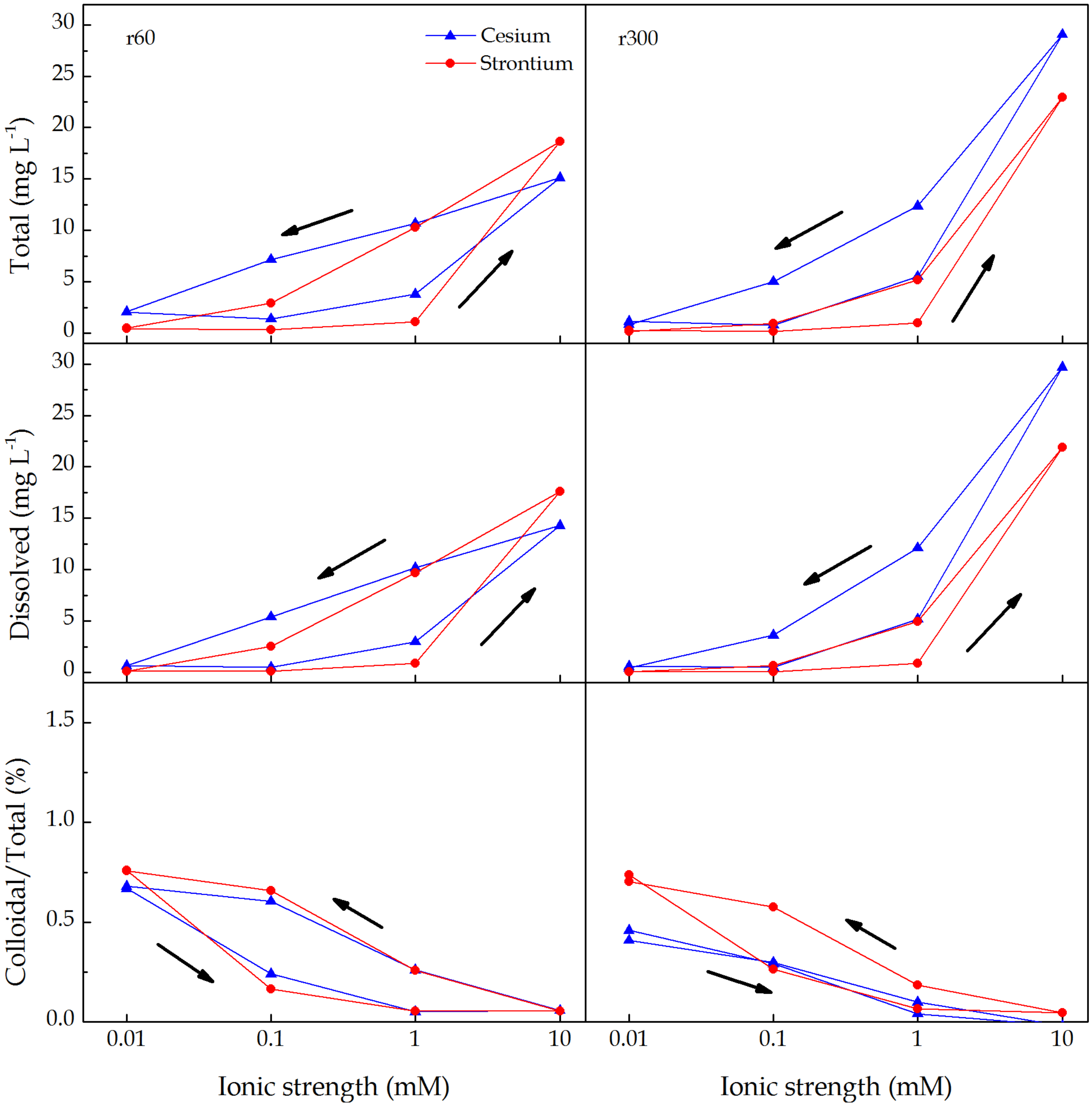


Figure 4.8. The fraction of cesium and strontium in the dissolved (left axis) and colloidal (right axis) forms as a function of the ionic strength of the rainfall application showing hysteresis in the mobilization of cesium and strontium in port r60 and r300 of core 2.

Discussion

***Exchange of solutes between pore water in the macropores and the matrix*:** In order to study the exchange of solutes between the bedding plane fractures and the matrix of the shale saprolite soil, we measured the relative saturation, distribution of infiltrating water flow, and bromide breakthrough times in all of the actively-flowing ports in both cores. A difference in relative saturation of the two soil cores indicates that the cores may have different physical properties (Figure 4.2). The fractures in the soil are expected to conduct water and a difference in saturation may occur between different regions of soil. The relative saturation was measured only at one location of the soil cores, which may not reflect the local moisture content in regions farther from probe. Caution should be maintained in direct comparison of the results of soil cores due to inherent heterogeneity of soil core.

The physical heterogeneity of the soil is evident because water flowed through only six ports in core 1 and five ports in core 2 (Figure 4.4). These results indicate that water was not flowing through 69% of the total area sampled by the 19 ports at the bottom surface of core 1 and 74% of total area of core 2. Because small regions of the soil cores were conducting most of the rainwater, the flux through each active port was higher than rainfall application rate.

An exchange of water between fractures and the surrounding matrix occurred during the transport of water. We measured the variation of breakthrough times of bromide to examine the nature of flow paths leading to each port. A variation in arrival times of bromide breakthrough between 0.7 h to 1.6 h in core 1 and between 1.3 h to 2.5 h in core 2 indicates a difference in the rate of exchange of bromide between the fractures and the matrix (Figure 4.3). Heterogeneous soil can be approximated as a medium with dual permeability – the macropores or fractures with higher permeability and the matrix with low permeability – and the transport of a solute in a heterogeneous soil occurs at different rates in the macropores and the soil matrix (Gerke and van Genuchten, 1993; Bundt *et al.*, 2000). In our soil cores, the infiltrating water quickly replaced the pore water in the fractures, which created a concentration gradient for bromide between the pore water in the fractures and the pore water in the matrix. Diffusion of bromide into the matrix dilutes the bromide concentration in the fracture pore water and causes slower breakthrough of bromide.

Interrupting the flow of the infiltrating water ended the advective transport of bromide; therefore, decreases in the concentration of bromide were attributed to the diffusion of bromide from the macropores into the soil matrix (Brusseau *et al.*, 1997). Stopping the flow during the tail of the bromide breakthrough increased the concentration of bromide in pore water due to diffusion of bromide from the soil matrix back to the macropores. The difference in the concentration of bromide in the pore waters before and after the flow interruption was greater in port R30 than in port R150 of core 1. The bromide breakthrough time in port R30 was also longer than that in port R150, which indicates that the exchange of pore water between the macropores and the matrix caused a late arrival of bromide and the change in the concentration of bromide in the pore water during the flow interruption. Previous studies found similar results using flow interruption techniques. Changes in the concentration of bromide due to the flow interruptions suggested an exchange of bromide from infiltrating water between the macropores and the soil matrix (Elci and Molz, 2009). The diffusion of a solute into the soil matrix from the macropores during a flow interruption reduces the concentration of solutes in the macropore (Reedy *et al.*, 1996). A decrease in the ionic strength of pore water by diffusion of solute into the matrix could increase the mobilization of colloids in pore water during a flow interruption.

***Mobilization of colloids*:** During each rainfall application, the concentration of mobilized colloids increased rapidly to a peak and decreased over time (Figure 4.5). The rapid increase in the concentration of mobilized colloids is the result of the pause in rainfall, which results in transient moisture content conditions. These transients enhance colloid mobilization (Ryan *et al.*, 1998; El-Farhan *et al.*, 2000; Saiers and Lenhart, 2003; Zhuang *et al.*, 2007; Majdalani *et al.*, 2008; Cheng and Saiers, 2010). The increase in colloid mobilization caused by wetting and drying transients has been attributed to the disintegration of pore wall under capillary stress generated by the preferential drainage of water from the macropores (Majdalani *et al.*, 2008; Michel *et al.*, 2010).

Greater amounts of colloids were mobilized in core 2 than in core 1. The difference between core 1 and core 2 was further evident by a higher relative saturation of core 2 and an unstable flow through the ports in core 2 (Figure 4.4). Unstable flow in fractures could occur due to the combined effects of negative water potential in capillaries of the matrix and positive water potential in the fractures during a rapid infiltration of rainwater (Wang *et al.*, 2004).

Colloid mobilization increased when the ionic strength of the rainwater solutions was decreased and decreased when the ionic strength was increased. A decrease in the ionic strength causes greater electrostatic repulsion between colloid and soil grain surfaces, and greater electrostatic repulsion causes colloid mobilization (DeNovio *et al.*, 2004). An increase in the ionic strength reduces colloid mobilization. Ionic strength dependent colloid mobilization fails to explain the difference in the colloid mobilization through the five ports in core 1 and the five ports in core 2. All active ports had similar conductivity, but a larger difference in colloid concentrations (Figure 4.5). The lack of differences in the conductivity of the pore waters should have resulted in the mobilization of similar amounts of colloids through each port. The discrepancy in mobilization of colloids among the ports in two cores indicates that the physical heterogeneity of the Oak Ridge soil affected the mobilization of colloids.

***Hysteresis in colloid mobilization*:** Mobilization of colloids was hysteretic in response to changes in ionic strength – the concentration of colloids mobilized at a given ionic strength was not matched when the experiment was repeated following exposure to pore water of higher or lower ionic strengths (Figure 4.6 and 4.7). The difference in the concentration of colloids could be due to a difference in residual ionic strength of pore water in macropore contributing to the colloid release. The residual ionic strength of pore water in the macropores depends on the ionic strength of the preceding rainfall and diffusion of solutes from surrounding matrix. The residual ionic strength of pore water during pause is high if rainwater of high ionic strength was injected before the pause. Diffusion of solute between the macropores and the matrix could change the ionic strength of pore water in the macropores and thus affect the release of colloids.

We used bromide breakthrough time to quantify the exchange of solute between the macropores and the matrix during a pause. The breakthrough time of bromide was high in port R30 of core 1 and port r60 of core 2. The hysteretic nature of colloid mobilization was also the greatest in port R30 of core 1 and port r60 of core 2. These results suggest that hysteresis in colloid mobilizations may be related to bromide breakthrough times. A positive correlation was found between the hysteresis index and bromide breakthrough times in all ports in core 1 (Figure 4.9). The positive correlation between the hysteresis index and breakthrough time of bromide indicates that the exchange of bromide, the cause of longer bromide breakthrough times, contributed to hysteresis in the mobilization of colloids.

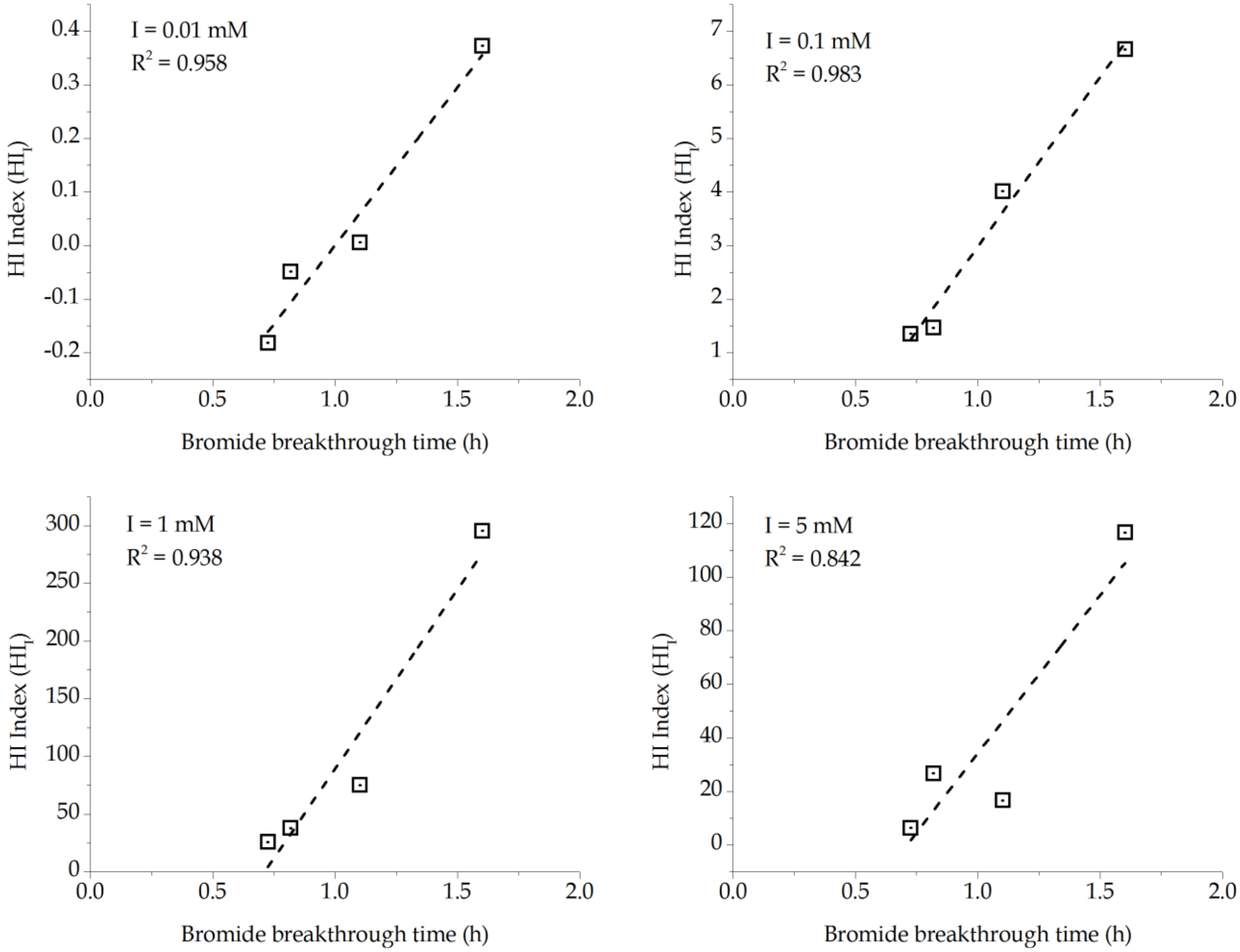


Figure 4.9. Hysteresis index (HI_I) as a function of the breakthrough time of bromide through the six active ports in core 1 at different ionic strengths.

We attribute hysteresis in colloid mobilization to the exchange of solute from or into the matrix that contains water from a previous rainfall. An illustration of the proposed mechanism for hysteresis in colloid mobilization is provided in Figure 4.10. The first rainfall at high ionic strength mobilizes a minimal amount of colloids and the macropores and the matrix are filled with rainwater of higher ionic strength. Decreasing the ionic strength of rainwater mobilizes a greater amount of colloids during the second rainfall. Most of these colloids must have come from the fractures, which were exposed to the infiltrating water of lower ionic strength, but few of the colloids would have mobilized from the matrix because the matrix still contains water of higher ionic strength from the previous rainfall. At the end of the second rainfall, the macropores and most pores in the matrix are filled with infiltrating water of lower ionic strength. The third rainfall is carried out by increasing the ionic strength of rainwater similar to the first rainfall. During the third rainfall, the macropores are immediately filled with rainwater of high ionic strength and contribute similar amount of colloids as the first rainfall. The contribution of the matrix to mobilizing colloids is greater during the third rainfall than the first rainfall because matrix still contains rainwater of low ionic strength from the second rainfall. Thus, hysteresis occurs because ionic strength of pore water in the matrix is dependent on the ionic strength of the previous rainfall. It should be noted that the rainfall events in the conceptual model did not follow the sequence of rainfall events in actual experiments.

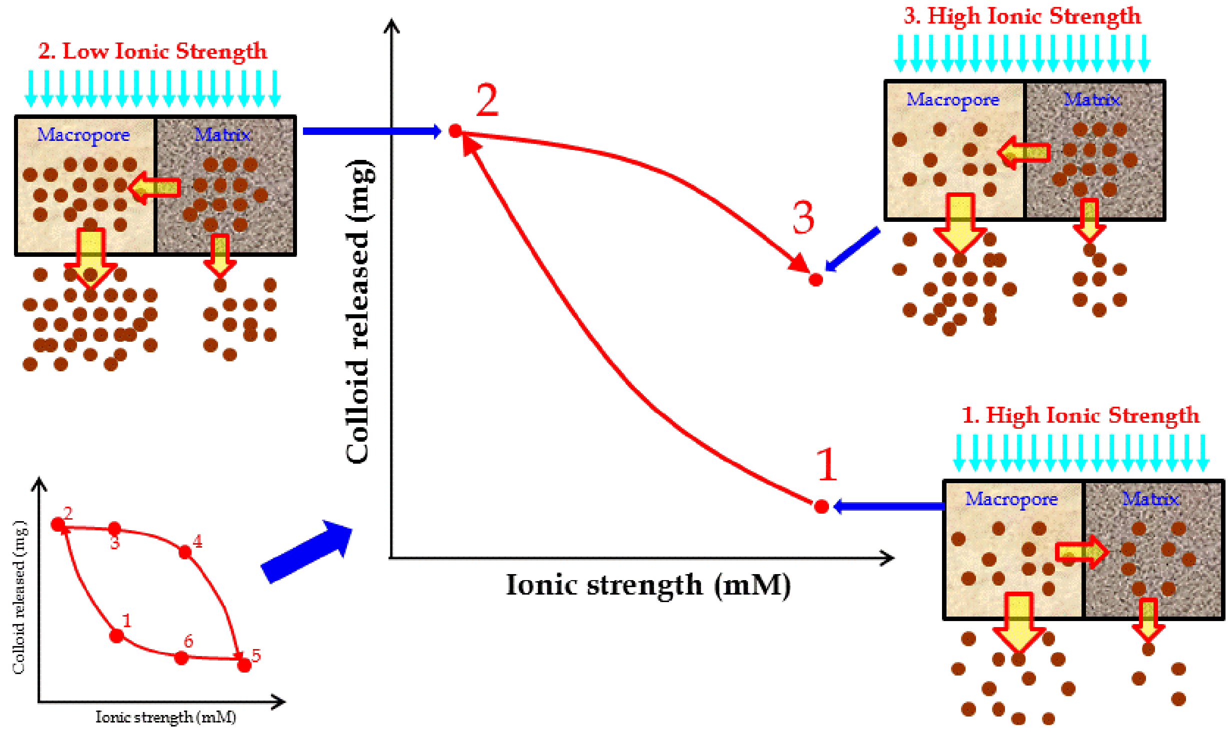


Figure 4.10. An illustration of exchange of pore water with infiltrating rainwater of different ionic strengths and its effect on the mobilization of colloids.

In core 1, the hysteresis index was smaller at ionic strengths below 0.1 mM and above 5 mM. The results indicate that the mobilization of colloids is insensitive to changes in the ionic strength below 0.1 mM and above 5 mM. The insignificance of hysteresis above 5 mM was due to limited mobilization of colloids at ionic strength greater than 5 mM. Repeating the rainfall at 0.01 mM did not mobilize greater amounts of colloids because there is no additional change in the residual conductivity of pore water during consecutive rainfalls at 0.01 mM. Ion exchange at an ionic strengths of 0.01 mM contributed to lack of changes in the conductivity of pore water.

Mobilization of cesium and strontium: The mobilization of colloidal strontium and cesium was hysteretic in the same way (Figure 4.8) as the mobilization of colloids (Figure 4.7). The total, dissolved, and colloidal fractions of cesium and strontium showed hysteresis in mobilization. The colloidal fraction of cesium and strontium mobilized in the same way as that of colloids indicating the hysteresis in colloid mobilization caused the hysteresis in mobilization of colloidal fractions of cesium and strontium.

The dissolved fractions of cesium and strontium were mobilized by cation exchange. At high ionic strength, more cesium and strontium are released as dissolved cations due to an increase in cation exchange. At lower ionic strength, desorption by cation exchange is minimal. An exchange of solute during a pause caused the variation in the concentration of cations. A variation in the concentration of cations (Na^+ in our experiment) caused a variation in the release of cesium and strontium by cation exchange. Therefore, an exchange of solutes between the macropores and the matrix led to a hysteresis in the mobilization of cesium, strontium, and colloids in heterogeneous soil.

The exchange of solute between the macropores and the soil matrix (i.e., the mobile and immobile zones) has implications to the mobilization of contaminants from the soil matrix. We showed that the exchange of solute indirectly affected the mobilization of colloids by changing the ionic strength of pore water. Hysteresis in colloid mobilization was found in a previous study (Torkzaban *et al.*, 2010). The results of our study suggest that the exchange of solute between the macropores and the matrix causes the hysteresis in the mobilization of colloids and metal cations in response to changes in ionic strength of rainwater. The results of our study have implications for colloid mobilization in natural conditions since we used intact soil core and *in situ* colloids to investigate the effect of pore water exchange on the mobilization of colloids and metal cations.

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CHAPTER 5

COLLOID FACILITATED-TRANSPORT OF CESIUM AND STRONTIUM IN A FRACTURED SOIL: EFFECT OF IONIC STRENGTH AND SOIL PHYSICAL HETEROGENEITY

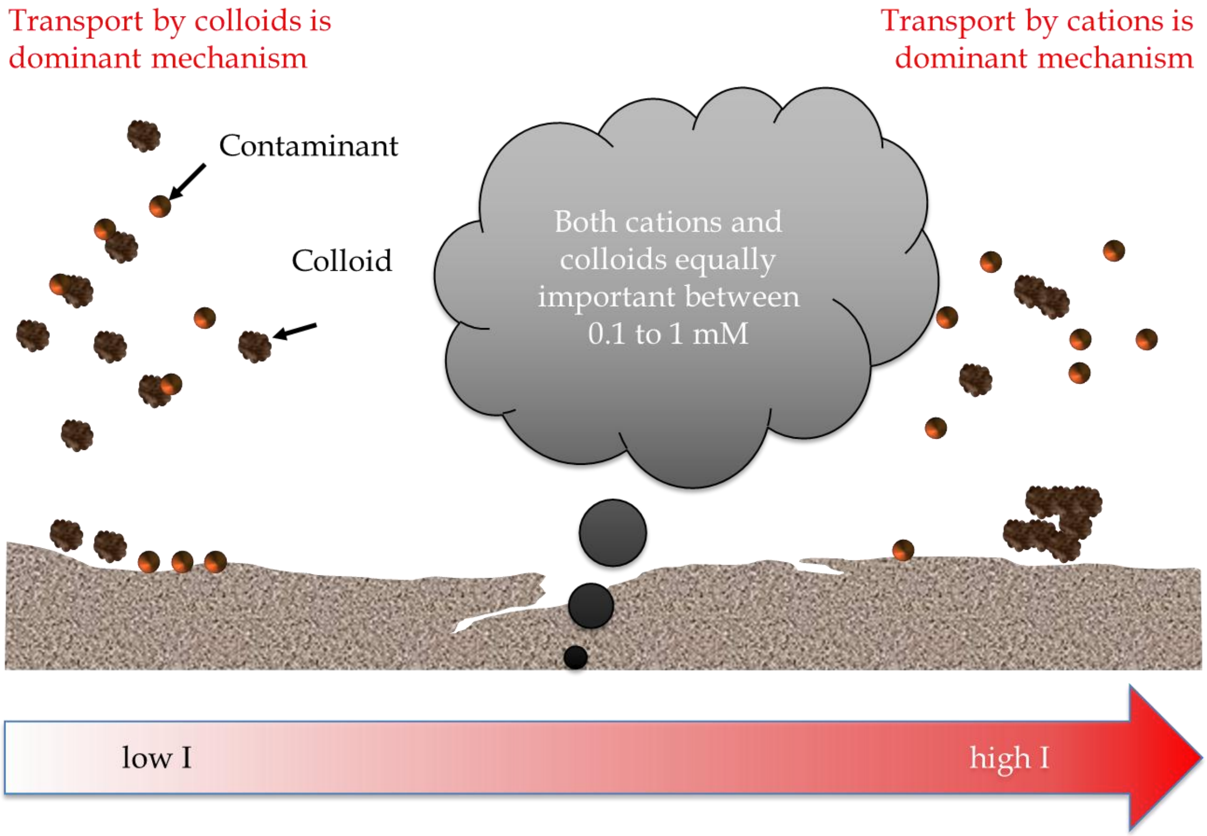

Illustration showing relative importance of cation exchange and colloid-facilitated transport at low and high ionic strength

Abstract

The aim of this work was to evaluate the effect of physical heterogeneity on cation exchange and colloid-facilitated mobilization of cesium and strontium from an intact core of a fractured soil. Cesium and strontium were added to the soil by simulated rainfall before applying rainwater of increasing ionic strengths from 0.01 mM to 10 mM. Water samples were collected using a 19-port grid at the bottom of the soil core to resolve the effect of physical heterogeneity on the mobilization of colloids and cations. Below 1 mM ionic strength, the metal cations were mobilized in the colloidal form by colloid-facilitated transport. Above 1 mM ionic strength, the metal cations were mobilized in the dissolved form by cation exchange. The amount of the metal cations mobilized by cation exchange at higher ionic strengths was much greater than the amount mobilized by colloid-facilitated transport at lower ionic strengths. Physical heterogeneity of the soil affected the release of cesium and strontium by influencing the exchange of solutes between the fractures and the soil matrix. For cation exchange, the release of the metal cations was greater in the fractures in which exchange of solutes with the matrix was minimal. For colloid-facilitated transport, the mobilization of metal cations was greater in fractures with greater exchange of solutes with the matrix. Colloid-facilitated transport through the macropores was less though a greater quantity of the mobilized colloids originated from the macropores. These results indicate a need to incorporate transient geochemical conditions and soil heterogeneity into models of metal transport in the vadose zone.

Introduction

The release of radioactive cations like cesium-137 and strontium-90 at nuclear facilities is a concern due to the potential of these contaminants to move through the vadose zone to ground water (DOE, 2006). Infiltrating rainwater carries cations and colloids that are known to mobilize metal cations from contaminated sites (McCarthy and Zachara, 1989). Metal cations can be released by cation exchange or colloid-facilitated mobilization process during infiltration of rainwater. Transport of metal cations by colloids is affected by physical (e.g., grain size distribution) and chemical conditions (e.g., ionic strength and pH) during a rainfall (Jardine and Donald, 2008). The relative importance of cation exchange and colloid-facilitated mobilization of metal cations under natural soil conditions may depend on the coupled effects of both physical and chemical conditions.

The relative importance of cation exchange and colloid-facilitated mobilization depends on the ionic strength of rainwater (McCarthy and Zachara, 1989). Colloid-facilitated transport of contaminants can be important when the colloids are abundant, when the colloids are more mobile than the contaminants, and when the contaminants desorb slowly from the colloids relative to the rate of transport (McCarthy and Zachara, 1989; DeNovio *et al.*, 2004). These conditions may be met at low ionic strength when colloids are released and transported in water due to an increase in the net repulsive forces between colloids and soil minerals (Ryan and Elimelech, 1996; DeNovio *et al.*, 2004; Sen and Khilar, 2006). A low ionic strength also favors the binding of the metal cations by the colloids. The release of metal cations by cation exchange is important at high ionic strength, which causes colloids to remain attached to soil grains due to a decrease in the electrostatic repulsion between colloids and grains. The decrease in colloid mobilization at high ionic strengths reduces the likelihood that colloid-facilitated transport would contribute to contaminant transport. The relative importance of colloid-facilitated mobilization and cation exchange on release of metal cations from soil is not clear at intermediate ionic strengths where both processes could be important.

For colloid-facilitated transport to be an important process for the mobilization of metal cations, the colloids need to be mobilized in association with metals cations. For cation exchange to be important, pore water of high ionic strength must reach locations where metal cations are adsorbed on soil. Soil physical heterogeneity or the distribution of the macropores and the matrix in soil influences the mobility of colloids and cations in soil. Colloids and associated metal cations move slower in the soil matrix due to an increase in colloid removal by physicochemical filtration and straining (Ryan and Elimelech, 1996; Wan and Tokunaga, 1997; Torkzaban *et al.*, 2008). Colloids can be mobilized quickly by advection through the macropores or preferential flow paths during a rainfall. A difference in infiltration rates between the macropores and the matrix could cause a difference between ionic strengths of pore waters in the macropores and the matrix. The difference in ionic strength could cause diffusion of solute between macropore and matrix. The ionic strength of pore water could vary based on the ionic strength of rainwater and the diffusion of solute between macropore and matrix. Thus, soil heterogeneity influences the ionic strength of pore water. Soil heterogeneity may indirectly influence cation exchange by changing the ionic strength of the pore water (Ma and Selim, 1997). The importance of cation exchange and colloid-facilitated transport of metal cations have been examined in separate experiments. However, both processes could occur simultaneously under natural conditions. Limited studies have been carried out to examine the mobilization of metal cations simultaneously by cation exchange and colloids under environmentally relevant geochemical conditions.

We hypothesized that the ionic strength of pore water and physical heterogeneity of the soil would affect the relative importance of colloid-facilitated transport and cation exchange in the mobilization of metal cations from soil. We applied rainfall of increasing ionic strengths from 0.01 to 10 mM to mobilize adsorbed cesium and strontium with *in situ* colloids from intact cores of a fractured shale saprolite soil. Cesium and strontium were used because they show different desorption kinetics from colloids (Turner *et al.*, 2006). Water samples were collected through multiple ports at the bottom of an intact core of a fractured shale saprolite soil to resolve the effect of physical heterogeneity on mobilization of cesium and strontium. Water passing through the fractures and the matrix were identified based on bromide breakthrough of infiltrating rainwater. The physical and chemical conditions where cation exchange outcompeted colloid-facilitated mobilization of metal cations were presented.

Experimental details

Intact soil core sampling: Intact soil cores were collected from the bottom of a hill slope in the Melton Branch watershed on the grounds of the Oak Ridge Reservation, Tennessee (Luxmoore and Abner, 1987). The field site and soils were described in detail by Jardine *et al.* (1993). The soil consists of fractured shale saprolite that has been weathered by 130 cm y^{-1} of rainfall. Infiltrating water predominantly passes through the bedding planes and fractures, which dip at an angle of 30° (Jardine *et al.*, 1993). The bedding planes and fractures are coated with iron(III) and manganese oxyhydroxides and translocated clay minerals.

Intact soil cores were collected using a hand-sculpting method (Jardine *et al.*, 1993). Vegetation and the O-layer of the soil were removed from the sample sites. Cylinders of soil in the A-horizon were excavated and trimmed to fit inside polyvinylchloride (PVC) pipes of 30.5 cm height and 25.4 cm width. In some cases, the top and sides of the soil cylinders were coated with melted paraffin wax to prevent the fractured soil from falling apart. The gap between the PVC pipe and the soil cylinder (approximately 1.2 cm) was filled with polyurethane expandable foam (US Composites). The soil collection method preserved the structural integrity of soil. Preliminary experiments confirmed no leaching of dissolved organic carbon from the paraffin wax and foam.

Experimental Setup**:** Colloid mobilization experiments were conducted using a rainfall simulator consisting of a reservoir, a peristaltic pump, a rainfall distributor, the soil core, a sampling grid, and sample collection tubes (Figure 5.1). The peristaltic pump transferred rainfall solutions (0.01 mM NaCl) from the reservoir to the rainfall distributor. Rainfall was simulated by dripping water through 85 needles (25 gauge) at the bottom of the rainfall reservoir. A stainless steel mesh (# 200) was installed at the bottom surface of the intact core. The intact core was placed under the rainfall reservoir on a sampling grid with 19 ports to resolve spatially the flow of water through macropore (fractures) and matrix. The arrangement and the numbering of ports in the grid and arrangement of needles below the rainfall reservoir are described in Figure 5.1. The ports delivered samples of infiltrating water to 19 sample collection tubes (glass, 2.5 cm diameter × 25 cm length). Each port captured water flowing through an area of 11.4 cm^2; the total collected area was 340 cm^2. Water flowing near the perimeter of the soil cores was collected in a channel (1.3 cm width) around the sample ports to be discarded. The water flows to each port from the bottom surface of soil under zero tension.

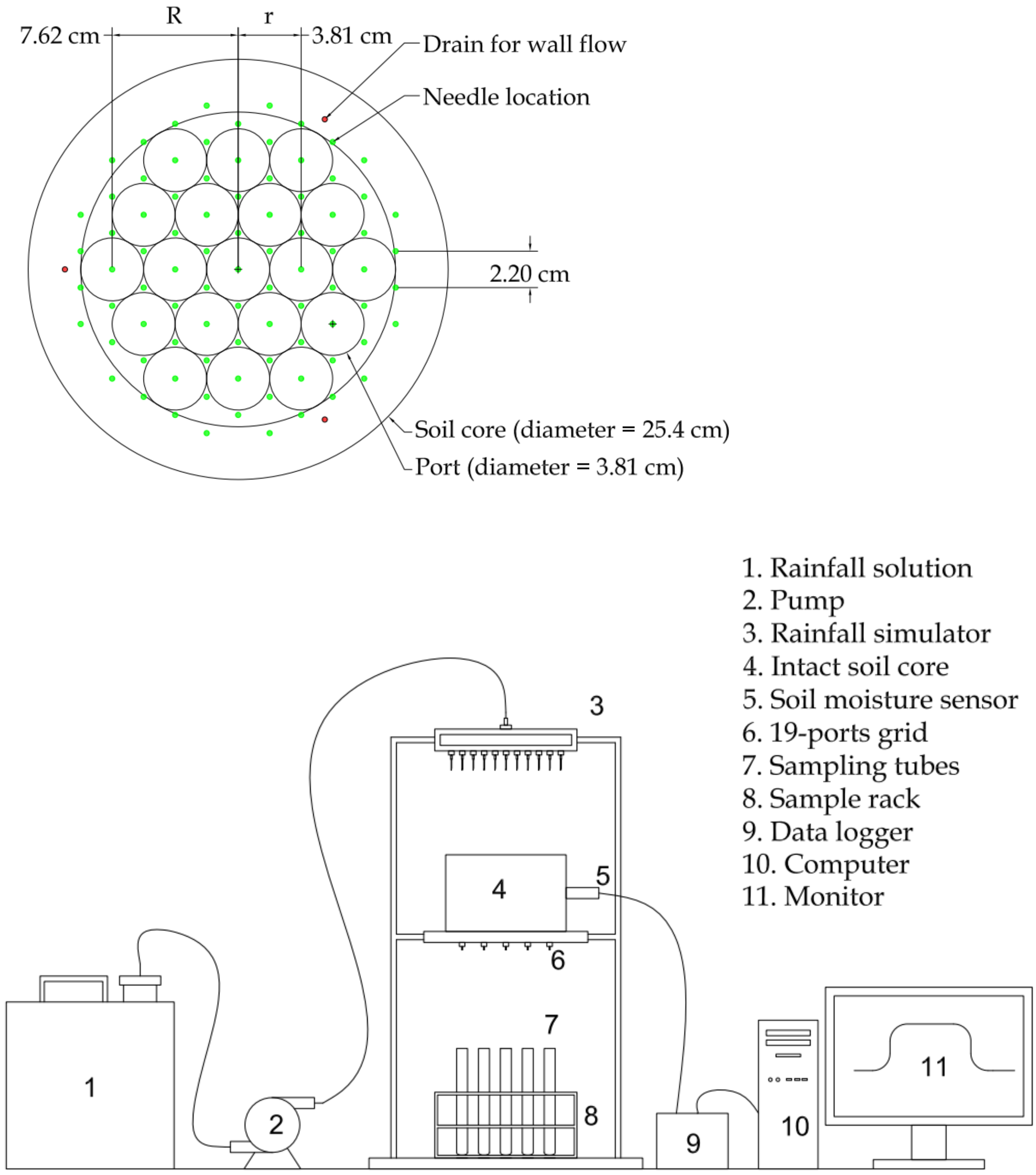

Figure 5.1. Column setup to examine the mobilization of colloid from intact core of a fractured soil. The 19 ports were arranged in a hexagonal pattern. The ports (diameter of 3.81 cm) were arranged in two concentric hexagons around a center port. The center port is designated as “00”. The inner hexagon contains six ports at a center-to-center distance of maximum 3.81 cm from port 00 and is designated as “r” followed by an angle. The outer hexagon contains 12 ports at center-to-center distance of maximum 7.62 cm and is designated as “R” followed by an angle. The 85 needles of the rainfall reservoir were arranged in hexagonal pattern with closest distance between two needles as 2.2 cm.

In preliminary rainfall experiments with the full-height (30.5 cm) soil cores, we observed that the bedding plane fractures carried most of the infiltrating water to the walls because the fractures intersected the core walls. To avoid this problem, the soil cores were cut to a height of 15 cm. A soil moisture probe (Delta-T Devices, Theta Probe MLX2) was inserted in the side of the soil core to monitor relative saturation of soil. The probe was located 7.5 cm below the soil surface and extended 6 cm into the soil. The probe was interfaced with a computer through a data logger (DATAQ Instruments, DI 710) to record and store relative saturation reading at 1 min intervals.

Two cores were used in this study. Bromide, cesium, and strontium were applied to both soil cores as a rainfall solution using a rainfall simulator. The bromide was used to examine the heterogeneity of soil contributing water to each port. Rainfall solutions of increasing ionic strengths were applied on each core on contaminated soil cores to investigate the mobilization of cesium and strontium by colloid-facilitated transport and cation exchange. The experimental conditions in this study are presented in Table 5.1.

Table 5.1. Conditions used for rainfall applications on cores 1 and 2.

Input Solution	Flux (cm h^{-1})	Ionic strength (mM)	Starting time (h)
1 mM CsBr + 1 mM $SrBr_2$	2.5	4	0
4 mM $NaNO_3$	2.5	4	50.0
Flow interruption start	0	4	55.7
Flow interruption end	0	4	67.9
0.003 mM $Ca(NO_3)_2$	2.5	0.01	68.5
0.033 mM $Ca(NO_3)_2$	2.5	0.1	72.5
0.333 mM $Ca(NO_3)_2$	2.5	1	77.1
3.333 mM $Ca(NO_3)_2$	2.5	10	81.8

***Application of rainfall containing cesium and strontium*:** Rainfall solutions containing cesium and strontium were applied to the soil core as the first step in assessing the effect of rainfall ionic strength on the mobilization of cesium and strontium from soil. A rainfall solution containing 1 mM CsBr (99.99%, Argo Chemical) and 1 mM $SrBr_2$ (99.9%, MP Biochemicals) in high-purity water (>18.2 MΩ cm) was applied at a rate of 1.8 cm h^{-1} for 50 h. A rainfall application rate greater than 1.8 cm h^{-1} led to water pooling on top of the soil cores used in the study. After the application of cesium and strontium, the rainfall was switched to 4 mM $NaNO_3$ (the same ionic strength as the cesium and strontium solution) until the concentrations of cesium and strontium did not decrease any further in the effluent, which required about 5.7 h. After the 4mM $NaNO_3$ rainfall application, flow was interrupted for 12.2 h. After the flow interruption, the flow was resumed for 0.6 h with rainfall solution of 4 mM $NaNO_3$.

***Characterization of physical heterogeneity of soil core*:** We investigated the effect of physical heterogeneity on cation exchange and colloid-facilitated transport of cesium and strontium. Based on previous experiments (Jardine *et al.*, 1993), we expected rapid infiltration through the bedding plane fractures (the macropores) and slow infiltration through the shale saprolite (the matrix) under heavy rainfall. In order to resolve the effect of physical heterogeneity on cation exchange and colloid-facilitated transport of cesium and strontium, two ports were chosen based on a difference in flow rate, breakthrough time of bromide, and long tailing of bromide. We assumed that a port receiving water from a region dominated by matrix flow would have characteristics that include slow flow rate and bromide breakthrough and tailing of the bromide breakthrough (Clothier *et al.*, 1998; Nielsen *et al.*, 2011). The bromide breakthrough time was estimated as the time at which the bromide concentration in a port reached 50% of bromide concentration in the rainfall solution. A change in concentration of bromide during flow interruption, where transport due to advection is zero, was used to investigate the effect of physical heterogeneity, especially matrix diffusion, on concentration of bromide (Brusseau *et al.*, 1989; Koch and Flühler, 1993).

Mobilization of colloids, cesium, and strontium: To release cesium, strontium and colloids, rainfall solutions of $Ca(NO_3)_2$ of increasing ionic strengths (0.01, 0.1, 1, and 10 mM) were applied to the cesium- and strontium-contaminated core. The ionic strength was adjusted by varying the amount of $Ca(NO_3)_2$ in solution. Calcium was chosen as the cation to maximize the release of cesium and strontium by cation exchange. Each solution was applied for 4 h before switching to a solution of higher calcium concentration. The flow was stopped for 5 min during switching of the rainwater solution from lower to higher ionic strength. Samples were collected from two ports receiving the highest and lowest flows for analysis of pH, conductivity, turbidity, and bromide, cesium, and strontium (total and dissolved) concentrations.

Batch desorption experiment: Batch experiments were conducted to estimate the effect of ionic strength on the desorption of cesium and strontium and to compare the effect of sodium and calcium concentrations to desorb cesium and strontium from soil. A mixture of 3 g of dry soil and 30 mL of high-purity water were mixed in polypropylene vials (50 mL) for 16-18 h on an orbital shaker (Lab Companion, SK-300) at 200 rpm. The soil-water suspensions were spiked with 300 μL of a solution containing 0.1 M CsBr and 0.1 M $SrBr_2$ to achieve initial cesium and strontium concentrations of 0.1 mM. The soil-water suspensions were mixed for 24 h at 200 rpm and centrifuged at 3400 rpm (1600 g) for 20 min. The solutions were decanted from the centrifuged suspensions and the vials were filled with solutions of $NaNO_3$ at concentrations of 0.01, 0.1, 1, and 10 mM or $Ca(NO_3)_2$ at concentrations of 0.01, 0.1, 1, and 10 mM. The soil-water suspensions were mixed for 24 h at 200 rpm and centrifuged at 3400 rpm (1600 g) for 20 min. The solutions were decanted from the centrifuged suspensions and analyzed for turbidity, cesium and strontium (total and dissolved). The batch desorption experiment was conducted in triplicate.

Analysis of water samples: The samples collected from all active ports were analyzed for pH, conductivity, turbidity, and bromide concentration. The pH was measured using a pH/ion-selective electrode meter (Orion 720A) and a combination electrode (Orion 8102BNU). Conductivity was measured using a conductivity meter (Orion 105) and a cell (Orion 011050). Bromide was measured using the pH/ion-selective electrode meter and a combination bromide-selective electrode (Accumet 13-620-524). Turbidity was measured using a turbidity meter (Hach 2100N). Turbidity was converted to colloid concentration (mg L^{-1}) using a calibration curve of total suspended sediment concentration versus turbidity. The total suspended sediment concentration was measured by drying colloid suspensions (20 mL) of increasing turbidity in pre-weighed aluminum cups in an oven at 104 °C and weighing the mass of the dried colloids. The contribution of total dissolved solids to the suspended sediments concentration was estimated to be less than 1% based on a conversion of the maximum conductivity (25 μS cm^{-1}) to total dissolved solids. Effluents from two ports in both cores were analyzed for cesium and strontium using inductively coupled plasma-mass spectrometry (ICP-MS; Perkin Elmer SCIEX Elan DRC-e). Cesium and strontium were measured as total and dissolved concentrations, with dissolved defined as passing through a 0.2 μm nylon filter (VWR, 25 mm diameter). The concentration of cesium and strontium associated with colloids was calculated as the difference between the total and dissolved concentrations. The detection limits for cesium and strontium were 1.9 and 0.9 μg L^{-1}, respectively. For ICP-MS, indium was used as an internal standard. Four standards (blank, 100, 500 and 1000 ppb) made by accurately diluting certified standards were used for calibration.

Results

***Effect of physical heterogeneity on flow of water*:** A rainfall application rate at 1.8 cm h^{-1} caused a relative saturation of 85 % in core 1 and 86% in core 2 during the rainfall application of cesium and strontium (Figure 5.2). However, the relative saturation of core 1 fluctuated during the rainfall application of $Ca(NO_3)_2$ of increasing ionic strengths. The flow interruption for 12.2 h led to decreases in relative saturation to 66.7% in core 1 and to 81% in core 2. Core 1 was drained faster than core 2 during the flow interruption. A short pause (0.1 h) in flow during the switching of rainwater to lower or higher ionic strengths caused fluctuation of moisture content in both cores. The changes in moisture content due to the short pause were higher in core 1 than in core 2.

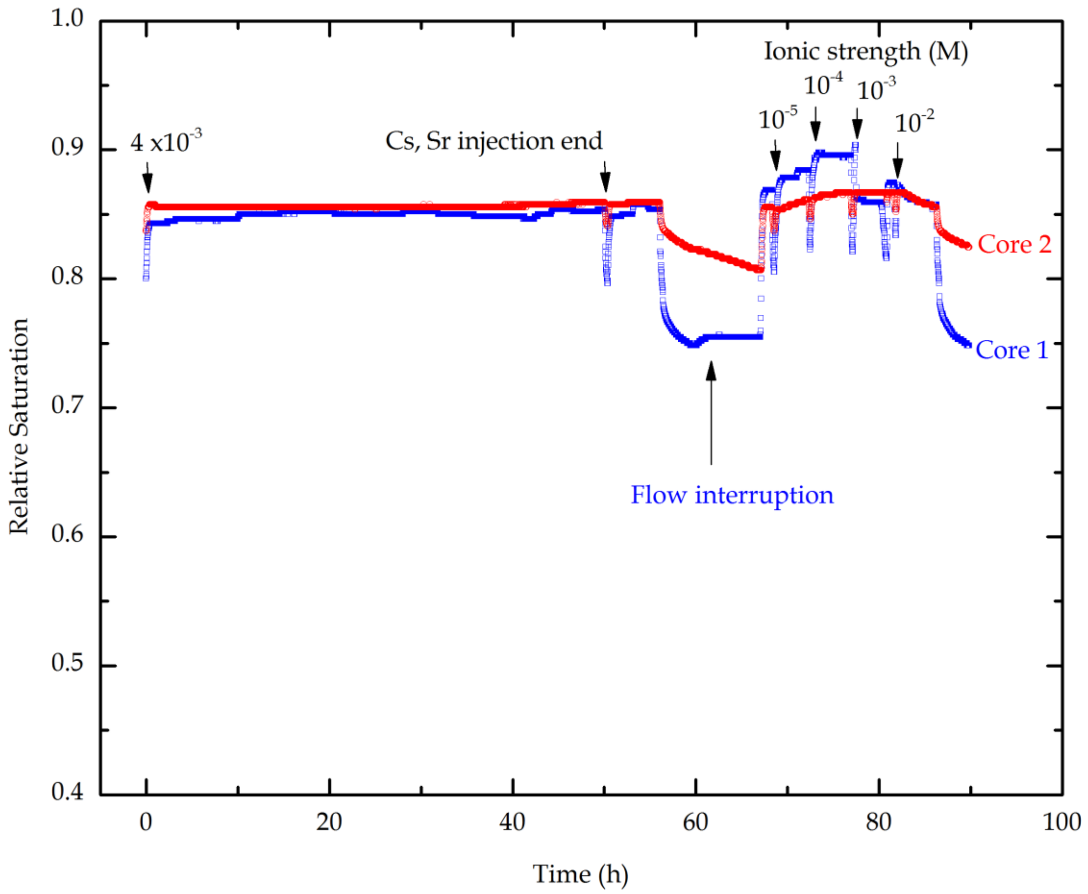

Figure 5.2. Average moisture content of cores 1 and 2 during rainfall experiments.

Of the 19 ports in the sample grid below the cores, water flowed through seven ports in core 1 and four ports in core 2 during the first 7.3 h of rain (Figure 5.3). The flow rates of the infiltrating water varied among the ports by a maximum factor of 12 in core 1 and 18 in core 2. We monitored the flow rates in two ports (r0 and r60) in core 1 and two ports (r30 and r90) in core 2 throughout the experiments.

The breakthrough time of bromide and conductivity varied in both sampled ports of core 1 and core 2 (Figure 5.4). The increase in the concentration of bromide due to flow interruption was used as an indicator of the diffusion of bromide between the macropores and the matrix. The increases in the concentration of bromide due to a flow interruption were higher for one of the sampled ports (r0 in core 1 and R30 in core 2) in each core. These two ports had slower flow rates and lesser variation of conductivities than the other sampled ports (r60 in core 1 and R90 in core 2). The long bromide breakthrough times, slow variation of conductivities, and a low flow rate at port r0 in core 1 and at port R30 in core 2 indicate a high diffusion of solute between the macropores and the matrix. A short bromide breakthrough times, fast variation of conductivities, and a high flow rate at port r60 in core 1 and at port R90 in core 2 indicate a low diffusion of solute between the macropores and the matrix.

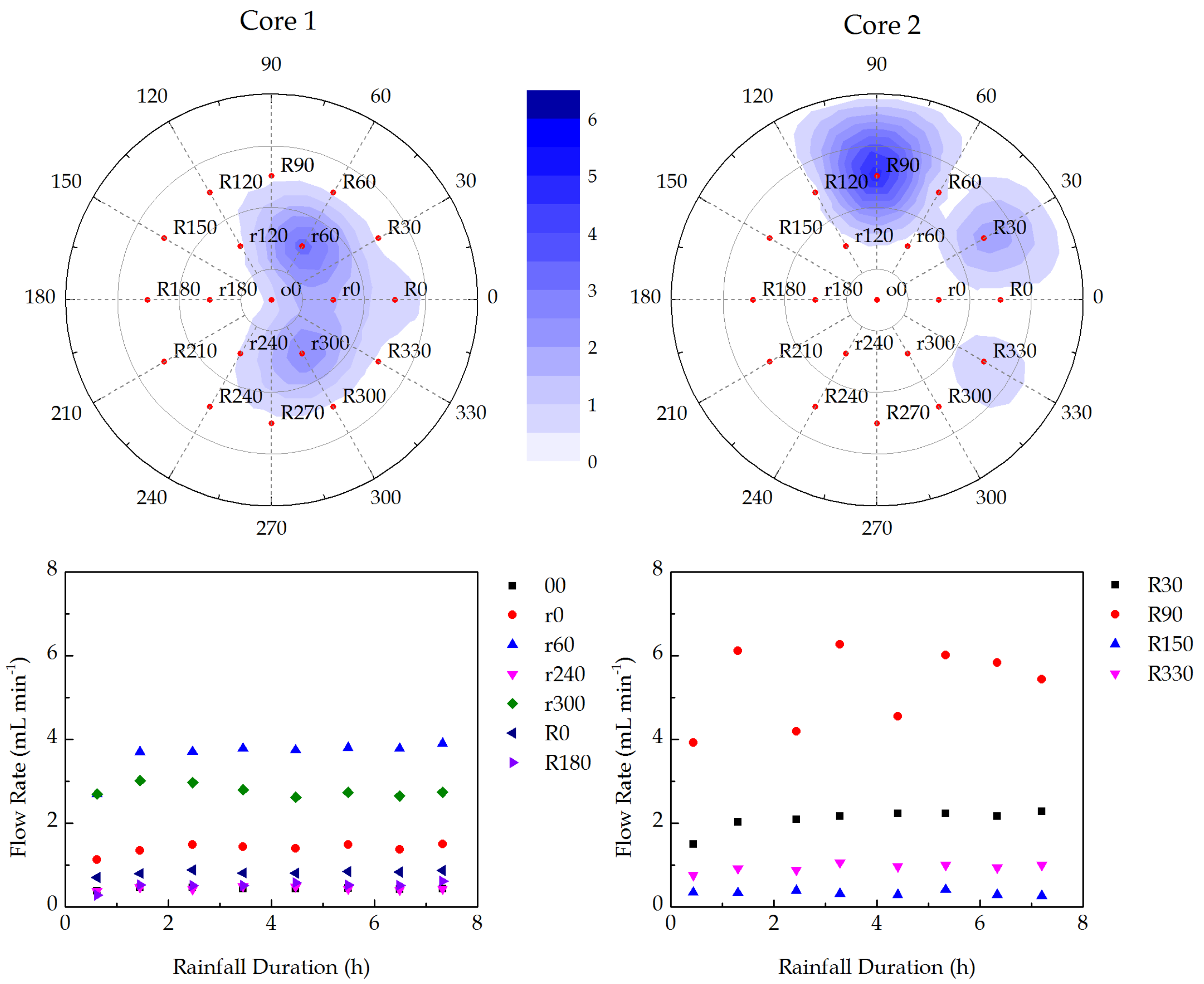

Figure 5.3. Flow distribution during first 7.3 h rainfall at an application rate of 2.5 cm h^{-1} on core 1 (left column) and core 2 (right column).

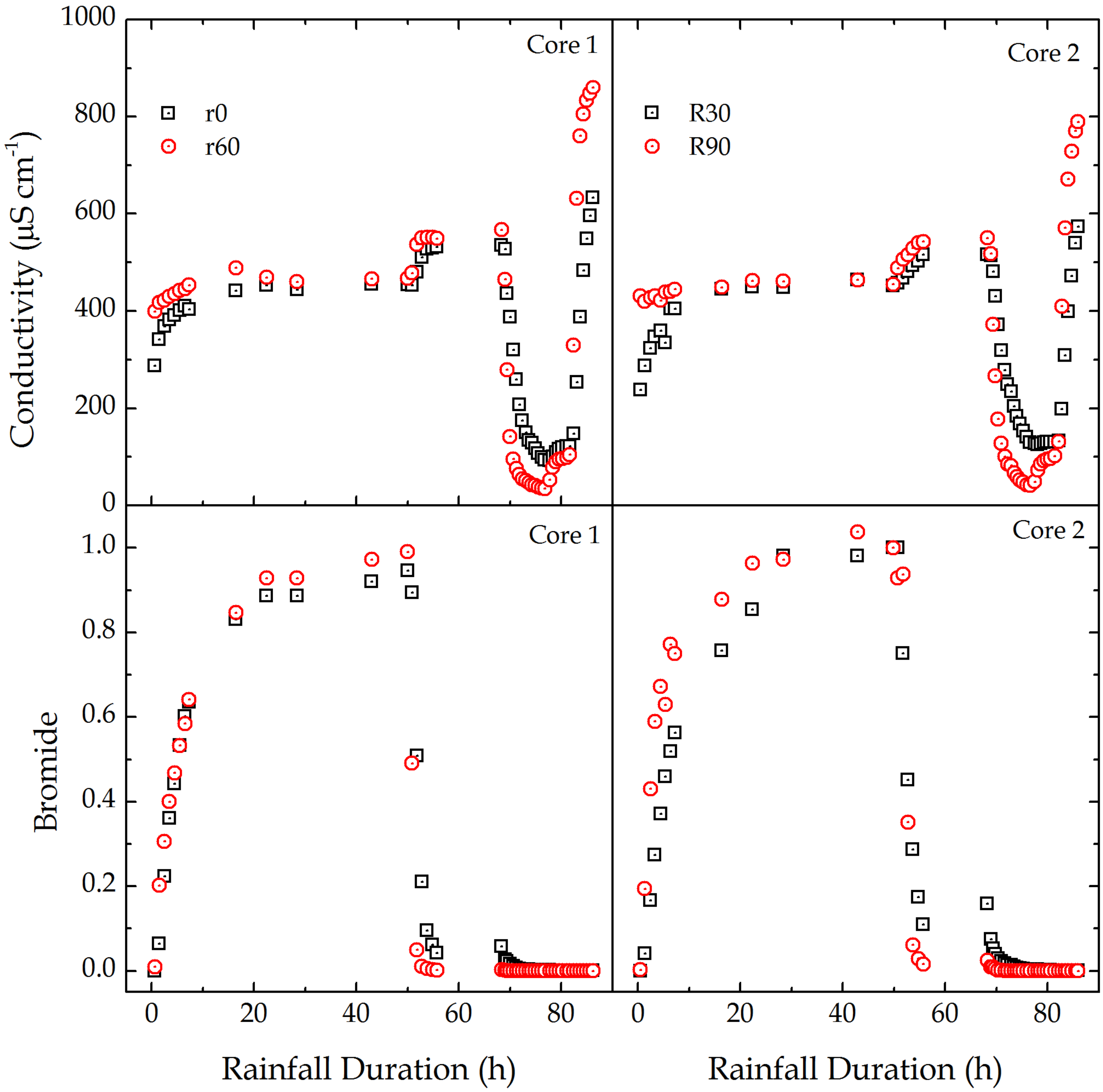

Figure 5.4. Conductivity (top) and bromide (bottom) breakthrough curves in two sampled ports for core 1 and core 2. The breakthrough times for r0 and r60 in core 1 were estimated 5.0 and 5.2 h, respectively. The breakthrough times for R30 and R90 in core 2 were estimated 2.8 and 6.0 h, respectively. Flow was interrupted between 55.7 h to 67.9 h. The ionic strength of rainwater was decreased from 4 mM to 0.01 at 68.5 h followed by an increase in the conductivity of rainwater to 0.1 mM at 72.5 h, to 1 mM at 77.1 h, and to 10 mM at 81.8 h during the rainfall.

***Mobilization of colloids*:** The mobilization of colloids decreased with increasing calcium concentration as indicated by the ionic strength of the rainfall solution in core 1 (Figures 5.5) and in core 2 (Figure 5.6). More colloids were mobilized from core 1 than from core 2. More colloids were mobilized in port r60 than port r0 in core 1 and more colloids were mobilized in port R90 than port R30 in core 2. It should be noted that port r60 in core 1 and port R90 in core 2 had a higher flow rate and a shorter breakthrough time of bromide.

***Application of cesium and strontium*:** The transport of cesium and strontium was faster in core 1 (Figure 5.5) than in core 2 (Figure 5.6) during a 50 h injection of cesium and strontium. Transport occurred through the dissolved phase of cesium and strontium. In both cores, strontium moved faster than cesium. The mobilities of cesium and strontium were different through each of the sampled ports in both cores. Cesium and strontium were transported faster through port r60 than port r0 in core 1. In core 2, cesium and strontium were transported faster through port r90 than port r30. Port r60 in core 1 and port R90 in core 2 had higher flow rates and shorter breakthrough times of bromide.

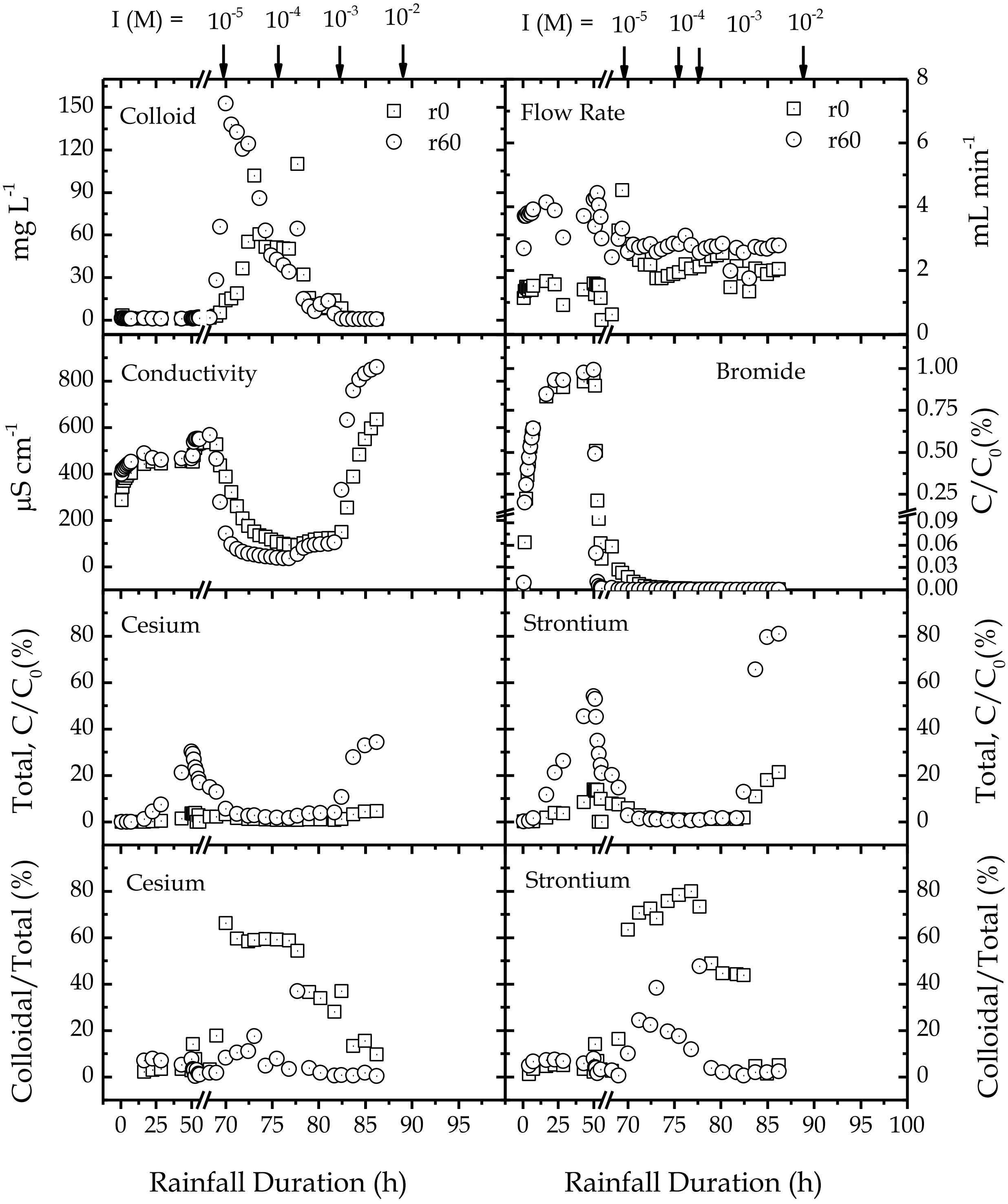

Figure 5.5. Mobilization of cesium, strontium, colloids, and bromide in core 1 by solutions of different ionic strengths. The arrows indicate a switch in rainfall solutions of different ionic strengths.

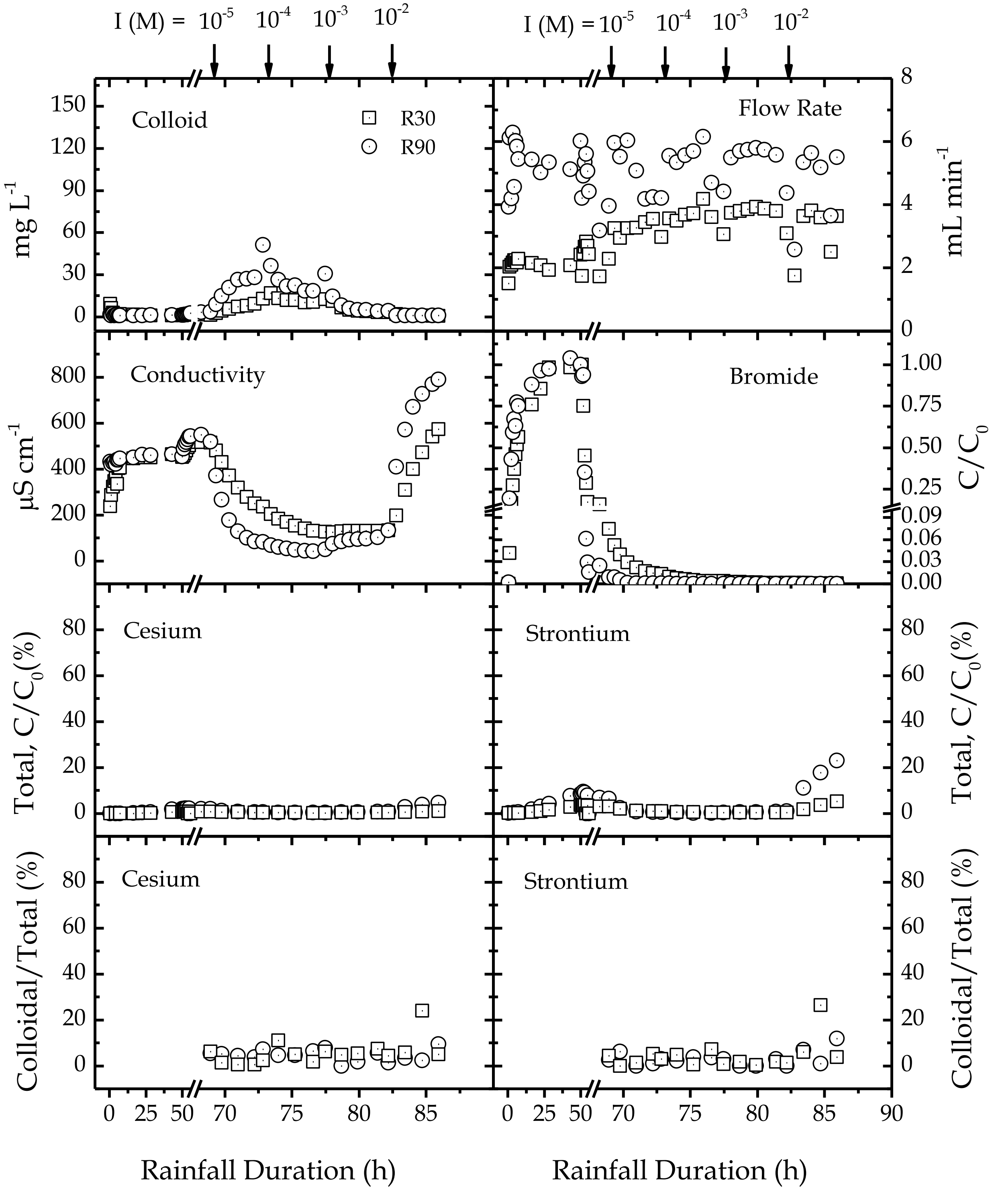

Figure 5.6. Mobilization of cesium, strontium, colloids, and bromide in core 2 by solutions of different ionic strengths. The arrows indicate a switch in rainfall solutions of different ionic strengths.

***Mobilization of cesium and strontium*:** The release of cesium and strontium increased with increases in the calcium concentrations of rainwater in core 1 (Figure 5.5) and in core 2 (Figure 5.6). A summary of the average concentration of cesium and strontium mobilized at each ionic strength solution is provided in Figure 5.7. The colloidal fraction of mobilized cesium and strontium decreased with increasing ionic strength in core 1. The colloidal fraction of cesium and strontium was higher in port r0 than in port r60 in core 1. Port r0 in core 1 had slower flow rate and longer breakthrough time of bromide. The colloidal fraction of cesium and strontium did not show any trend in core 2. The total concentration of cesium was consistently below that of strontium at all ionic strengths in both cores.

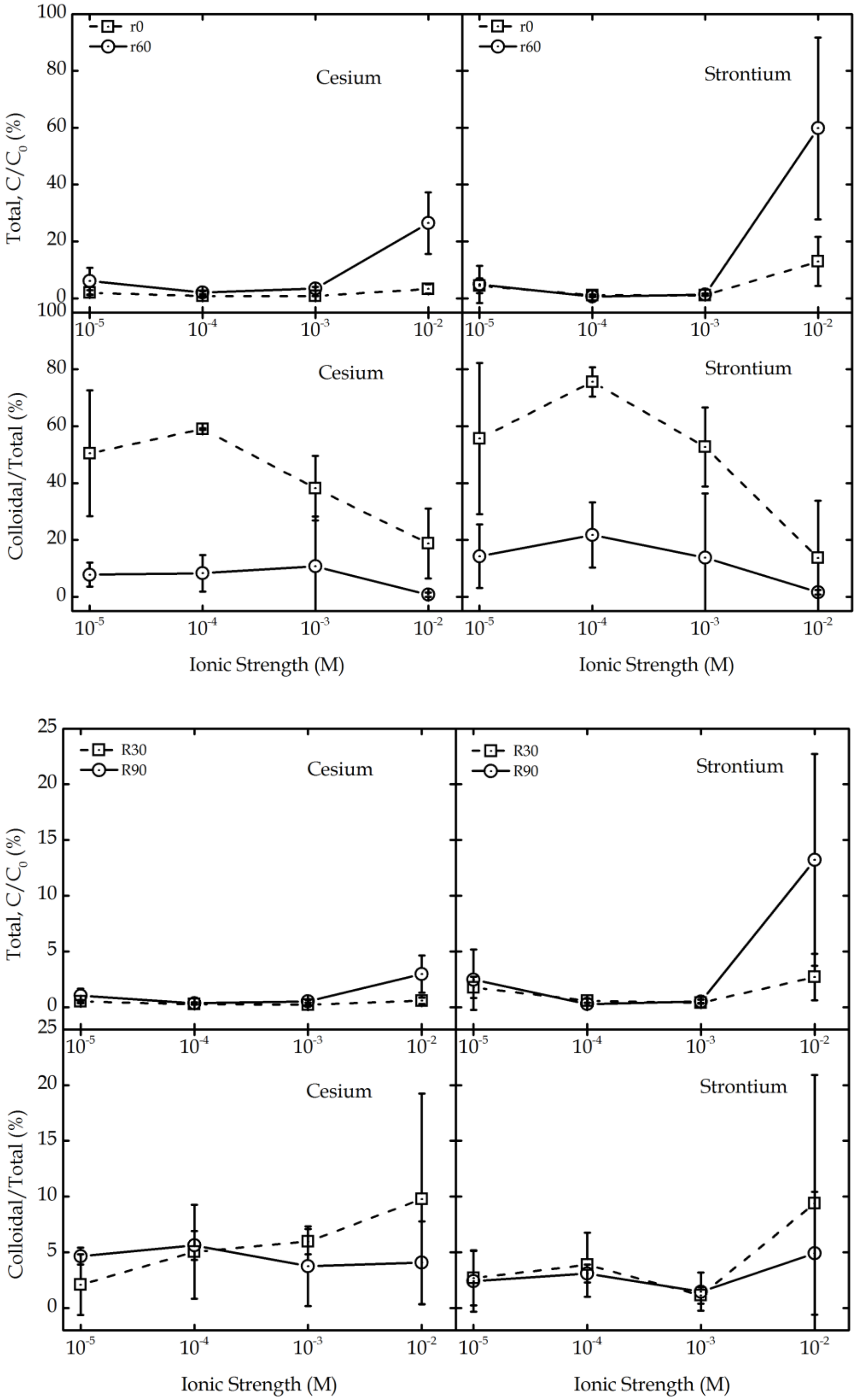

Figure 5.7. Summary of cesium and strontium fractionation at different ionic strengths in core 1 (top) and core 2 (bottom).

***Release of cesium and strontium in batch studies*:** The release of cesium and strontium increased with increases in the calcium concentrations of the solution (Figure 5.8). Release was not significant until the ionic strength of the solution was raised to 0.1 mM. Strontium was more readily released than cesium. The colloid concentration of the decanted soil suspensions decreased with increasing ionic strength and remained constant between 1 and 10 mM ionic strength. The released concentrations of cesium and strontium were higher in the presence of calcium than in the presence of sodium.

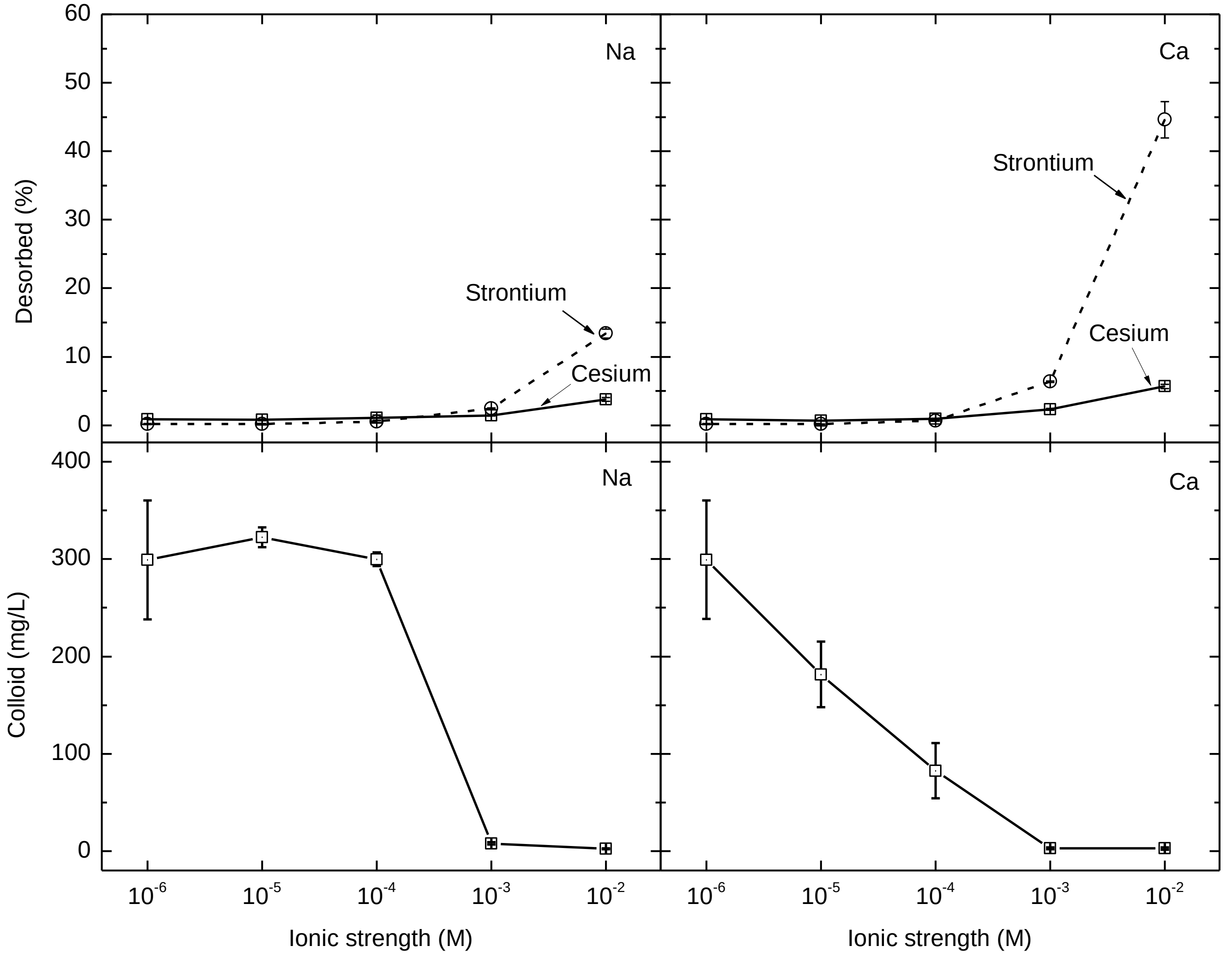

Figure 5.8. Desorption of cesium and strontium by $NaNO_3$ (left) and $Ca(NO_3)_2$ (right) at different ionic strengths in batch studies. Colloid concentration was measured from decanted solution isolated from centrifuged soil mixture.

Discussion

***Characterization of physical heterogeneity of soil*:** The physical heterogeneity of the soil was examined based on relative saturation of soil core and the distribution of flow rate in the cores. A difference in the rate of decrease of the relative saturation between the two cores during the 12.2 h flow interruption indicates that the cores have different physical properties (Figure 5.2). The relative saturation in core 1 was sensitive to long pauses (12.7 h) and short pauses (0.1 h) in flow during the switching of rainwater to lower or higher ionic strengths. This result suggests that the fractures in core 1 drain water faster than fractures in core 2. Compared to the four active ports in core 2, seven ports were conducting water in core 1, which indicates a more uniform distribution of water in core 1. Water was flowing through more than 37% of the total bottom surface of core 1 in comparison to less than 21% of the total bottom surface of core 2 covered by 19 ports (Figure 5.3). These results suggest that preferential flow occurred through the fractures. A variation of moisture content during the pauses indicates that water was exchanged between the fractures and the surrounding matrix.

We measured the variation of bromide breakthrough times to examine the nature of flow paths leading to the two sampled ports in each core. The breakthrough times of bromide were similar in both ports in core 1. A variation in arrival times of bromide breakthrough between 2.8 h to 6.0 h in core 2 indicates a difference in the exchange rate of bromide between the fractures and the surround matrix in both ports (Figure 5.4). The two ports sampled in core 1 have similar bromide breakthrough times. The rate of decrease of conductivity of the pore water was smaller in ports r0 in core 1 and R30 in core 2 than the other sampled port in the respective cores. Interrupting the flow of infiltrating water through the soil cores ruled out the contribution of advection-dominated transport; therefore, increases in the concentration of bromide were attributed to the diffusion of solute from the matrix into the soil macropore (Brusseau *et al.*, 1997). A difference in concentration of bromide before and after a flow interruption was greater in port r0 than port r60 of core 1 and in port R30 than port R90 in core 2. Changes in the concentration of bromide due to flow interruptions suggest an exchange of bromide between the macropores and the soil matrix (Elci and Molz, 2009). The diffusion of a solute into the soil matrix from the macropores during a flow interruption reduces the concentration of a solute in the macropores (Reedy *et al.*, 1996). Therefore, diffusion of solute into surrounding matrix decreased the ionic strength of pore water in the macropores. On the other hand, diffusion of solute from the matrix increased ionic strength of pore water in macropore.

***Mobilization of colloids*:** Colloid mobilization increased when calcium concentration of the rainwater solutions was decreased, and decreased when the calcium concentration increased (Figure 5.5 and 5.6). An increase and decrease in calcium concentration was indicated by corresponding increase and decrease in the conductivity of pore water. A decrease in the calcium concentration causes greater electrostatic repulsion between colloid and soil grain surfaces, which results in greater colloid mobilization (DeNovio *et al.*, 2004). An increase in calcium concentration reduces colloid mobilization. More colloids were mobilized from ports (r60 in core 1 and R90 in core 2) where conductivity decreased gradually in response to lowering calcium concentration of rainwater. Each port responded differently to changes in calcium concentration due to a difference in hydraulic property of soil through which water flows (Compere *et al.*, 2001). A rapid decrease in calcium concentration in fractures mobilized more colloids, which indicates a strong correlation between the rate of exchange of calcium between the fractures and the matrix, and the amount of colloids mobilized. This result has important implications for the mobilization of colloids from heterogeneous soil driven by transients in geochemical conditions that typically occur during a rainfall.

Within the same core, the ports with higher flow rates mobilized greater amounts of colloids than the ports with lower flow rates. If flow rate is an indication of greater mobilization of colloids, more colloids should be mobilized from both ports in core 2 than the ports in core 1. A lower amount of colloids in core 2 indicates that the conductivity of water, and not just the flow rate, contributed to the mobilization of colloids in all ports. The results of a field experiment suggested a lack of relationship between the quantity of colloids mobilized and the discharge rate of infiltrating water (Ryan *et al.*, 1998). Our study highlights the importance of matrix diffusion in mobilizing colloids in macroporous soil.

***Removal of cesium and strontium from rainwater*:** **C**esium and strontium adsorbed more strongly in core 2 (Figure 5.6) than core 1 (Figure 5.5). Stronger adsorption of cesium and strontium could be due to changes in physical and chemical heterogeneity of soil (Jackson and Inch, 2002; Pace *et al.*, 2007). The soil used in this study is composed of fractured saprolite and clay minerals where clays are coated with a large quantity of amorphous Fe(III) and Mn oxides (Jardine *et al.*, 1993). A variation of clays and iron oxides (chemical heterogeneity) and fracture sizes (physical heterogeneity) could lead to a different removal rate of cesium and strontium in both cores.

The adsorption of cesium was stronger than strontium in both cores. Greater quantities of cesium were adsorbed on soil minerals compared to strontium due to a difference in the strength of binding to soil minerals. The strength of adsorption of cations to soil minerals depends on whether adsorption occurs through the formation of either inner-sphere or outer-sphere surface complexes, or the simple accumulation of an ion swarm near the mineral surface without complex formation (Bostick *et al.*, 2002). For example, Cs^+ forms stronger surface complexes with illite by ion exchange and inner-sphere complexation to frayed-edge (surface hydroxyl) sites, whereas Sr^{2+} binds with illites by ion exchange only (Turner *et al.*, 2006).

***Mobilization of cesium and strontium*:** Release of cesium and strontium increases with increases in ionic strength of rainwater, which indicates the importance of cation exchange on the release of cesium and strontium at high ionic strengths. Cation exchange is favorable at high ionic strengths due to stronger competition of calcium with cesium and strontium for the available adsorption sites. Batch desorption results also indicated a higher release of cesium and strontium by 10 mM of sodium or calcium, though calcium was more effective in removing both cesium and strontium from soil (Figure 5.8). Lichtner *et al.* (2004) examined the transport of cesium in a mixture of cations including Na^{+}, K^{+} and Ca^{2+} and found that cesium was mobilized to a greater extent in presence of other cations. Increase in mobilization of cesium and strontium by ion exchange was attributed to an increase in the ionic strength of rainwater in several previous studies (Flury *et al.*, 2002; Torkzaban *et al.*, 2010; Chang *et al.*, 2011).

In addition to confirming the release of cesium and strontium at high ionic strengths by cation exchange, we provided further evidence on the effect of heterogeneity on cation exchange. The release of cesium and strontium by cation exchange was higher in ports with lower diffusion of solute to the matrix (e.g. port r60 in core 1 and R90 in core 2) than that of the macropores. A rapid infiltration of rainwater of high ionic strength and low diffusion of calcium to the surrounding matrix increased the concentration of calcium in both ports. A higher concentration of calcium in port r60 and R90 released greater quantity of cesium and strontium than the other ports in the respective cores. Cation exchange was less effective for the release of cesium and strontium in port r0 and R30 because matrix diffusion decreased the concentration of calcium in pore water and decreased the cation exchange process.

In contrast to high ionic strength, less cesium and strontium were mobilized by low ionic strength rainwater. A greater fraction of total cesium and strontium mobilized at low ionic strengths are colloidal, which indicates the importance of colloid-facilitated transport of cesium and strontium at low ionic strengths. The colloidal fractions decreased with increases in ionic strength. A decrease in colloidal fraction was attributed to a decrease in amount of colloids mobilized at higher ionic strengths as well as an increase in the desorption of cesium and strontium from colloids by calcium. Colloid-facilitated transport was found to be significant at a lower concentration of cesium possibly because of saturation of strong sites on colloids (Zhuang *et al.*, 2003). Cations adsorbed on weak sites may desorb at higher ionic strengths making colloid-facilitated transport less important. For example, Steefel *et al.* (2003) observed that 95% of cesium was desorbed when cesium was weakly bound to Hanford sediments. Our results confirmed a decrease in the importance of colloid-facilitated transport at high ionic strengths.

We provided evidence of the effect of heterogeneity on colloid-facilitated transport of cesium and strontium. A greater fraction of cesium and strontium was associated with colloids in samples collected from port r0 than port r60 in core 1. Slow flow, long bromide tailing, high dispersion of conductivity were the characteristic of port r0. Even though more colloids were mobilized in core r60, the fraction of colloids carrying cesium and strontium was lower in port r60 than the colloids in r0. Two explanations were suggested for the increase in colloid-facilitated transport of cesium and strontium through regions of soil with higher matrix diffusion. First, a long residence time at r0 as indicated by bromide breakthrough curve enabled a strong association of cations with colloids and resulted in a slow release of cesium or strontium. The role of residence time and ionic strength was observed in previous studies (Flury *et al.*, 2002; Chen *et al.*, 2005). Less cesium was desorbed from colloids when residence time of colloids increased in Hanford sediments (Chen *et al.*, 2005). Second, the colloids were released from soil where cesium and strontium were strongly adsorbed during injection period (first 50 h). The colloids released from these regions were expected to have higher concentrations of cesium and strontium during the injection. Slower flow rate during injection allowed the cesium and strontium to diffuse into the soil-water interface and to adsorb strongly on soil minerals as well as colloids. Cations associated with colloids in matrix desorbed slowly due to the strength of the bond between the cations and colloids (McCarthy and Zachara, 1989). Therefore, colloid-facilitated transport could be effective in fractures with higher solute exchange with the soil matrix in contrast to fracture with low exchange rate even though larger quantities of colloids were mobilized from the macropores.

Comparison between the releases of cesium and strontium: Similar to release of cesium and strontium in the column experiment, a stronger adsorption or weaker removal of cesium than strontium was observed in batch release experiments (Figure 5.8). For the same reason, cesium was expected to be mobilized by colloids in a greater amount compared to strontium. However, our result contradicted our assumption and a greater faction of strontium was associated with colloids than cesium at lower ionic strength (Figure 5.5). The results indicated a formation of outer sphere complex for both cesium and strontium. In a previous study, we characterized the colloids by X-ray diffraction analysis and found that the colloids were primarily composed of clays, predominantly illite (Chapter 3). A larger fraction of iron oxides may have coated the frayed edge sites of illite (Jardine *et al.*, 1993).

Our study improves the understanding of the role of soil heterogeneity and changes in ionic strength on the release of contaminants by ion exchange or colloids. Colloid-facilitated mobilization of cesium and strontium was found to be important at low ionic strengths in fractures where there is high exchange of pore water with the surrounding matrix. Release of cesium and strontium by cation exchange appears to be important at high ionic strengths in the fractures where there is a little exchange of pore water with the surrounding matrix. The comparative study between colloid-facilitated transport and cation exchange is useful to predict the release of contaminant from heterogeneous soils.

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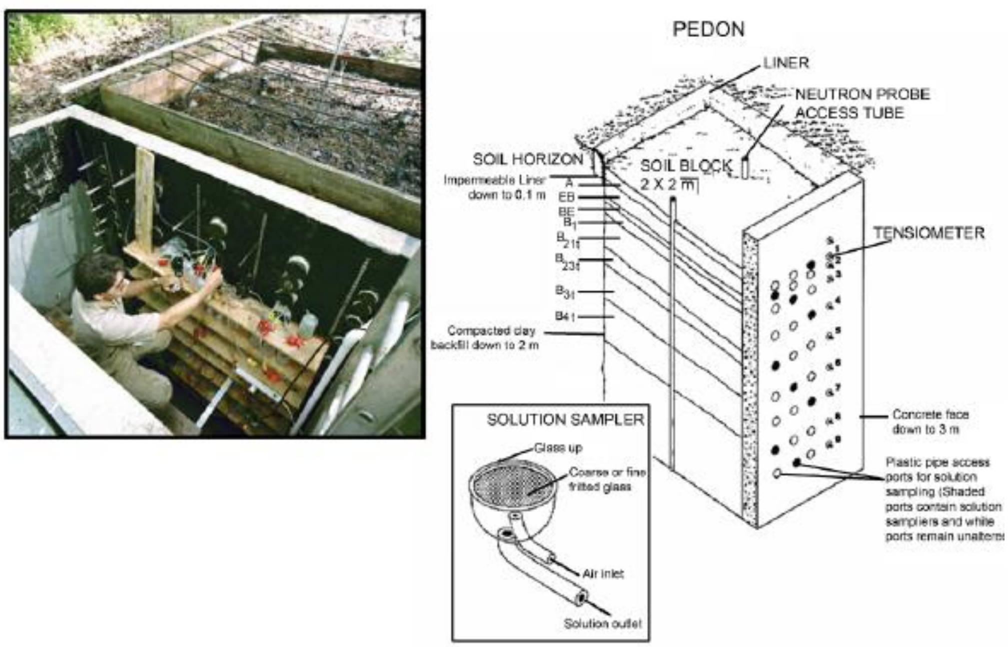
CHAPTER 6

FIELD STUDY OF THE ROLE OF CATION EXCHANGE, ORGANIC MATTER, AND COLLOIDS IN THE MOBILIZATION OF CESIUM AND STRONTIUM FROM A FRACTURED UNSATURATED SOIL



A schematic of instrumented soil pedon to examine transport process of contaminants

Abstract

The relative importance of cation exchange, organic matter-facilitated transport, and colloid-facilitated transport of cesium and strontium was evaluated under transient flow conditions in a fractured, unsaturated soil pedon in the Melton Branch watershed on the Oak Ridge Reservation. The soil pedon was instrumented with tensiometers and samplers at multiple depths to collect water from macropores, mesopores, and the soil matrix. Rainwater containing cesium and strontium were applied at 2.5 cm h^{-1} for 5 h. Cesium and strontium were mobilized from the soil pedon at low and high ionic strengths (0.01 and 5 mM) and two concentrations of dissolved organic matter (2 and 8 mg C L^{-1}). Under heavy rainfall (2.5 cm h^{-1}), infiltrating water passed predominantly through the macropores. Organic matter- and colloid-facilitated mobilization of the cations were not effective in the macropores. Infiltrating water of low ionic strength mobilized organic matter and colloids, but did not mobilize much cesium or strontium. Mobilization of cesium and strontium was greatest when the ionic strength of the infiltrating water was increased from 0.01 mM to 5 mM. We surmise that cation exchange at high ionic strength, and not organic matter- or colloid-facilitated transport, is the main mechanism for the mobilization of cesium and strontium through the macropores of the fractured soil.

Introduction

Predicting the transport of contaminants in the vadose zone under natural conditions is essential to access and protect groundwater from radioactive waste. Metal cations from radioactive wastes are mobilized by a combination of processes that include, but are not limited to, cation exchange, mobilization by organic matter, and mobilization by colloids (McCarthy and Zachara, 1989). The contributions of each process to the transport of metal cations in porous media have been independently estimated under controlled laboratory conditions (Chen *et al.*, 2005; Cheng and Saiers, 2010; Chang *et al.*, 2011; Zhao *et al.*, 2011), but under natural conditions, these processes occur simultaneously. The relative importance of each process has not been tested under conditions of physically and geochemically heterogeneous soil during a transient rainfall.

Colloids and organic matter are known to enhance the transport of metal cations in soils (Ryan *et al.*, 1998; Cheng and Saiers, 2010; Zhao *et al.*, 2011). In order to mobilize metal cations, colloids and organic matter must move faster than the contaminants through soil. Colloids and organic matter are mobilized by rainwater in contrasting physical and geochemical conditions. Rainwater passes through a network of larger and smaller pores, where flow paths depend on rainfall intensity, water content, and the pore size distribution of the soil (Anderson *et al.*, 1997; Jardine and Donald, 2008). The mobilization of colloids and organic matter can be directly affected by the nature of rainfall and the physical heterogeneity of soil. Colloids are mobilized through macropores, but removed from pore waters due to physicochemical filtration at pores and interfaces between water, air and solids (DeNovio *et al.*, 2004). Since organic matter is much smaller in size than colloids, organic matter may move readily through both macropores and the matrix. The ionic strength of rainwater influences the mobility of colloids and organic matter (Ryan and Gschwend, 1994; DeNovio *et al.*, 2004; Hruska *et al.*, 2009; Torkzaban *et al.*, 2010). Low ionic strength promotes greater mobilization of colloids as a result of an increase in the repulsive interaction between colloids and soil minerals. Unlike colloids, organic matter mobilization is less sensitive to changes in ionic strengths (Jardine *et al.*, 1989). Organic matter enhances the mobility of colloids by competing for adsorption sites and increasing the negative surface charges of mineral surfaces.

Metals are mobilized by major cations in water of high ionic strength through cation exchange (McKinley *et al.*, 2007). However, a recent study indicated that mineral dissolution competes with ion exchange to remove metal cations from soil. Chang *et al.* (2011) found ion-exchange as the dominant mechanism for removal of cesium and mineral dissolution as the major pathway for releasing strontium in waste-weathered Hanford sediment. This evidence is contrary to earlier findings where removal of cesium was greater than that of strontium due to formation of an inner-sphere complex with the minerals (Turner *et al.*, 2006). However, the relative importance of cation exchange or colloid-facilitated transport appears to depend on the ionic strength of rainwater (Chapter 5). Ionic strength also affects the release of metal cations from soil by colloids and other cations. Higher ionic strengths mobilized more metal cations by cation exchange. On the other hand, colloid-facilitated transport is inhibited by high ionic strength of pore water, because colloids are removed from the pore water at higher ionic strengths (DeNovio *et al.*, 2004). More work is needed to evaluate the importance of ion exchange mechanism under field conditions where release of metal cations by other processes cannot be ruled out.

The objective of our study was to identify the relative importance of three mechanisms – ion exchange, organic matter-facilitated transport, and colloid-facilitated transport – to the mobilization of cesium and strontium from a fractured soil under transient flow conditions.

The experiments were conducted at an instrumented soil pedon in order to evaluate the role of heterogeneity on the transport of cesium and strontium by all three processes. The role of pore-scale heterogeneity was evaluated by collecting samples from macropores, mesopores, and the soil matrix using samplers at different suction pressures.

Experimental details

***Description of field site*:** The field experiment was conducted at an instrumented soil pedon located on a hill slope in the Melton Branch watershed on the grounds of the Oak Ridge Reservation, Tennessee (Luxmoore and Abner, 1987). The soil consists of fractured shale saprolite that has been completely weathered under heavy rains that exceed 130 cm y^{-1}. Rainwater is infiltrated through the bedding planes and fracture that are usually coated with Fe and Mn-oxides and translocated clays (Jardine *et al.*, 1993).

We used an instrumented soil pedon that was built in 1987 by hydrologically isolating a 3 m deep and 2×2 m^2 area soil block from surrounding soil by a rubber liner on three sides of the block (Luxmoore and Abner, 1987; Jardine *et al.*, 1989). The three sides were filled with compacted clay-rich soil from the site. A concrete wall supported the fourth side where polyvinylchloride (PVC) access ports sealed by rubber stoppers were installed for instrumentation and sample collection. Nine tensiometers and twenty-seven plate-type fritted glass solution samplers were instrumented laterally within the pedon as a function of depth with three samplers installed at each of nine depths (Figure 6.1). At any sampling depth down to 2.8 m, two coarse- and one fine-porosity fritted glass samplers were installed as described by Jardine *et al.* (1990). The coarse- and fine-fritted glass samplers have bubbling pressures of 2.5 kPa and 50 kPa, respectively. The tube collecting samples was attached to a glass bottle maintained under constant suction using a vacuum pump and pressure regulators. The fine samplers were placed under 10 kPa tension to collect samples from matrix. The coarse samplers were placed under 2 kPa tension to collect water from the mesopores. Water was also collected at zero tension in other samplers. The zero-tension samplers are expected to get water from the macropores.

High-purity water (>18.2 MΩ cm) prepared on site using deionized water purification tanks was used to prepare rainfall solution in a 250 gallon tank (high density polyethylene). Rainfall solution was delivered from the tank to a rainfall simulator using a peristaltic pump. A rainfall simulator was designed by connecting multiple PVC pipes (1.3 cm diameter and 2 m length) with t-joints so that the distance between two adjacent PVC pipes was 15 cm. The PVC pipes were perforated (1 mm hole diameter) at approximately every 15 cm of their length to allow water to drip from a total of 225 holes on the soil pedon surface.

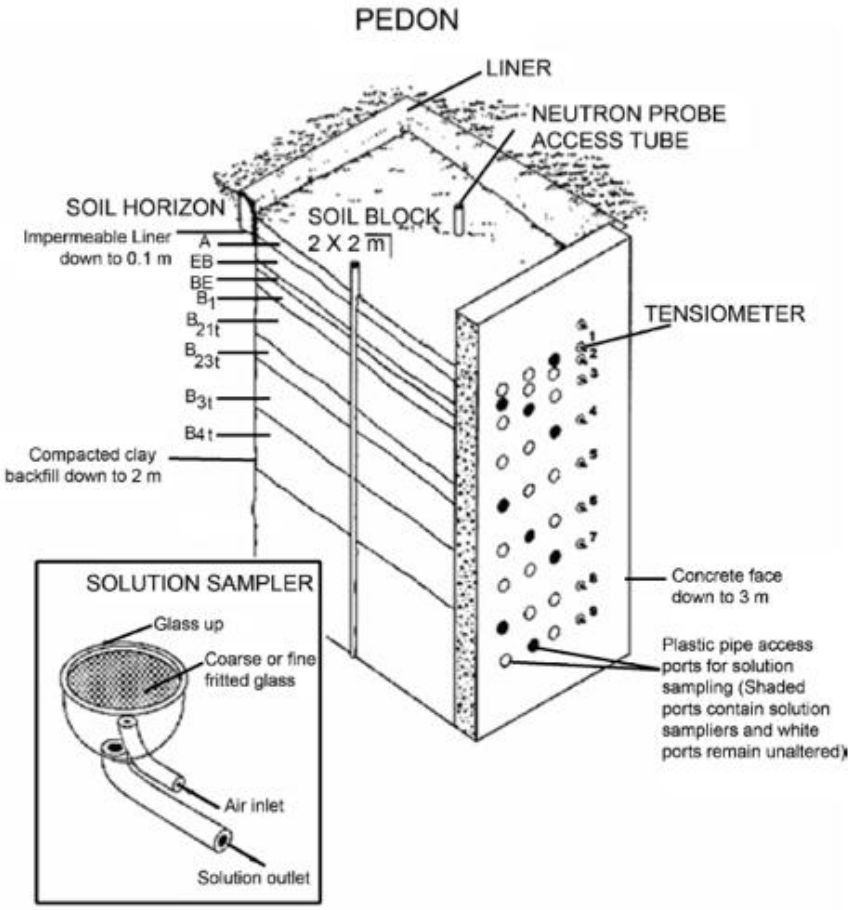


Figure 6.1. The schematic view of instrumented soil pedon showing the location of solution samplers and tensiometer with depth and an example of solution samplers installed laterally into the pedon (Jardine *et al.*, 2006).

***Rainfall and cation mobilization experiments*:** The instrumented soil block was contaminated with cesium and strontium by applying a solution of 1 mM of $CsNO_3$ (99.9%, MP Biochemicals), 1 mM $Sr(NO_3)_2$ (99.9%, MP Biochemicals), and 1 mM NaBr at a infiltration rate of 2.5 cm h^{-1} for 5 h before switching the solution to 5 mM $NaNO_3$ for another 2 h. The flow was stopped for 17 h before application of solutions of either low ionic strength (0.01 mM of $NaNO_3$) or higher ionic strength (10 mM of $NaNO_3$) with different concentrations of dissolved organic matter (0, 2.0, and 7.9 mg C L^{-1}). The sequence of experiments conducted on the soil pedon is summarized in Table 6.1. We used natural organic matter previously isolated from brown water from a wetland pond in Georgetown, SC (Gu *et al.*, 1994). Briefly, the water from the pond was filtered through a 0.1 μm Amicon hollow-fiber filter and the filtered solution was passed through a cation exchange resin (Na^+ form) to isolate natural organic matter. The natural organic matter had been stored at 4 °C prior to use in the experiment. The properties of the dissolved organic matter used in this study are summarized in Table 6.2. The infiltrating water was collected from 27 samplers located at multiple depths.

Table 6.1. Composition of rainwater solutions injected on the Melton Branch soil pedon.

Day	Conditions	DOM (mg C L^{-1})	Ionic strength (mM)	Rainfall time [chemical composition]
1	injection (High I, no DOC)	0	5	1.0 [5.0 mM $NaNO_3$] 5.0 [1.0 mM $CsNO_3$, 1.0 mM $Sr(NO_3)_2$, 1.0 mM NaBr], 2.0 [5.0 mM $NaNO_3$]
2	Release (Low I, no DOC)	0	0.01	7.0 [0.01 mM $NaNO_3$]
3	Release (Low I, low DOC)	1.97	0.01	6.5 [0.01 mM $NaNO_3$]
4	Release (Low I, high DOC)	7.86	0.01	5.8 [0.01 mM $NaNO_3$]
5	Release (high I, high DOC/no DOC)	7.86	5	6.5 [5.0 mM $NaNO_3$], 3.2 [4 mM $NaNO_3$,

Table 6.2. Physical and chemical properties of organic matter used in the study (Gu *et al.*, 1994).

Elemental Analysis	Weight %[a]	Property	Fraction[b]
C	48.3	Acidity[c]	12 mmol g^{-1} C
O	42.1	Hydrophobic acid fraction	42%
H	3.3	Hydrophobic acid neutral fraction	18%
N	1.6	Hydrophilic fraction	40%
S	3.1		

Release of cesium and strontium from soil in batch study: Batch experiments were conducted to evaluate the effect of dissolved organic matter concentration on the release of cesium and strontium from soil collected from the field site. A mixture of 3 g of dry soil and 30 mL of high-purity water were mixed in 50-mL polypropylene vials for 16 to 18 h on an orbital shaker (Lab Companion, SK-300) at 200 rpm. The soil-water suspensions were spiked with 300 μL of a solution containing 0.1 M CsBr and 0.1 M $SrBr_2$ to achieve cesium and strontium initial concentrations of 0.1 mM. The soil-water suspensions were mixed for 24 h at 200 rpm and centrifuged at 1600 *g* for 20 min. The solutions were decanted from the centrifuged suspensions and the vials were filled with solutions of Georgetown dissolved organic matter at four concentrations (0, 1.1, 2.2, 4.2, and 7.9 mg C L^{-1}) to desorb cesium and strontium from the soil. The dissolved organic matter solutions were prepared at two ionic strengths (0.01 and 10 mM) where ionic strength was adjusted by adding $NaNO_3$. The soil-water suspensions were mixed for 24 h at 200 rpm and centrifuged at 1600 g for 20 min. The solutions were decanted from the centrifuged suspensions and analyzed for cesium, strontium, and turbidity. The batch desorption experiment was conducted in triplicate.

***Analysis of water samples*:** The samples collected from samplers were analyzed for pH, conductivity, turbidity, bromide, dissolved organic carbon, total major cations, and total and dissolved cesium and strontium concentration. The pH was measured using a pH/ion-selective electrode meter (Orion 720A) and a combination electrode (Orion 8102BNU). Conductivity was measured using a conductivity meter (Orion 105) and a cell (Orion 011050). Bromide was measured using the pH/ion-selective electrode meter and a combination bromide-selective electrode (Accumet 13-620-524). Dissolved organic carbon (filtered by 0.45 µm nylon syringe filter) was measured using a high-temperature platinum-catalyzed combustion organic carbon analyzer (Shimadzu TOC-5000). Turbidity was measured using a turbidity meter (Hach 2100N). Turbidity was converted to colloid concentration (mg L^{-1}) using a calibration curve of total suspended sediment concentration versus turbidity. The total suspended sediment concentration was measured by drying colloid suspensions (20 mL) of increasing turbidity in pre-weighed aluminum cups in an oven at 104 °C and weighing the mass of the dried colloids. The contribution of total dissolved solids to the suspended sediments concentration was estimated to be less than 1% based on a conversion of the maximum conductivity (25 µS cm^{-1}) to total dissolved solids. Water samples were analyzed for cesium and strontium using inductively coupled plasma-mass spectrometry (ICP-MS; Perkin Elmer SCIEX Elan DRC-e). Cesium and strontium were measured as total and dissolved concentrations, with dissolved defined as passing through a 0.2 µm nylon filter (VWR, 25 mm diameter). The concentration of cesium and strontium associated with colloids was calculated as the difference between the total and dissolved concentrations. The detection limits for cesium and strontium were 2.1 and 1.0 µg L^{-1}, respectively. For ICP-MS, indium was used as an internal standard. Four standards (blank, 100, 500 and 1000 ppb) made by accurately diluting certified standards were used for calibration.

***Colloid characterization*:** The size and morphology of the colloids were examined using scanning electron microscopy and energy dispersive X-ray analysis (SEM/EDX; JEOL JSM6480LV low-vacuum; 20 kV accelerating voltage). The water samples were dispersed by vortex-mixing (100 rpm, 30 s). One drop of the sample was added on a copper grid (#200 mesh) mounted on the end of needle-sharp forceps and air-dried overnight. The grid was stored in a dust-free environment before the SEM/EDX analysis.

Results

***Distribution of water in the soil pedon*:** Water samples were collected from three zero-tension (macropore) samplers (0.3, 1.2, and 2.7 m depth) and one coarse (mesopore) sampler (1.2 m depth) where the flow rates through zero-tension samplers were higher than the coarse sampler by a factor of 3 to 10 (Figure 6.2). Other samplers, including all of the fine (matrix) samplers were not active during the rainfall period. The bromide and conductivity breakthrough in the zero-tension sampler at the 0.3 m depth is provided in Figure 6.3. The breakthrough times of bromide decreased with increases in depth of samplers (Figure 6.4). The bromide breakthrough time was greater in the coarse sampler than in the zero-tension sampler at a depth of 1.2 m. The conductivity in samples from all samplers showed trends similar to that of the bromide breakthroughs in response to changes in the chemical conditions of the rainfall solution.

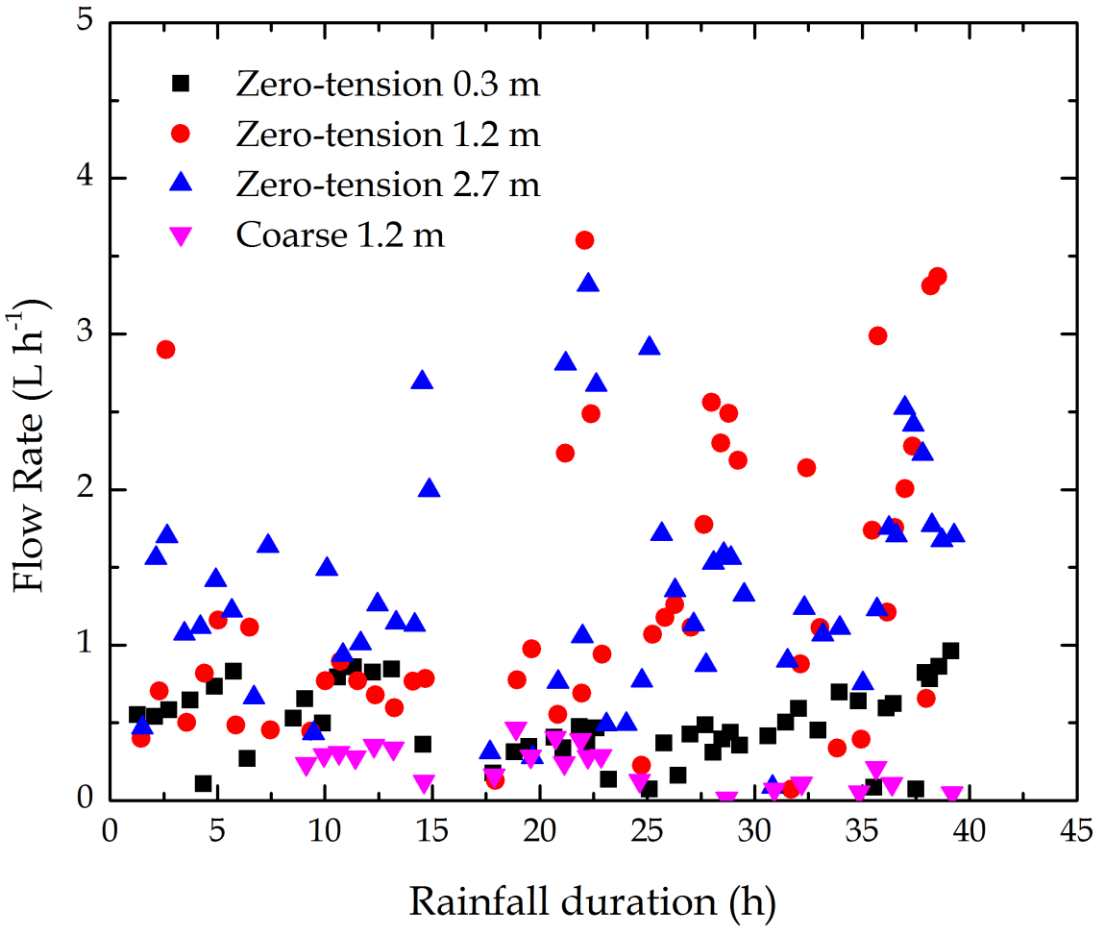


Figure 6.2. Flow rates through four samplers during rainfall experiments.

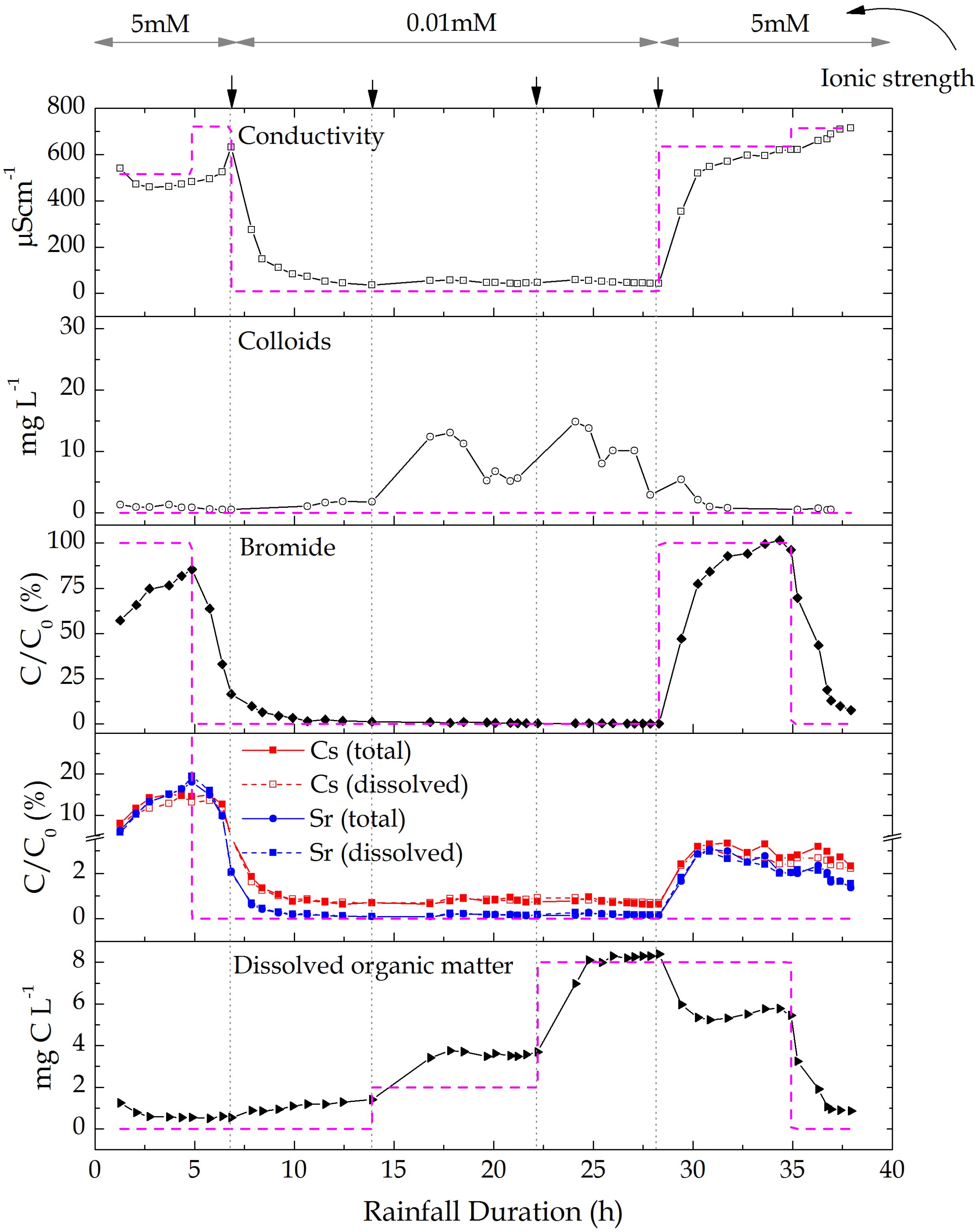


Figure 6.3. Mobilization of cesium and strontium as measured in a zero-tension sampler at 0.3 m depth by rainfall solutions of different ionic strengths and organic matter concentrations. The vertical dotted lines represent 17 h pause between consecutive rainfall events. The input concentrations of each parameter are presented as a horizontal dotted line.

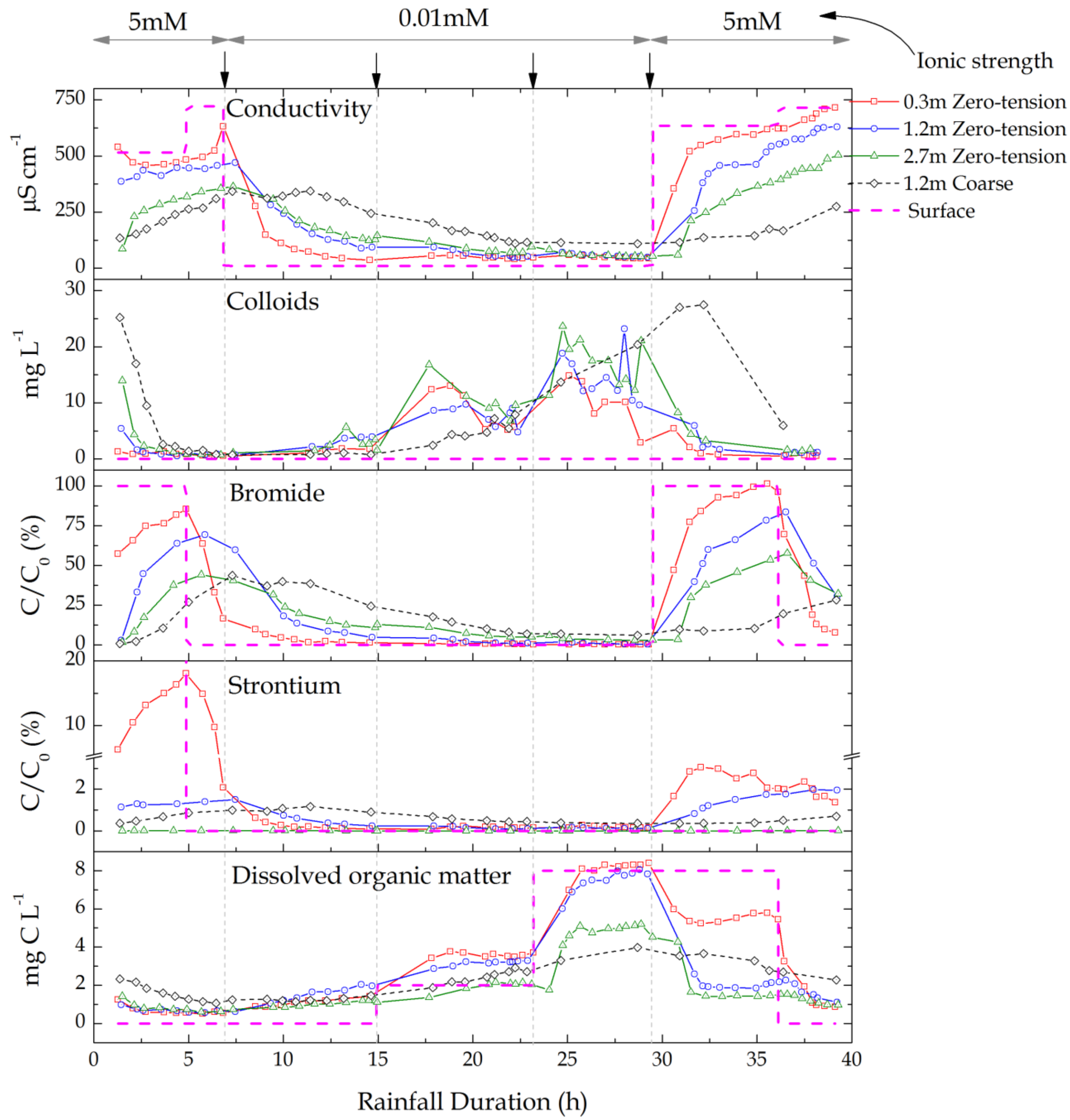


Figure 6.4. Mobilization strontium as a function of travel distance during infiltration of rainwater solutions of different ionic strength and organic matter concentrations. Arrow marks represents 17 h pause between consecutive rainfall events. The input concentrations of each parameter are presented as horizontal dotted line. Cesium was not detected in any sample below 0.3 m.

***Mobilization of dissolved organic carbon with changes in ionic strength*:** The concentration of dissolved organic carbon (DOC) in the zero-tension sampler at 0.3 m below surface was within 1 mg L^{-1} during the application of rainwater at 5.0 mM (Figure 6.3). The DOC in the samples represented the organic matter naturally mobilized from soil by the organic matter -free rainfall solution. The concentration of DOC increased when the ionic strength of the rainfall solution was decreased from 5.0 mM to 0.01 mM. Injection of organic matter of 2.0 mg C L^{-1} increased the concentration of organic matter in the zero-tension sampler to 4.0 mg C L^{-1}. Approximately 100% breakthrough of organic matter was obtained within the first 2 h when rainwater containing 7.9 mg C L^{-1} was injected at an ionic strength of 0.01 mM. The peak value of the organic matter breakthrough decreased by 40% (from 7.9 mg C L^{-1} to 5.2 mg C L^{-1}) when the ionic strength of the rainfall solution was increased from 0.01 mM to 5 mM.

The concentration of DOC mobilized during rainfalls decreased with the depth of the sampler locations (Figure 6.4). The mobilization pattern of organic matter observed in the zero-tension sampler at a depth of 0.3 m was consistent with that observed in the other samplers. During the injection of DOC, the concentrations of DOC decreased in all samplers when the ionic strengths of the feed solution increased from 0.01 mM to 5 mM. Injection of DOC led to a gradual increase in the concentration of DOC in pore water sampled by a coarse sampler than that sampled by zero-tension sampler at a depth of 1.2 m.

***Mobilization of colloids with changes in ionic strength*:** The colloid concentration in infiltrating water collected at a zero-tension sampler (0.3 m depth) was nearly zero during the high ionic strength (5 mM) rainfall in day 1 (Figure 6.3). The colloid concentration of the infiltrating water did not change when the ionic strength of the rainfall was decreased to

0.01 mM on the second day. The colloid concentration increased in the sampler when the concentration of organic matter in the rainfall solution was increased from 0 to 2.0 mg L^{-1} on the third day and to 7.9 mg L^{-1} on the fourth day at constant ionic strength (0.01 mM). The mobilization of colloids was similar among the three zero-tension samplers (Figure 6.4). The concentration of colloids gradually increased with the injection of organic carbon in a coarse sampler at a depth of 1.2 m. The concentrations of colloids in all samplers were significantly lower than the concentration expected based on laboratory studies at low ionic strengths. It is possible that the fritted ceramic cups of the samplers became clogged over years and may have blocked colloids from passing through.

Application of cesium and strontium to the soil pedon: A relative breakthrough of 15-18% for cesium and strontium was achieved after a 5 h injection of rainwater containing 1 mM of cesium and strontium (Figures 6.3 and 6.4). Cesium, strontium, and bromide concentrations decreased sharply after switching the rainfall to a cesium- and strontium-free solution of the same ionic strength (5 mM). The strontium was retarded with an increase in the depths of sampler's location (Figure 6.4). The concentration of cesium was below the detection limit in all samplers below 0.3 m from the surface.

Mobilization of cesium and strontium in the soil pedon: A decrease in the ionic strength of the rainfall solution from 5 mM to 0.01 mM on the second day mobilized colloids and organic matter, but did not mobilize significant amounts of cesium and strontium (Figures 6.2 and 6.4). An increase in the organic matter concentration of the rainfall solution from zero to 2.0 mg C L^{-1} on the third day to 7.9 mg C L^{-1} on the fourth day at the same low ionic strength (0.01 mM) did not mobilize cesium and strontium from soil. An increase in the ionic strength of the rainfall solution from 0.01 mM to 5 mM without changing the organic matter (7.9 mg C L^{-1}) on the fifth day resulted in an increase in the relative breakthrough of both cesium and strontium from 0.5% to 2.5%. The concentration of cesium and strontium did not change when the rainwater was switched to a solution with no organic matter at a similar ionic strength.

Batch experiments**:** Cesium and strontium were not released from soil by increasing the dissolved organic carbon concentration from 0 mg C L^{-1} to 7.9 mg C L^{-1} in batch studies (Figure 6.5). Release of cesium and strontium was small in batches at ionic strength of 0.01 mM. Increasing the ionic strength of the solution to 10 mM increased the release of both cesium and strontium in all batches. More strontium was released than cesium at an ionic strength of 10 mM.

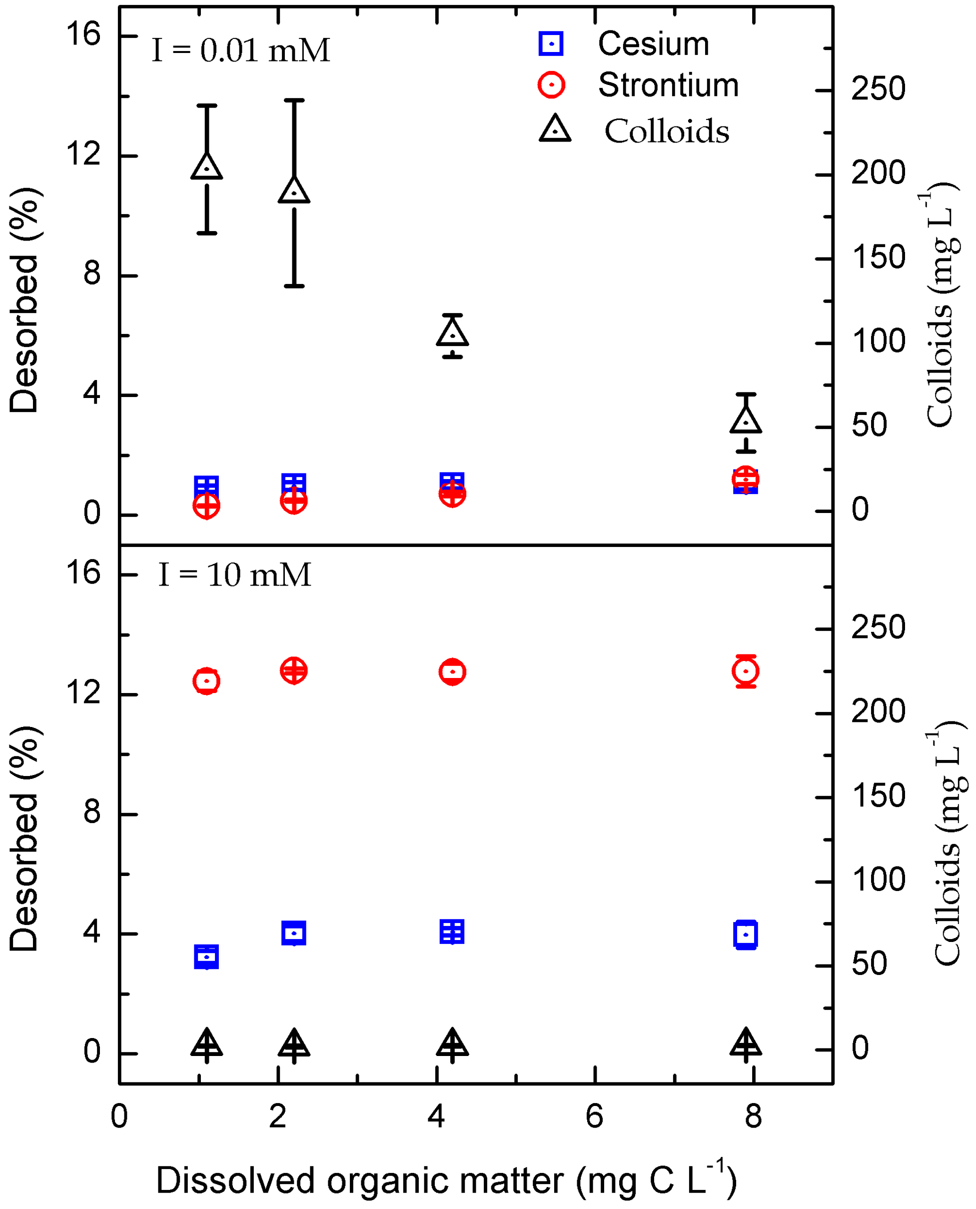


Figure 6.5. Cesium and strontium desorbed at different organic matter concentrations prepared at two ionic strengths (0.01 mM and 10 mM NaNO3). The error bar represents one standard deviation from the triplicates.

***Colloid Characterization*:** The average size of colloids found in the total sample was below 200 nm (Figure 6.6).

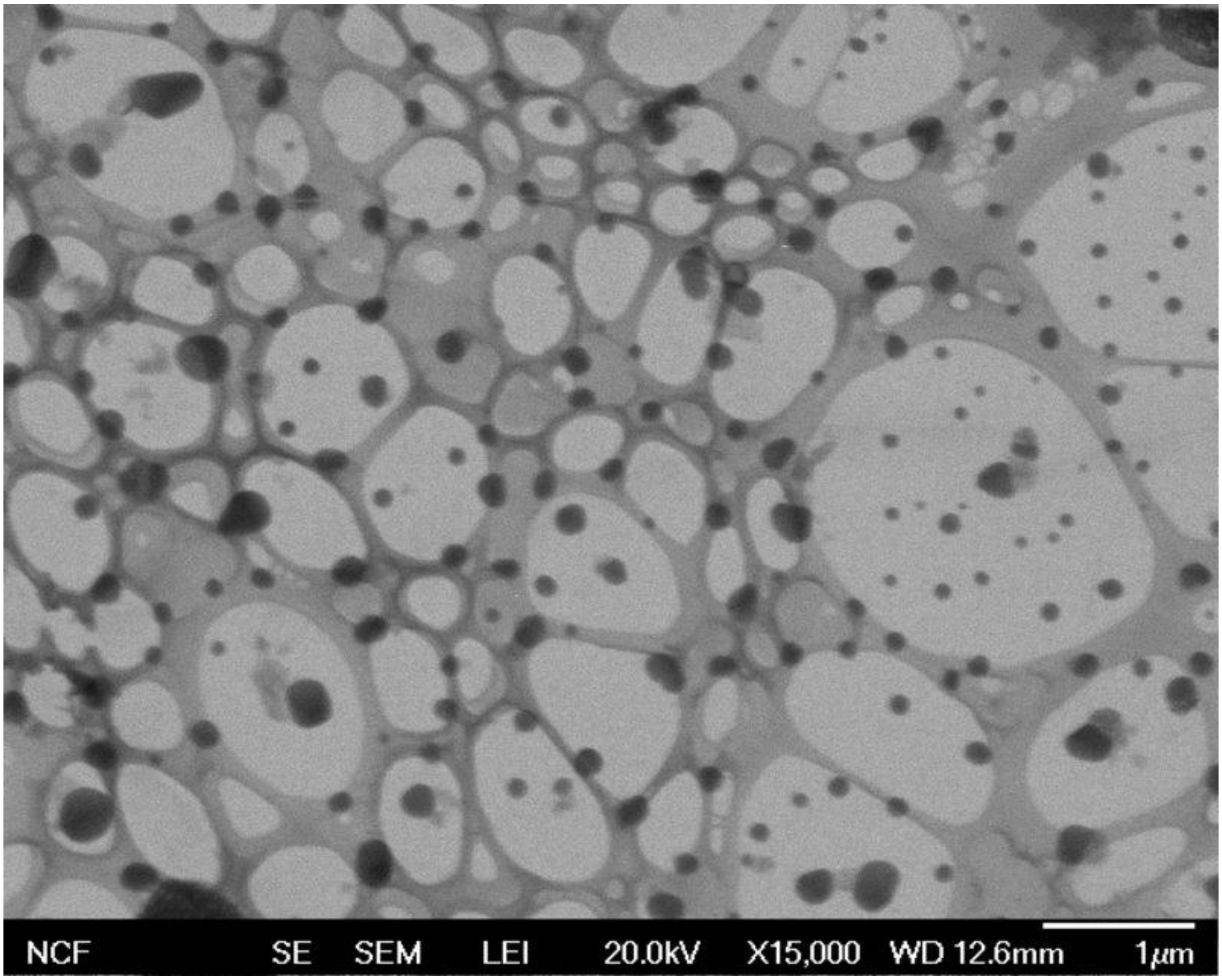


Figure 6.6. Colloid size measured by SEM. The colloids are the black spots on carbon (larger white spots) supported on the copper grid.

Discussion

Effect of physical heterogeneity of soil on the movement of water: Four out of 27 samplers received water during rainfall, which indicates that preferential flow occurred in the pedon (Figure 6.2). The flow rates in zero-tension samplers were one order of magnitude greater than the flow rate in the coarse sampler and no samples were obtained from fine samplers. Breakthrough curves of bromide and conductivities at all sampling ports indicate that an increase in depth results in a greater dispersion of the solutes in water (Figure 6.4). The dispersion of solutes was higher in the flow path leading to the coarse sampler than that leading to the zero-tension sampler at the 1.2 m depth. Higher dispersion of solutes in the coarse sampler than in the zero-tension sampler indicates a greater diffusion of the solute into the surrounding matrix. The slow exchange of solutes is evident from a lag time of conductivity of rainwater as well as the longer breakthrough time of bromide in the coarse sampler.

Mobilization of organic carbon: Increasing the ionic strength from 0.01 to 5 mM reduced the mobility of organic matter at all depths on the fifth day (Figure 6.4). A decrease in the mobility of the organic matter at higher ionic strengths can be attributed to an increase in the adsorption of organic matter onto mineral surfaces at higher ionic strengths. An increase in the mobilization of organic matter was observed when the ionic strength of stream water decreased (Hruska *et al.*, 2009). Two mechanisms could be suggested to explain an increase in the adsorption in solutions of higher ionic strength: (1) higher ionic strength resulted in a favorable entropy change for physical adsorption (Jardine *et al.*, 1989) and (2) a decrease in the repulsion between organic carbon and the mineral surface due to reduction of similar charges (Shen, 1999). Limited field experiments addressed the transport of organic matter under natural conditions (McCarthy *et al.*, 1993; Jardine *et al.*, 2006; Hruska *et al.*, 2009). The effect of ionic strength on organic matter sorption was minimal in the soil matrix compared to the macropores. This may be due to slow diffusion of the solutes between water in the macropores and the matrix.

A complete breakthrough of organic matter indicates that the soil minerals have limited absorption capacity for organic matter. Kothawala *et al.* (2009) found that organic matter predominantly adsorbed on iron or aluminum oxide instead of clays. In our study, water passed through the macropores where iron oxides have been relocated (Jardine *et al.*, 1990). The breakthrough of organic matter was lower in the coarse sampler than in the zero-tension sampler at the 1.2 m depth, which points to a greater adsorption of organic matter in the soil mesopores (coarse samplers) than in the macropores (zero-tension samplers). The longer residence time of infiltrating water in the soil matrix could cause adsorption of the organic matter onto weak sites that were kinetically ruled out in the macropores.

Mobilization of colloids: Decreasing the ionic strength and increasing the organic matter concentration mobilized greater amounts of colloids (Figure 6.4). A decrease in ionic strength mobilized colloids by increasing the repulsive interactions between similarly charged mineral colloids and soil minerals.

Increases in the concentration of organic matter resulted in increases in the mobilization of colloids at both low and high ionic strength. Adsorption of organic matter on the surfaces of colloids and soil minerals could increase the negative surface charge of both surfaces resulting in an increase in the repulsive interactions between the colloids and the soil minerals (Shen, 1999). At low ionic strengths and high organic matter concentrations, conditions that should promote colloid mobilization, the colloid concentrations measured in this soil pedon were lower than values reported in other field studies in unsaturated soil (Marley *et al.*, 1993; Ryan *et al.*, 1998; Novikov *et al.*, 2006; Utsunomiya *et al.*, 2009; Chawla *et al.*, 2010). A decrease in mobilization of colloids could be due to clogged samplers. The samplers were constructed with fritted glass cups of different porosities to collect water from the macropores and the soil matrix. Over the last two decades, the pores in the fritted glass may have become clogged and the transport of colloids into sampling bottles may have been inhibited, although the flow of water into the zero-tension samplers suggests that the zero-tension samplers were not sufficiently clogged to prevent colloids from entering the samplers. Only one coarse sampler at the 1.2 m depth and no fine samplers were active during the experiments. The peak concentration of colloids in coarse sampler was greater than the peak concentration of colloids measured in any of the zero-tension samplers; therefore, it is unlikely that this coarse sampler was clogged. However, no flow through fine samplers (5 µm size) indicates clogging of the porous sampling cup in fine samplers. Recent studies showed that soil pores of differential size contributed to generation of colloids during transient conditions (Majdalani *et al.*, 2008; Michel *et al.*, 2010). A higher concentration of colloids in the coarse samplers was because of the low flow rate of water in the coarse samplers (Figure 6.2). A larger flow rate in the zero-tension sampler diluted the total amount of mobilized colloids and decreased the concentration of colloids in the samples.

Mobilization of cesium and strontium by colloids: The transport of cesium and strontium by colloids was negligible at all ionic strengths and organic matter concentrations. The relative breakthroughs of both cesium and strontium were below 1.8% during the low ionic strength (0.01 mM) rainfall experiments. Colloid-facilitated transport was ruled out due to the small difference between the total and dissolved cesium and strontium concentrations. Colloid-facilitated transport may be important if high concentrations of colloids are present (McCarthy and Zachara, 1989), but in the low ionic strength experiment, the colloid concentrations were below 30 mg L^{-1}. The colloid concentrations that we measured could have been incorrectly low for two reasons: (1) the samplers may have been clogged and blocked the collection of colloids, or (2) the colloids were too small to be retained by the 0.2 μm filters used to separate dissolved from total cations. The size of the colloids was estimated to be below 0.02 μm by SEM analysis (Figure 6.6); therefore, the 0.2 μm filters were not small enough to remove the colloids from the infiltrating water samples.

Colloid-facilitated transport of cesium and strontium did not occur during this study. In contrast to our study, colloid-facilitated transport of radionuclides has been observed in numerous field studies (Marley *et al.*, 1993; Ryan *et al.*, 1998; Novikov *et al.*, 2006; Utsunomiya *et al.*, 2009; Chawla *et al.*, 2010). We added cesium and strontium to soil before one day of mobilization test. In the previous studies, colloids were aged with the dissolved fraction of radionuclides. Therefore, aging of colloids might have contributed to colloid-facilitated transport in the previous studies. Colloids moving at relatively high velocity through macropores may not have interacted with the soil minerals long enough to adsorb cesium or strontium. Colloids may have been more effective in mobilizing contaminants in the systems examined in the previous studies because of longer residence times for the colloids compared to the residence time of the colloids in our studies. In this study, the short time between the addition of the cesium and strontium to the soil pedon and the applications of rainfall to mobilize the cesium and strontium might have limited the association of the metals with the mobilized colloids. The preferential migration of rainwater in the macropores limited the contribution of colloid-facilitated transport of cesium and strontium in the soil pedon.

Mobilization of cesium and strontium by organic matter: The addition of organic matter to the rainfall solution had very little effect on the mobility of cesium and strontium in the soil pedon. Increasing the organic matter concentration from 2.0 to 7.9 mg C L^{-1} did not mobilize more cesium and strontium. The soil pedon results were supported by the laboratory batch release experiments in which less than 2% of the total cesium and strontium were desorbed from the soil in the presence of dissolved organic matter concentrations up to 7.9 mg L^{-1} (Figure 6.5). Cesium is associated with natural organic matter by a weak outer-sphere complexation that may not be sufficiently strong to remove the cesium associated with soil minerals (Xu *et al.*, 2006). Limited release of strontium and no release of cesium were observed when organic matter was injected through a contaminated quartz column (Solovitch-Vella and Garnier, 2006). Bunzl *et al.* (1998) examined the association of cesium and strontium with different fractions of dissolved organic matter isolated from soil as determined by gel filtration and found that cesium was associated with organic matter of smaller size (molecular weight between 560 and 1300 Da) and strontium was associated with inorganic compounds. In our study, frequent sampling within 6 h of the rainfall application limited the sampling volume and the possible use of ultrafiltration to identify the size fraction of dissolved organic matter with which cesium and strontium were associated. The total fraction of cesium and strontium released during the injection of organic matter was less than 1% of injected concentration. The result indicates little role of organic matter in mobilizing cesium and strontium in the field site.

Mobilization of cesium and strontium by cation exchange: Cation exchange was the dominant mechanism in releasing cesium and strontium from the soil pedon. Both cesium and strontium were mobilized in greater amounts by the application of rainfall of high ionic strength (5 mM). The batch release experiments produced the same results – that an increase in ionic strength (to 5 mM) most effectively desorbed cesium and strontium from the soil. The fine fraction of Melton Branch soil is composed of predominantly illite with entrapped ferric iron and manganese(IV) oxides (Chapter 3). The oxide minerals and edge of clays adsorb cesium and strontium by cation exchange or specific complexation (Jackson and Inch, 2002). The importance of the cation exchange mechanism on mobilizing cesium and strontium has been identified in laboratory experiments using sediments from the Hanford site (Flury *et al.*, 2002; Rod *et al.*, 2010; Chang *et al.*, 2011).

A difference between the release of cesium and strontium was also an indication of cation exchange mechanism. Cesium forms a stronger complex owing to its smaller hydrated size than strontium. The weakly hydrated cesium ion binds strongly by forming an inner-sphere complex and the more strongly hydrated strontium binds weakly by forming an outer-sphere complex with clay minerals (Turner *et al.*, 2006). This explains the deeper migration of strontium compared to cesium at the field site. A higher mobility of strontium in the zero-tension samplers than in the coarse samplers suggests an increase in the residence time in the matrix may lead to slower release of strontium in the coarse samplers. The high flow rate through preferential flow paths made the role of cation exchange much more important than colloid-facilitated and organic matter-facilitated transport in the mobilization of cesium and strontium.

The results of the current study demonstrated the mobilization of organic carbon and colloids in response to transient conditions. We have demonstrated that organic carbon could potentially migrate through preferential flow paths without interacting with the soil matrix under transient conditions. The result has implications on the transport of organic contaminants as well as facilitated transport of other contaminants by natural organic carbon. Both cesium and strontium were not affected by organic carbon because of the limited interaction of organic carbon with the soil matrix that usually acts as a sink for metals. Transports of cesium and strontium by colloids cannot be entirely ruled out since major fractions of colloids are smaller than 100 nm. Further study is required to address the transport of contaminants by nano-sized colloids. Cesium and strontium were mobilized due to cation exchange in the field study.

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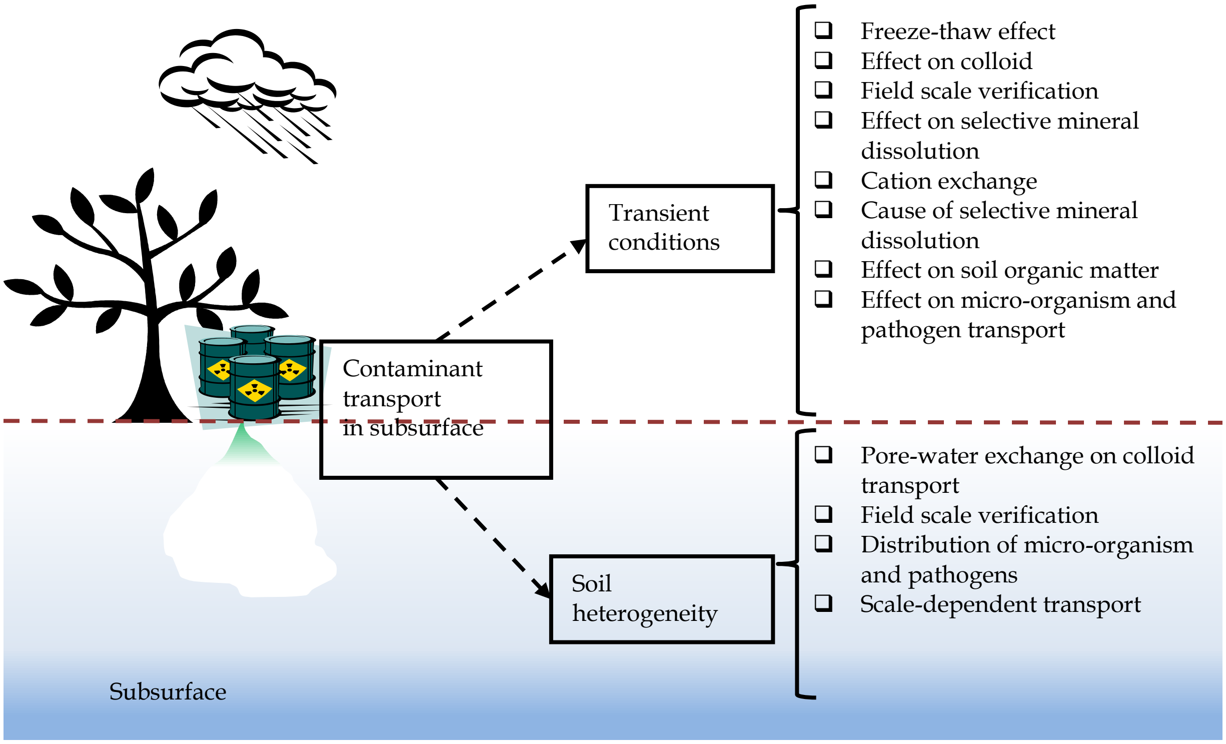
CHAPTER 7

CONTRIBUTIONS OF THE CURRENT WORK AND A ROADMAP TO FUTURE STUDY OF THE TRANSPORT OF CONTAMINANTS IN THE VADOSE ZONE



An illustration of the status of our understanding of subsurface contaminant transport

Summary and conclusions

The objective of this work was to investigate the mobilization of colloids, organic matter, cesium, and strontium through a fractured soil under transient flow conditions. The objective was achieved by investigating three components of the mobilization process (Figure 7.1): (1) rainfall characteristics that included frequency and duration of pauses between rainfalls, (2) geochemical properties (in particular, ionic strength) of rainwater, and (3) soil physical heterogeneity (macropore and micropore flow). The work addressed the following specific questions:

a) What is the mechanism of colloid mobilization from unsaturated heterogeneous soil under transient flow conditions?

b) What is the effect of freeze-thaw cycles on the transport of colloids and metal contaminants?

c) What is the effect of the exchange of solute in pore water between macropores and the matrix on the mobilization of metal contaminants from physically heterogeneous soils?

d) How do geochemical conditions coupled with soil physical heterogeneity affect the mobility of colloids and metal cations?

e) What processes are most important for mobilizing metal cations at the field scale under transient flow conditions?

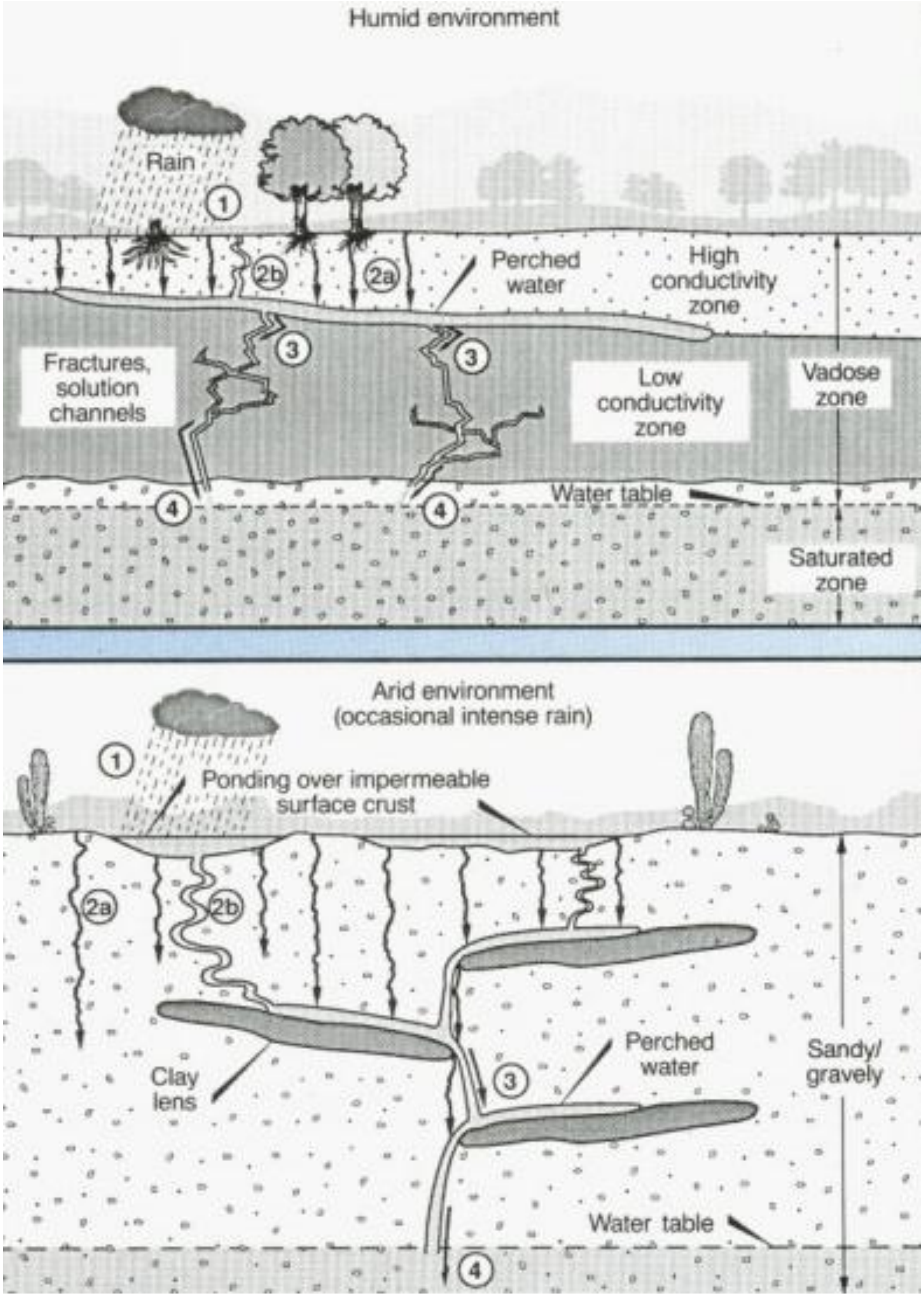


Figure 7.1. Transport of colloids and metal cations through the vadose zone (McCarthy and Zachara, 1989). The pathways of water is depicted according to the following regions: (1) rainwater on the surface, (2) advection through fractures and matrix in subsurface, (3) flow between perched water and ground water, and (4) groundwater.

Role of transient flow conditions: We investigated the effect of rainfall frequency and pauses between rainfalls on the mobilization of colloids from an intact soil core. We suggested and verified a mechanism to explain the mobilization of colloids under transient flow conditions. Greater amounts of colloids were mobilized in frequent rainfalls of short duration than in one rainfall of longer duration. Increases in the duration of pauses between rainfall leads to drying of larger pores and to increasing in the capillary stress, which breaks the walls of dried pores and generates colloids from the broken walls. The colloids are mobilized into the nearest water-filled pores before being transported by the infiltrating rainwater. A pause of 2.5 d optimally mobilized colloids from the soil. Increasing the duration of pauses beyond the optimal duration promoted the generation of more colloids as well as inhibited the mobilization of the colloids due to a lack of water-filled pores. We attributed the effect of pauses between rainfalls on colloid mobilization to changes in the moisture content of the soil.

Implications: The current study provides the conceptual framework to predict the mobilization of colloids after a pause in rainfall. The results of the current study highlight the importance of residual moisture content after a pause in rainfalls on the mobilization of colloids from a physically heterogeneous soil. The residual moisture content in a soil depends on the grain size distribution of the soil. For example, soils with higher fraction of clay can hold water for long time compared to sandy soils. Therefore, critical moisture content may be attained faster in sandy soil than clayey soil. Based on the soil property, the pause duration to attain critical moisture content can be estimated.

Effect of freeze-thaw cycles on colloid mobilization: We examined the effect of freeze-thaw cycles on the mobilization of colloids and colloid-facilitated transport of cesium and strontium through intact cores. Significantly greater amounts of colloids and colloid-associated cesium and strontium were mobilized from the cores subjected to freeze-thaw cycles than from the cores kept at room temperature. The mobilized colloids had higher fractions of clay minerals and iron oxides, and a lower fraction of quartz relative to the mineral distribution in the soil from which the colloids were mobilized. The freeze-thaw cycles created new flow paths through which colloids, cesium, and strontium were transported. These findings suggest greater colloid and colloid-associated contaminant mobilization in the vadose zone during temperature fluctuations near the freezing point of water.

Implications: The current study is the first to demonstrate that the enhanced mobilization of colloids and metal contaminants from the soil due to freeze-thaw of soil. In the advent of climate changes, more regions in North America can face rapid fluctuations of temperature around freezing. Changes in the dynamics of freeze-thaw cycles in soil as a result of climate change will have widespread implications on the dynamics of contaminants that includes soil organic carbon, metals, pathogens and colloids in soil. Our findings are applicable to better understanding of the risk of contaminant transport in climates subject to freezing and thawing conditions in the soils.

Exchange of solute between pore waters in macropores and matrix: We conducted rainfall experiments in the laboratory to evaluate the effect of pore water exchange in mobilizing cesium, strontium, and colloids from intact soil cores. The ionic strength of the rainfall was varied between 0.01 to 10 mM to promote the exchange of pore water between the macropores and the matrix. A 19-port sampling grid was used to provide spatial resolution of the infiltrating water flow paths. Using this apparatus, water passing through macropores and the matrix were identified and differentiated. Bromide breakthrough time through each port was used as an indicator to quantify the rate of exchange of pore water between macropores and the matrix. Mobilization of metals and colloids was hysteretic in response to changes in the ionic strength of infiltrating water – the amount of metals and colloids mobilized at a given ionic strength was not matched when the experiment was repeated following an exposure to rainwater of higher or lower ionic strengths. The extent of hysteresis was positively correlated with the breakthrough time of bromide. We attributed the hysteretic behavior to an exchange of pore water between macropores and the soil matrix. These results provided evidence that metals might be mobilized with colloids from the soil matrix due to pore water exchange between macropores and the matrix.

Implications: The current study demonstrates the importance of residual ionic strength of pore water on the mobilization of colloids and metal contaminants from a physically heterogeneous soil. The residual ionic strength of pore water depends on the nature of the preceding rainfall as well as the physical heterogeneity of soil. Therefore, it is important to incorporate the history of rainfall events as well as soil property to predict the mobilization of colloids and contaminants in any soil.

Importance of physical heterogeneity: We examined the importance of colloid-facilitated transport in comparison with the cation exchange process for remobilizing cesium and strontium under transient geochemical conditions. The ionic strength of rainwater was varied from 0.01 mM to 10 mM to quantify metal cations mobilized by colloids and cation exchange. The colloidal and dissolved fraction of cesium and strontium were measured from samples collected from macropore and matrix. Rainwater above 1 mM ionic strength effectively mobilized cesium and strontium by cation exchange. Below 1 mM, the metal cations were mobilized in the colloidal form by colloid-facilitated transport. The physical heterogeneity of the soil influenced the mobilization of metal cations by both processes. More metal cations were mobilized in macropores than in the soil matrix by cation exchange. The rapid exchange of infiltrating rainwater with the pore water in the macropores promoted the cation exchange process in the macropores. Limited interaction of colloids with soil minerals caused colloids to move without remobilizing metal cations from the macropores. In contrast to colloids in the macropores, colloids in the matrix contained greater amounts of cesium and strontium. These results indicated that the physical heterogeneity of soils plays an important role in mobilization of cesium and strontium.

Implications: The current study highlights the importance of physical heterogeneity and ionic strength of rainwater on the mobilization of metal cations by cation exchange and colloid-facilitated mobilization. Mobilization by both these processes has not been studied simultaneously. The current study demonstrated that both processes could simultaneously occur during environmentally relevant conditions. We also reported that macropores and matrix could influence the mobilization of metal cations by cation exchange or colloid-facilitated mobilization. Therefore, it is important to incorporate the soil physical heterogeneity to predict the mobilization of metal cations under natural conditions.

Coupled processes for mobilization of metal cations: We conducted field experiments to evaluate the relative importance of cation exchange, organic matter-facilitated transport, and colloid-facilitated transport of cesium and strontium under heavy rainfall. Under these heavy rainfall conditions, infiltrating water passed predominantly through the macropores. Infiltrating water of low ionic strength mobilized colloids, but did not mobilize much cesium and strontium. Rainwater at 5 mM mobilized significant amounts of cesium and strontium by cation exchange. Increasing the organic matter concentration from 0 to 8.0 mg C L^{-1} did not mobilize cesium or strontium from the soil. Under heavy rainfall, cesium and strontium were mobilized by ion exchange through the macropores. Under this condition, organic matter- or colloid-facilitated transport of cesium and strontium were less important.

Implications: The result of current study highlighted the importance of cation exchange on the mobilization of metal cations. We also reported the transport of organic carbon in soil as a function of ionic strength of rainwater as well as soil physical heterogeneity. These results were important to improve our understanding of the transport processes in field conditions.

Roadmap to future work

Transport of organic matter: The importance of colloids or organic matter in the facilitated transport of cations has been evaluated separately in previous studies. Colloids and organic matter coexist in soil pore waters and are capable of transporting cations in soil. The transport of colloids and organic matter may differ because colloids and organic matter may follow different paths owing to a difference in their size ranges. Only two studies have demonstrated that organic matter and colloids facilitate the transport of cations to different extents under given laboratory conditions (Bradford *et al.*, 2004; Singh *et al.*, 2009). The difference has not been evaluated under natural conditions that account for transient flow and physical heterogeneity of soil.

Under natural conditions, the surfaces of most inorganic colloids are coated by organic matter, which changes the interaction of cations with the surfaces of mobile colloids (Mylon *et al.*, 2004; Laegdsmand *et al.*, 2005; Harbour *et al.*, 2007; Mibus *et al.*, 2007). Absorption of organic matter increases the stability of colloids (Nelson *et al.*, 1985; Harbour *et al.*, 2007; Janot *et al.*, 2011). Fewer studies have been conducted to systematically investigate the effect of organic matter on colloid-facilitated transport in natural conditions. In contrast to colloid-facilitated transport, fewer studies have examined organic matter-facilitated transport of metals in the subsurface, though evidence of organic matter-facilitated transport in saturated media has been observed (McCarthy, 1998; Mibus *et al.*, 2007). We examined the mechanism of colloid mobilization during transient conditions. The transport of organic matter under transient flow conditions is not clear and should be investigated further.

Freeze-thaw cycles: Freeze-thaw cycles are known to increase the erosion of soil (Van Klaveren and McCool, 2010). We demonstrated that freeze-thaw cycles promoted colloid-facilitated transport of metal contaminants. The results of our study indicate that contaminants are more mobile than previously identified without taking freeze-thaw into account. We also observed a preferential release of clay and iron oxide from soil. The cause of release is not known. Preliminary results of our study also suggested an increase in the concentration of organic matter, nitrate, and phosphate during the thawing of frozen soil. A recent review paper emphasized the key role of freeze-thaw cycles in the persistence of soil organic matter in soil (Schmidt *et al.*, 2011). Freeze-thaw has the potential to mobilize larger fractions of soil organic matter by mineralization (Schmitt *et al.*, 2008). The mineralization of soil organic carbon increases nitrogen availability in soil and amplifies microbial activity. All these results have implications on nutrient cycles, climate change, and chemical concentrations in the atmosphere (van Groenigen *et al.*, 2011). For example, a recent study indicates soil nitrite can release nitrous acid to the atmosphere, which then produces hydroxyl radicals during photolysis (Su *et al.*, 2011). Previous studies indicated that our knowledge on the effect of freeze-thaw cycles on soil environment is limited. Further study is needed to investigate the role of freeze-thaw cycles on microbial life, mineralization of soil organic carbon, dissolution of minerals (Svensson and Hansen, 2010), and contaminant transport in soil.

Role of transient flow conditions on pathogen transport: Microbial transport in the subsurface is a concern and evidence for colloid-facilitated transport of pathogens has been shown in previous work (Ginn *et al.*, 2002; McGechan and Lewis, 2002; Sen, 2011). Transient flow conditions promote mobilization of colloids that may carry the pathogens to uncontaminated regions. To the best of our knowledge, the effect of transient conditions on pathogen transport has not been investigated. Pathogens are known to adsorb strongly on clay and iron oxide by electrostatic interactions (Jiang *et al.*, 2007). Clay and iron oxide were preferentially leached out during transient flow conditions (Chapter 3). The removal of clay and iron oxides may limit the retention capacity of soils as well as mobilize pathogens attached to clay and iron oxides. Increasing the iron oxide coating on sand surfaces resulted in higher removal of bacteriophage PRD1 and *Cryptosporidium parvum* from solution (Abudalo *et al.*, 2005). Exchange of pore water between the macropores and the soil matrix mobilized colloids from the interface between macropores and the matrix (Chapter 4). These interfaces are rich in pathogens (van Veen *et al.*, 1997). Disruption of the interface by transient conditions may have severe implications for pathogen contamination in unsaturated soil. These results indicate a need to examine the effect of transient flow conditions on pathogen mobilization in unsaturated soil.

Rainwater picks up nutrients like PO_4^{3-} and NO_3^- from the soil surface during runoff. Nutrients may adsorb on to pathogens and soil surfaces to increase the negative charge on both surfaces. An increase in negative surface charge was shown to increase pathogen mobility in sand (Wang *et al.*, 2011). These nutrients may also promote mobilization of pathogens in response to a nutrient gradient by a process known as chemotaxis (Ginn *et al.*, 2002). Chemotaxis has been shown to enhance the mobility of microorganisms in porous media (Roush *et al.*, 2006). These results suggest that pathogenic microbe transport may be controlled by the nutrient gradient in heterogeneous soil. A difference in flow rate between the macropores and the soil matrix caused the nutrient gradient in heterogeneous soil. Therefore, nutrients in pore water could mobilize pathogens by chemotaxis or by release of pathogen due to the adsorption of nutrients. Distinguishing the impacts of surface modification and chemotaxis on pathogen mobility is essential to assess the contamination by infiltration of nutrient-rich infiltrating water. A difference in the mobilization of pathogens in rainwaters with and without nutrients (e.g., PO_4^{3-}) at the same ionic strength could be used as an indicator to separate mobilization by chemotaxis from mobilization by surface modification. Another method is to monitor the concentration of phosphate-binding proteins in the matrix and macropores (Medveczky and Rosenberg, 1970). This research will have implications on the viability of reusing wastewater.

The accomplishments of the current work and scope for future work are summarized in Figure 7.2.

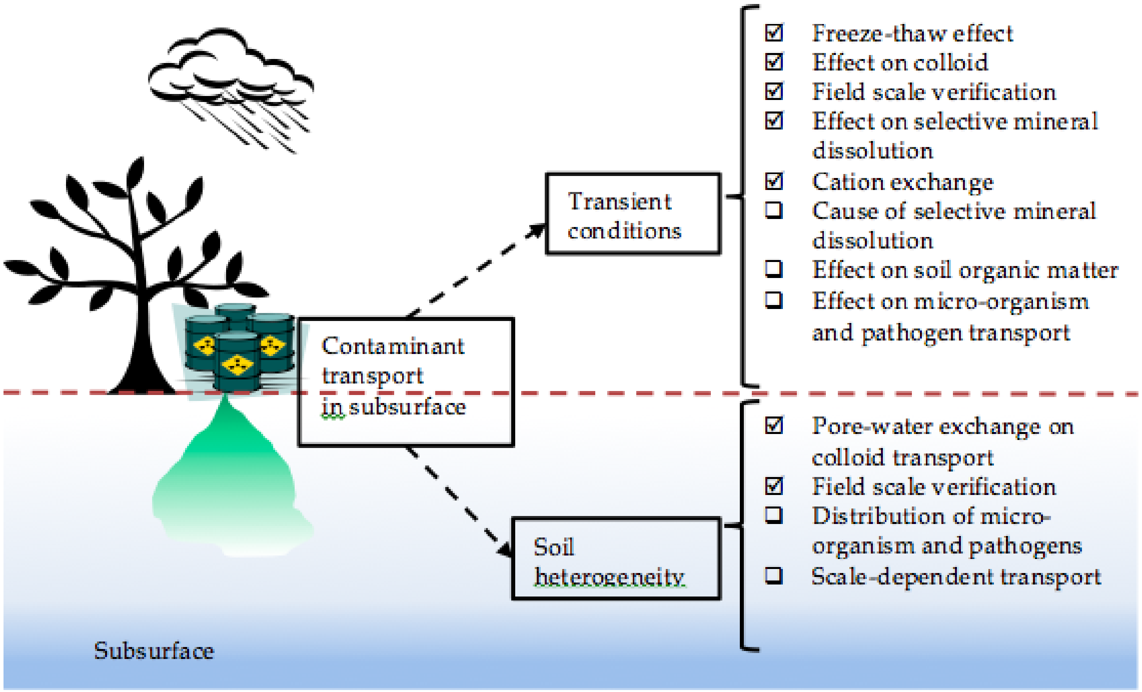


Figure 7.2. An illustration of the status of our understanding of subsurface contaminant transport including a list of completed and future work. The checked squares indicate current understanding and the hollow squares indicate future work.

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CHAPTER 8

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CHAPTER 9

APPENDIX

A. Injection of dye in soil core to identify preferential flow paths

Dye injection in intact soil core has been used to trace the preferential flow paths in unsaturated soil (Allaire *et al.*, 2009; Hardie *et al.*, 2011). We applied a dye on top of a soil core and assumed that regions around preferential flow path would be colored by dye. The rhodamine B (90%, Sigma) solution (1 mM) was prepared in 8 L of high-purity water. The solution was applied on the top of the soil core at 2.5 cm h^{-1}. The soil core was dried at room temperature for 48 h. A hand saw was used to cut the soil core horizontally at multiple depths (2.5, 10.1, 15.2, 20.3, and 25.4 cm) from surface of soil core. The photographs of top and bottom surface of soil cores along with top surface of each cross-section were taken using a digital camera. The preferential flow was observed through the cracks in the soil (Figure 9.1). The region colored by the dye decreased with an increase in the depth. Preferential flow paths were limited to less than 50% of the total surface area at 15.2 cm (half of the column height). Therefore, we cut the column horizontally into half. The upper half of the column was used for all laboratory experiments due to higher hydraulic conductivity of upper half.

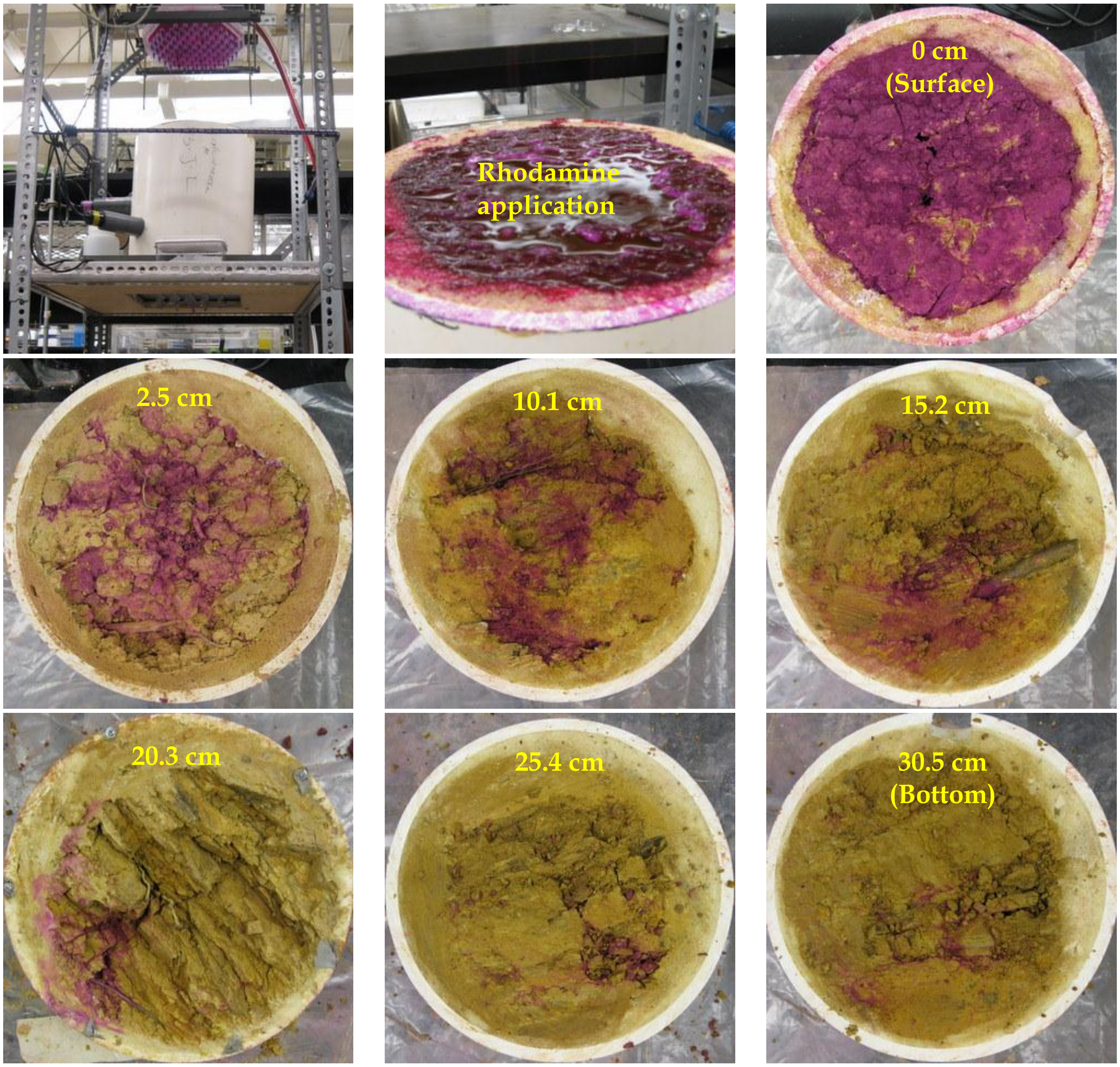

Figure 9.1. Rhodamine dye applications on the soil core. The horizontal cross-sections of soil core at multiple depths from surface of soil core are shown.

B. Correlation between turbidity and colloid concentration

Water samples were measured for turbidity which was used to estimate the colloid concentration (mg L^{-1}). The total suspended sediment concentration was measured by drying colloid suspensions (20 mL) of increasing turbidity in pre-weighed aluminum cups in an oven at 104 °C and weighing the mass of the dried colloids (Table 9.1). The conductivity (C, μS cm^{-1}) of samples were measured and total dissolved solids (TDS, mg L^{-1}) were estimated from conductivity of samples using Equation B1 (McNeil and Cox, 2000).

$$\log(TDS) = 0.154(\log C)^3 - 1.22(\log C)^2 + 4.12(\log C) - 2.76 \qquad \text{(B1)}$$

The colloid concentration (mg L^{-1}) was calculated by subtracting the dissolved solid concentration from the total solid concentration. The colloid concentration was correlated to turbidity of samples using a calibration curve (Figure 9.2).

Table 9.1. Turbidity, conductivity, and total solids measured in water samples. The concentration of total dissolved solid and colloid concentration were calculated.

Turbidity (NTU)	Total solid (mg L^{-1})	Conductivity (μS cm^{-1})	Total dissolved solids (mg L^{-1})	Colloids (mg L^{-1})
510.0	998	24	1.0	997.0
126.6	282	20	0.9	281.1
71.1	160	19	0.9	159.1
27.2	71	15	0.7	70.3
3.2	28	14	0.6	27.6
1.6	16	14	0.6	15.4

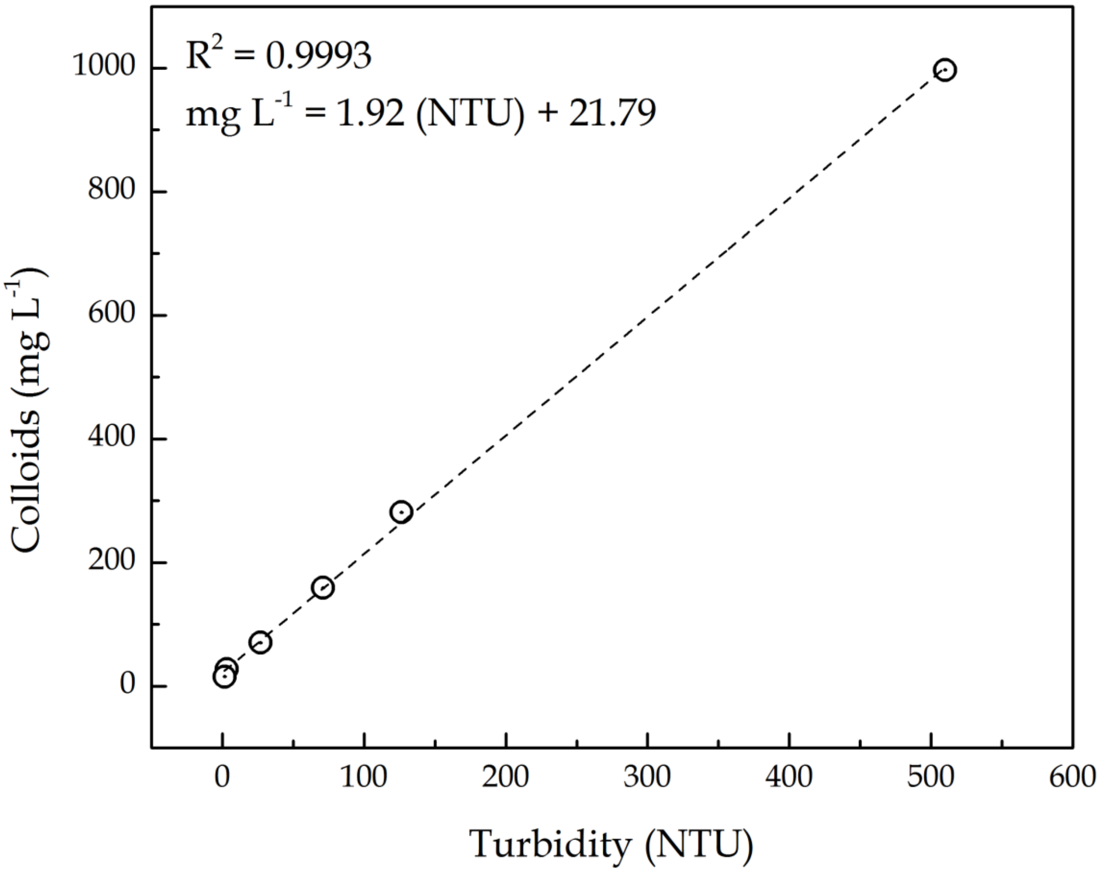

Figure 9.2. Correlation between colloids concentration (mg L^{-1}) with turbidity (NTU) of water samples.

C. Calibration of soil moisture probe

The soil moisture probe (ThetaProbe ML2x, Delta-T Devices) was calibrated in order to convert voltage reading (V) to volumetric moisture content (θ). The refractive index of water was related to volumetric moisture content using Equation C1 (see manual for soil moisture probe[1]).

$$\sqrt{\varepsilon} = a_0 + a_1\theta \qquad \text{(C1)}$$

The refractive index was related to voltage across sensors in soil moisture probe using Equation C2.

$$\sqrt{\varepsilon} = 1.07 + 6.4V - 6.4V^2 + 4.7V^3 \qquad R^2 = 0.998 \qquad \text{(C2)}$$

Equating C1 and C2, and solving for the moisture content, we obtained:

$$\theta = \frac{\left[1.07 + 6.4V - 6.4V^2 + 4.7V^3\right] - a_0}{a_1} \qquad \text{(C3)}$$

The coefficients, a_0 and a_1 were determined by measuring the voltage reading for a completely oven dry soil and completely saturated soil.

For completely dry soil, θ = 0 and $V = V_0$;

$$a_0 = \left[1.07 + 6.4V_0 - 6.4V_0^2 + 4.7V_0^3\right]$$

For completely wet soil, $\theta = \theta_{\text{Saturation}}$ and $V = V_{sat}$;

$$a_1 = \frac{\left[1.07 + 6.4V_{Sat} - 6.4V_{Sat}^2 + 4.7V_{Sat}^3\right] - a_0}{\theta_{sat}}$$

Approximately 300 g of soil was dried in a 250 mL beaker at 104° C for 24 h. The moisture probe was inserted in the dried soil to measure V_0 and to estimate a_0. The soil was

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[1] ftp://ftp.dynamax.com/Manuals/ML2x_Manual.pdf (accessed on November 29, 2011)

saturated with a known quantity of water and equilibrated for 1 h. The moisture probe was inserted into saturated soil to measure V_{sat} and to estimate a_1.

The values of the estimated coefficients were: a_0 = 1.533 and a_1 = 3.932.

References

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