

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/259497797>

# Colloid-Facilitated Mobilization of Metals by Freeze-Thaw Cycles

ARTICLE in ENVIRONMENTAL SCIENCE & TECHNOLOGY · DECEMBER 2013

Impact Factor: 5.33 · DOI: 10.1021/es403698u · Source: PubMed

---

CITATIONS

8

---

READS

103

3 AUTHORS, INCLUDING:



**Sanjay Mohanty**

University of Pennsylvania

11 PUBLICATIONS 65 CITATIONS

SEE PROFILE



**Joseph N Ryan**

University of Colorado Boulder

108 PUBLICATIONS 4,760 CITATIONS

SEE PROFILE

# Colloid-Facilitated Mobilization of Metals by Freeze–Thaw Cycles

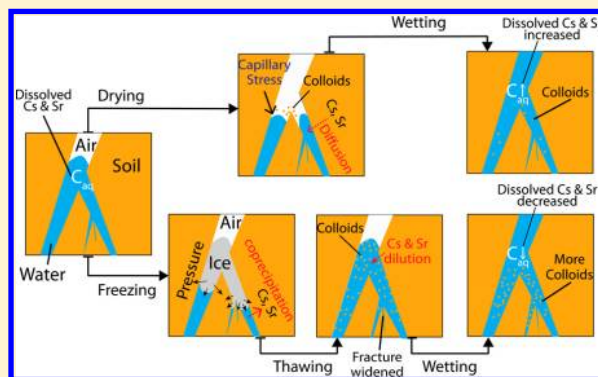
Sanjay K. Mohanty,<sup>\*,†,‡</sup> James E. Saiers,<sup>§</sup> and Joseph N. Ryan<sup>†</sup>

<sup>†</sup>Department of Civil, Environmental, and Architectural Engineering, University of Colorado Boulder, Boulder, Colorado 80309-0428, United States

<sup>§</sup>Yale School of Forestry and Environmental Studies, Yale University, New Haven, Connecticut 06511, United States

## S Supporting Information

**ABSTRACT:** The potential of freeze–thaw cycles to release colloids and colloid-associated contaminants into water is unknown. We examined the effect of freeze–thaw cycles on the mobilization of cesium and strontium in association with colloids in intact cores of a fractured soil, where preferential flow paths are prevalent. Two intact cores were contaminated with cesium and strontium. To mobilize colloids and metal cations sequestered in the soil cores, each core was subjected to 10 intermittent wetting events separated by 66 h pauses. During the first five pauses, the cores were dried at room temperature, and during last five pauses, the cores were subjected to 42 h of freezing followed by 24 h of thawing. In comparison to drying, freeze–thaw cycles created additional preferential flow paths through which colloids, cesium, and strontium were mobilized. The wetting events following freeze–thaw intervals mobilized about twice as many colloids as wetting events following drying at room temperature. Successive wetting events following 66 h of drying mobilized similar amounts of colloids; in contrast, successive wetting events after 66 h of freeze–thaw intervals mobilized greater amounts of colloids than the previous one. Drying and freeze–thaw treatments, respectively, increased and decreased the dissolved cesium and strontium, but both treatments increased the colloidal cesium and strontium. Overall, the freeze–thaw cycles increased the mobilization of metal contaminants primarily in association with colloids through preferential flow paths. These findings suggest that the mobilization of colloid and colloid-associated contaminants could increase when temperature variations occur around the freezing point of water. Thus, climate extremes have the potential to mobilize contaminants that have been sequestered in the vadose zone for decades.



## INTRODUCTION

Extreme weather patterns, including a warmer climate, increases in the frequency of heavy rainfall, and increases in the frequency of the freeze–thaw cycle, are altering hydrology above and below ground.<sup>1,2</sup> Freeze–thaw cycles have been shown to change the physical,<sup>3,4</sup> chemical,<sup>5,6</sup> and biological<sup>7</sup> properties of soils. Freezing and thawing break up soil aggregates,<sup>8,9</sup> and soil disaggregation is often linked to generation of colloids in soils.<sup>10</sup> Colloids can enhance the transport of certain contaminants,<sup>11</sup> including many of the radioactive elements found at U.S. Department of Energy (DOE) sites.<sup>12</sup> The effect of freeze–thaw cycles on the fate and transport of these contaminants is unknown.

Colloids and contaminants are mobilized by the water that infiltrates during rainfall and snowmelt. Typically, rainfall and snowmelt result in transient flow through soils. Transient flow is marked by wetting and drying cycles that result in high and low moisture contents. Variation of the moisture content promotes colloid mobilization.<sup>13</sup> Thus, transient infiltration mobilizes more colloids<sup>14–16</sup> and contaminants<sup>17</sup> than steady infiltration. The release of colloids during transient infiltration has been related to the antecedent moisture content of the soil, which depends upon the duration of the drying cycle.<sup>15</sup>

Prolonged drying decreases the soil moisture content and lowers the capillary pressure (toward more negative values), and this reduction in capillary pressure can contribute to the generation of colloids by collapsing soil pore walls.<sup>15,18</sup>

Similar to drying, freezing can alter the structure of soils. During freezing, water expands to form ice, and the expansion creates pressure on pore walls that breaks up soil aggregates.<sup>9</sup> Freeze–thaw cycles can increase the hydraulic conductivity of soil<sup>19</sup> and the transport of colloids, including bacteria, through soils.<sup>20</sup> Freeze–thaw cycles may generate soil colloids by (1) soil disaggregation and (2) differential freezing. Differential freezing is the freezing of water in macropores before water in the soil matrix, which occurs because of the higher (less negative) capillary pressure in the macropores compared to that of the soil matrix.<sup>21</sup> When the water in the macropores freezes, water moves from the soil matrix to the macropores and the capillary pressure in the soil matrix decreases or becomes more negative. The decrease in capillary pressure in the soil matrix

Received: August 19, 2013

Revised: December 27, 2013

Accepted: December 30, 2013

Published: December 30, 2013



may generate colloids, as it does when soil drying results in capillary pressure reduction.<sup>15</sup> These colloids can carry contaminants. Thus, freeze–thaw cycles could potentially mobilize colloids and colloid-associated contaminants.

This study aimed to evaluate the effect of freeze–thaw cycles on the mobilization of colloids and colloid-associated metal cations from soil. We hypothesized that freezing would generate more colloids and enhance the transport of colloids and colloid-associated contaminants through soil because the formation of ice during freezing can disrupt soil aggregates and mobilize colloid-containing contaminants. To test the hypotheses, we collected intact soil cores of a fractured soil and contaminated the cores with cesium and strontium. The contaminated cores were subjected to five dry–wet cycles at room temperature and five dry–wet cycles with intervening freeze–thaw cycles. The mobilization of colloids, dissolved metal cations, and colloid-associated metal cations was monitored during rainfall following each cycle. The results of the two treatments were compared to assess the effect of freezing and thawing on the fate and transport of colloids and contaminants.

## ■ EXPERIMENTAL SECTION

**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, TN.<sup>22</sup> The soil consists of fractured shale saprolite that has been weathered by 1300 mm year<sup>−1</sup> of rainfall. Infiltrating water predominantly passes through the bedding planes and fractures, which are coated with iron(III) and manganese oxyhydroxides and translocated clay minerals.<sup>23</sup> Intact soil cores were collected using a hand-sculpting method described elsewhere.<sup>23</sup> 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. The gap between the PVC pipe and the soil cylinder (approximately 1.2 cm) was filled with polyurethane-expandable foam (U.S. Composites, Inc., FL).

**Experimental Setup.** Colloid mobilization experiments were conducted using a setup consisting of a rainfall distributor, the soil core, and a sampling grid (see Figure S1 of the Supporting Information). Rainfall was simulated by dripping water from the rainfall distributor through 85 stainless-steel needles (25 gauge). The intact core was placed under the rainfall distributor and on top of a sampling grid with 19 ports to monitor the heterogeneity of infiltrating flow during a rainfall. The number of flowing ports was used as an indicator of the existence of preferential flow paths. Each port captured water flowing through an area of 11.4 cm<sup>2</sup>; the total collected area was 340 cm<sup>2</sup>. The water flowed to each port from the bottom surface of the soil core under zero tension and drained into a funnel (high-density polyethylene) connected to a 300 mL bottle. Water flowing near the perimeter of the soil cores, which may contact with foam or PVC pipe, was collected in a channel of 1.3 cm width around the sample ports to be discarded.

In preliminary rainfall experiments with soil cores of full height (30.5 cm), we observed that the bedding plane fractures carried most of the infiltrating water to the walls of the core because the fractures intersected the core walls.<sup>24</sup> To avoid this problem, the soil cores were cut to a height of 15 cm.

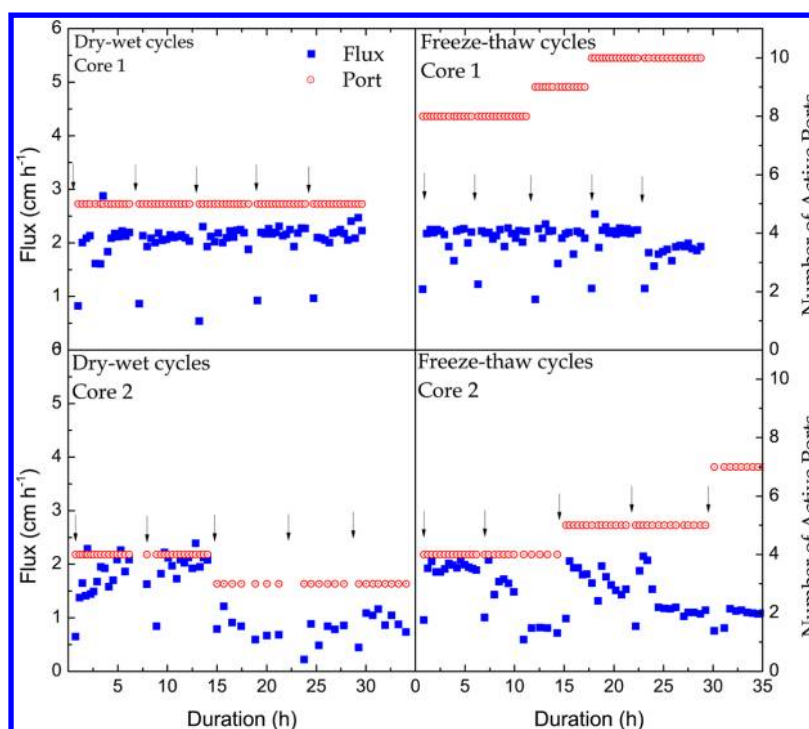
A soil moisture probe (Delta-T Devices, Theta Probe MLX2) was inserted through the side of the core at 7.5 cm

below the soil surface. The probe 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.

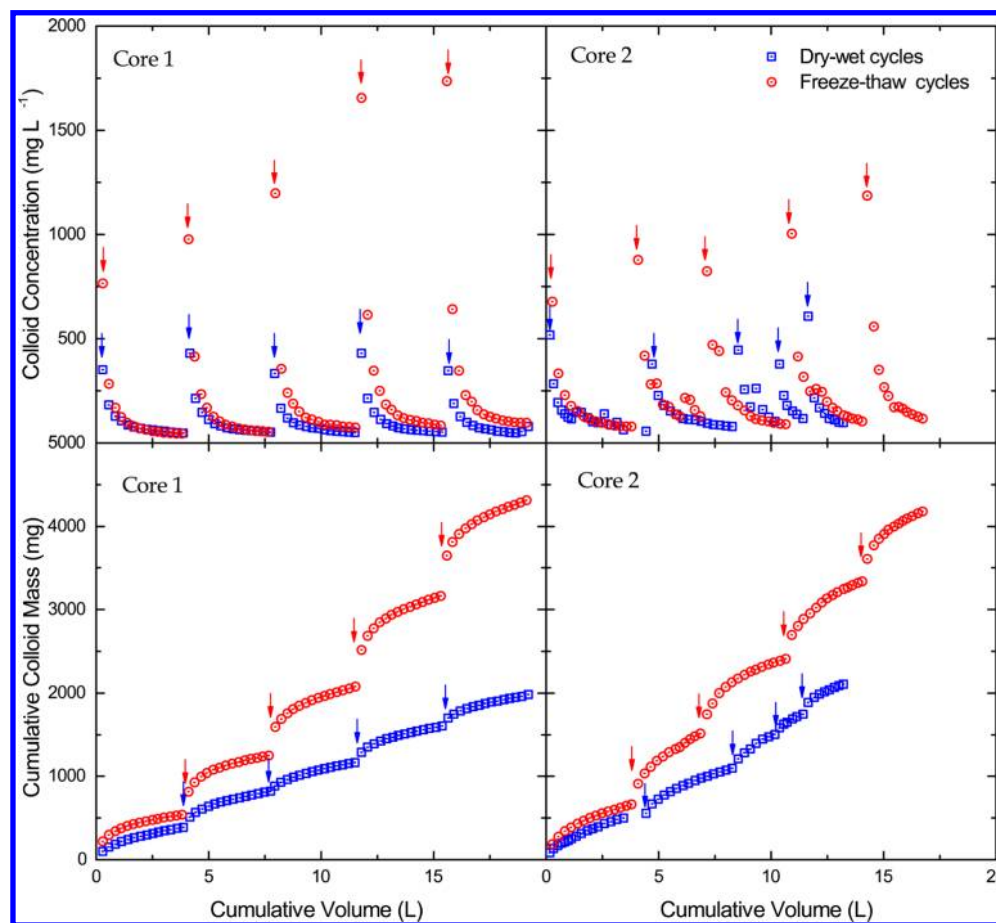
**Experimental Procedure.** To quantify the effect of freeze–thaw cycles on the mobilization of cesium and strontium with colloids, we subjected the soil cores to three treatments: (1) application of cesium and strontium on the soil core, (2) mobilization of cesium and strontium by five cycles of rainfall following drying intervals at room temperature (collectively referred as dry–wet cycles), and (3) mobilization of cesium and strontium by five cycles of rainfall following freezing and thawing intervals (collectively referred as freeze–thaw cycles). The sequences of treatment steps are provided in Figure S2 of the Supporting Information.

To contaminate the soil cores, a rainfall solution containing 1 mM CsBr (99.99%, Argo Chemical) and 1 mM SrBr<sub>2</sub> (99.9%, MP Biochemicals) in high-purity water (18.1 MΩ cm<sup>−1</sup>) was applied at a rate of 2.5 cm h<sup>−1</sup> for 51 h. The concentrations used in this study represent typical concentrations of cesium and strontium in a waste plume generated by leaking storage tanks at the Hanford Reservation.<sup>25</sup> The contaminant solution was followed by rainfall applications of 4 mM NaNO<sub>3</sub> for 17 h to flush the contaminants from pore water with solution of similar ionic strength and 0.01 mM NaNO<sub>3</sub> for 24 h to simulate the application of rainwater. During the application of the 0.01 mM NaNO<sub>3</sub> solution, the total concentrations of cesium and strontium decreased below 0.1% of the injected concentrations, which indicates that the contaminated pore water had been mostly displaced by the uncontaminated rainwater. Following contamination of the soil cores, the release of the metals accumulated in the soil matrix was monitored in five dry–wet cycles. During each cycle, the wet soil core was drained by gravity (for approximately 30 min) and left to dry in the laboratory at 22 ± 2 °C for 66 h prior to application of rainwater (0.01 mM NaNO<sub>3</sub>) for 6–7 h at 2.5 cm h<sup>−1</sup>. To compare the effect of freezing to drying on the release of metals and colloids, the same soil core was subjected to five freeze–thaw cycles after completion of dry–wet cycles at room temperature. A freeze–thaw cycle differs from a dry–wet cycle by additional freezing and thawing steps, which was carried out between two wetting events. A freeze–thaw interval was marked by freezing the soil core at −15 °C for 42 h after gravitational drainage followed by thawing in the laboratory at 22 ± 2 °C for 24 h. During freezing, the soil core was placed on a foam sheet and kept inside a freezer. Although we have not measured the direction of freezing, thermal insulation of the soil core by the PVC pipe and expandable foam along the sides and by the foam sheet at the core base may cause the freezing front to propagate from the surface of the soil core, similar to how soil freezes in nature. After each freeze–thaw interval, the release of metals and colloids was monitored by application of rainwater similar to that of dry–wet cycles. Samples collected during application of rainwater were analyzed, whereas no samples were analyzed after gravitational drainage as flow ceased. The experiments were repeated using a duplicate core.

**Analysis of Water Samples.** The water samples were analyzed for pH, turbidity, cesium, and strontium. Effluent pH was measured using a pH/ion-selective electrode meter (Orion 720A) and a combination electrode (Orion 8102BNU). Turbidity was measured using a turbidity meter (Hach 2100N). The measured turbidities were converted to colloid concentrations (mg L<sup>−1</sup>) using a calibration curve of the total

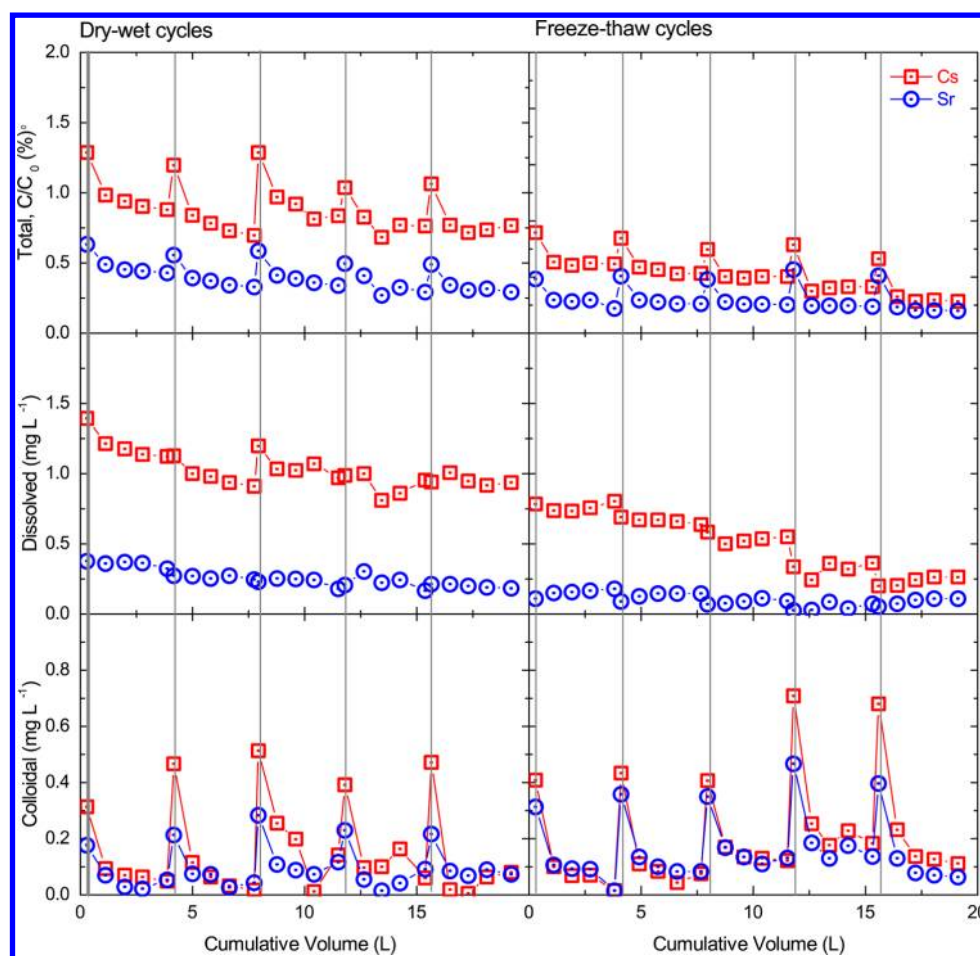


**Figure 1.** Flux and number of active ports in the dry–wet and freeze–thaw experiments. The arrows mark the start of rainfall after drying at room temperature or freeze–thaw intervals. The  $x$  axis represents cumulative duration of rainfall that does not account for the 66 h drying and 66 h freeze–thaw treatments.



**Figure 2.** Concentration and cumulative mass of colloids mobilized as a function of the total volume of water infiltrated through two cores during dry–wet and freeze–thaw experiments. The arrow marks indicate the start of rainfall after a freeze–thaw cycle or dry–wet cycle.





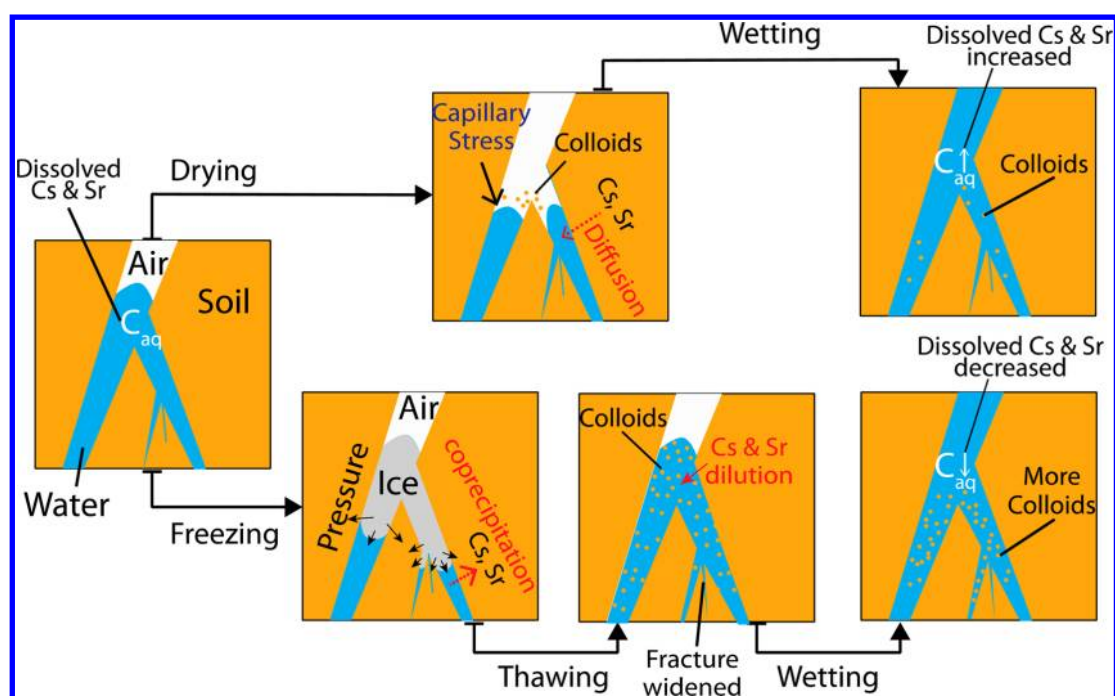
**Figure 3.** Total, dissolved, and colloidal concentrations of cesium and strontium mobilized from a soil core as a function of the cumulative volume of infiltrating water during the dry–wet and freeze–thaw experiments. The gray lines indicate the start of rainfall after a drying or freeze–thaw interval. The method detection limits for strontium and cesium are  $0.2$  and  $0.3 \mu\text{g L}^{-1}$ , respectively. Results from the duplicate core are provided in Figure S3 of the Supporting Information.

suspended sediment concentration versus turbidity. The suspended particle concentration was measured by drying colloid suspensions ( $20 \text{ mL}$ ) of increasing turbidity in preweighed aluminum cups in an oven at  $104^\circ\text{C}$  and weighing the mass of the dried colloids. The contribution of total dissolved solids to the suspended sediments was estimated as less than 1% based on a conversion of the maximum electrical conductivity ( $25 \mu\text{S cm}^{-1}$ ) to total dissolved solids. Cesium and strontium concentrations were measured using inductively coupled plasma–mass spectrometry (ICP–MS; Perkin-Elmer SCIEX Elan DRC-e) and reported as total (unfiltered samples) and dissolved (filtrate from  $0.2 \mu\text{m}$  nylon syringe filter) concentrations. The concentration of cesium and strontium associated with colloids was calculated as the difference between the total and dissolved concentrations. Cesium and strontium that passed through the  $0.2 \mu\text{m}$  filters, the smallest pore size that did not result in rapid clogging, were considered to be dissolved, which may result in an overestimation of dissolved cesium and strontium in the effluent. The mineralogy of the soil and the colloids mobilized during dry–wet and freeze–thaw cycles was characterized by X-ray diffraction (XRD) analysis and acid digestion test (see the Supporting Information).

## RESULTS

**Effect of Freezing on Preferential Flow of Water.** The number of active ports, an indicator of preferential flow, was higher in freeze–thaw experiments than dry–wet experiments (Figure 1). The number of active ports nearly doubled after five freeze–thaw cycles, although the flux of water through the entire core (sum of all ports) did not change during dry–wet and freeze–thaw experiments. During the wetting periods, the moisture content of cores was  $82 \pm 3\%$  (average  $\pm$  standard deviation), which was reduced to  $76 \pm 2\%$  after gravitational drainage because of evaporation of water from top and bottom surfaces of the soil cores. Following drainage, a 66 h drying at room temperature reduced the moisture content of cores to  $53 \pm 4\%$ , whereas a 42 h freezing and 24 h thawing process reduced the moisture content to  $68 \pm 3\%$ .

**Colloid Mobilization.** Successive dry–wet cycles at room temperature did not increase the amount of colloids mobilized, but successive freeze–thaw cycles increased the total amount of colloids mobilized in each rainfall event (Figure 2). Rainfalls after five freeze–thaw cycles mobilized twice the amount of colloids as rainfall after five dry–wet cycles. After five freeze–thaw cycles, the infiltrating water mobilized colloids with a cumulative mass of  $4.3 \text{ g}$  in the first core compared to  $2.0 \text{ g}$  of colloids mobilized during five dry–wet cycles. The results in the second core were consistent with the first core— $4.2 \text{ g}$  of



**Figure 4.** Illustration showing the effect of dry-wet and freeze-thaw cycles on the mobilization of colloids and metal cations. During drying, capillary pressure could break pore walls and generate colloids. The dissolved cesium and strontium increased because of their diffusion from the matrix to preferred flow paths. During freezing, pressure from expanding ice crystals could create or widen fractures or preferential flow paths in soil matrices and generate colloids. The dissolved cesium and strontium could decrease because of precipitation with secondary minerals and subsequent dilution during ice melt.

colloids were mobilized during the freeze-thaw cycles compared to 2.1 g mobilized during the dry-wet cycles (see Table S1 of the Supporting Information). The mineral properties of colloids mobilized after drying or freeze-thaw cycles are provided in Tables S2 and S3 of the Supporting Information.

**Colloid-Facilitated Transport of Cesium and Strontium.** Dissolved, colloidal, and total effluent concentrations of cesium were generally greater than those of strontium for both the dry-wet and freeze-thaw cycles (Figure 3 and Figure S3 of the Supporting Information). For both metal contaminants, colloid-facilitated transport was more apparent during freeze-thaw cycles compared to dry-wet cycles; that is, the relative fractions of cesium and strontium associated with colloids were greater in the freeze-thaw experiments than those in the dry-wet experiments (see Figure S4 of the Supporting Information). Following drying or freeze-thaw cycles, the total and colloidal concentrations of cesium and strontium peaked at the start of wetting events and decreased as the wetting event progressed. The dissolved concentrations show an opposite trend in response to both treatments—the dissolved concentrations dipped following drying at room temperature but peaked following freeze-thaw cycles.

## DISCUSSION

**Role of Freeze-Thaw Cycles on Preferential Flow of Water.** The presence of few active ports during dry-wet and freeze-thaw cycle suggests that water bypassed a major fraction of the soil matrix and flowed through preferential channels. Preferential flow occurred likely through the fractures located parallel to the bedding planes in the soil because the hydraulic conductivity in the fractures is several orders of magnitude

greater than the hydraulic conductivity in the clay-rich soil matrix.<sup>26</sup>

Nearly twice the number of active ports in the freeze-thaw experiments compared to dry-wet experiments indicates an increase in the preferential flow paths because of freeze-thaw. These results suggest that expansion and contraction of water during freeze-thaw cycles could create new fractures or widen the interconnected microfractures in the soil matrix, resulting in the formation of new preferential channels. An increase in the number of active ports with a successive freeze-thaw cycle further supports this idea. These new or widened fractures may provide a passage for rainwater from the existing fractures to the previously unexposed soil matrix.

Taber<sup>27</sup> provided a conceptual framework supported by experimental evidence to explain the propagation of the freezing front in soil during frost heave, which could also explain the link between freeze-thaw and the creation of preferential flow paths. The author showed that the growth of ice crystals inside soil depends upon the moisture content of soil and soil property. A higher moisture content favors greater ice formation. Once the ice is formed in one location, water flows from surrounding regions to support the growth of ice crystals. Consequently, the propagation of a freezing front depends upon how quickly water is supplied to the freezing front. Because nearly 70% of the soil cores were filled with water before the freeze-thaw cycles, the ice front could have penetrated into soil matrixes through water-filled fractures and microfractures. Additionally, a major fraction of soil core consisted of clay, which conducts water too slowly to sustain the growth of the freezing front.<sup>27</sup> Thus, the fractures created by the growth of ice crystals did not penetrate throughout the soil core, as was indicated by the large number of inactive ports in both cores.

**Role of Freeze–Thaw Cycles on the Mobilization of Colloids.** More colloids were released because of freeze–thaw cycles compared to dry–wet cycles at room temperature. DeNovio et al.<sup>11</sup> summarized various processes that mobilize colloids during intermittent flow. Because draining and wetting occur in dry–wet and freeze–thaw cycles, the difference in colloid mobilization is attributed to the generation of colloids during both treatments. We provide a conceptual figure illustrating the differences in the colloid mobilization mechanism during dry–wet and freeze–thaw cycles (Figure 4). On the basis of a capillary model proposed by Michel et al.,<sup>18</sup> the difference in capillary pressure between a drained pore and an adjacent undrained pore could be strong enough to break the wall between the pores and mobilized colloids. Because the mobilization of colloids depends upon the duration of the interval between rainfalls,<sup>15</sup> we expected a similar amount of colloids to be mobilized during successive rainfalls of the same interval. While successive dry–wet cycles did not change the amount of colloid mobilized in each cycle, each successive freeze–thaw cycle mobilized more colloids than the previous cycle, indicating a different colloid mobilization process during freezing. We suggest that propagation of the freezing front and the resultant disintegration of the soil could generate colloids. Freezing causes expansion of water in the soil pores, and the expansion may break up soil aggregates,<sup>8,9,28</sup> generating colloids. Colloids may also be mobilized by frost heave.<sup>29</sup> During frost heaving, water on the surface of soil freezes in contact with air at subfreezing temperatures. The nucleated ice is surrounded by a film of supercooled water that is gradually frozen. The water from nearby pores flows toward the freezing front and forms ice. The expansion of the freezing front may cause scouring and colloid formation. Because each freeze–thaw cycle created new fractures, indicated by the increase in the number of active pores, these fractures could expose a greater soil area to expansion by freezing, thereby increasing the colloid mobilization in successive freeze–thaw cycles.

XRD results show that the colloids contained larger fractions of clay minerals and iron oxide than the soil from which colloids were generated. This result indicates that clay and iron oxides are disproportionally mobilized from soil during dry–wet and freeze–thaw experiments. The iron(III) and manganese oxyhydroxides and clay minerals are translocated within the bedding planes and fractures in soil because of heavy weathering of soil over years.<sup>30</sup> Transient conditions during freeze–thaw and dry–wet cycles mobilized the colloids enriched with metal oxides and translocated clay minerals. These results have several environmental implications because metal oxides and clay minerals have larger surface areas than quartz and other minerals for sorption and mobilization of many contaminants.

Mineralogical and elemental analyses of the colloids further support our hypothesis that freeze–thaw could affect the soil matrix that is not accessed by infiltrating water during dry–wet cycles. The colloids mobilized during freeze–thaw experiments have more quartz and less clay minerals than the colloids mobilized during dry–wet experiments. It appears that the pressure generated because of successive expansion and contraction of water and ice during freeze–thaw cycles could break a fraction of the soil minerals dominated by quartz fragments. On the other hand, capillary pressure, which is the dominant force for the generation of colloids during dry–wet cycles at room temperature, may not mobilize quartz colloids.

**Mobilization of Cesium and Strontium by Freeze–Thaw.** Our results suggest that colloid-facilitated transport of cesium and strontium is greater because of the mobilization of greater amounts of colloids in the freeze–thaw experiments than that in dry–wet experiments at room temperature. Drying and freezing increased the mobilization of colloidal cesium and strontium but had a contrasting effect on the transport of the dissolved fractions. An increase in the contaminant concentration in pore water during flow interruption of the dry–wet cycles was expected because of diffusion of contaminants from matrix pore water to the preferred flow path in the soil core.<sup>31</sup> Interestingly, flow interruption during freeze–thaw cycles reduced the dissolved cesium and strontium. This reduction is attributed to three processes that occurred during freeze–thaw cycles. First, dissolved cesium and strontium could co-precipitate or sorb on secondary minerals that are precipitated as a result of salt exclusion from ice crystals during freezing.<sup>32</sup> Second, the dissolved cesium and strontium could adsorb on the soil exposed during the formation of new fractures. Third, melting of ice during thawing could further dilute the remaining dissolved cations in the pore water. The colloidal concentration increased because of dry–wet and freeze–thaw cycles, although the total amounts of colloidal cesium and strontium were greater during freeze–thaw than dry–wet cycles. A net increase in the concentration and cumulative mass of cesium and strontium associated with colloids during freeze–thaw cycles indicates that more colloids were generated from previously contaminated soil than from freshly exposed soil. Increases in the colloidal concentration of both strontium and cesium support the relevance of colloid-facilitated transport as a major process for the migration of contaminants in the subsurface under these extreme conditions.

Greater quantities of cesium were associated with colloids compared to strontium because of a difference in binding strengths to colloids. The strength of sorption of cations to colloids depends upon whether sorption 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. For example, cesium forms stronger surface complexes with illite by ion exchange and inner-sphere complexation to frayed-edge (surface hydroxyl) sites, whereas strontium binds with illite by ion exchange only. The transport of readily desorbing strontium is not effectively facilitated by colloids compared to slowly desorbing cesium.<sup>33</sup> XRD confirmed the presence of illite in the mobilized colloids, which could contribute to a larger fraction of cesium in the soil compared to strontium.

**Environmental Implications.** Our study provides evidence that freeze–thaw cycles enhance the mobilization of colloids and associated metal cations. We show that frequent freeze–thaw cycles could mobilize the contaminants sequestered in the soil matrix that is exposed by cracks formed during freezing of water. The implication of this study is relevant to the management of sites contaminated with heavy metals and radioactive wastes. Previous studies<sup>34,35</sup> that examined colloid-facilitated transport of radionuclides did not use antecedent conditions, in particular, freeze–thaw during winter, to estimate the long-term release of contaminants. Our results show that extreme weather patterns because of climate change could shift the equilibrium of contaminants and could potentially increase the mobilization of sequestered contaminants. Our experiments, however, simulate the effect of freeze–thaw cycles on the mobilization of colloids and contaminants under extreme



conditions, which may differ from many natural settings. For instance, deeper soil is not affected by freeze–thaw cycles because freezing of the forest floor under natural conditions is limited to a depth of 20 cm.

The results of this study are also relevant to remediation schemes that require accessing contaminants sequestered in the soil matrix.<sup>36</sup> For example, solidification or stabilization is an effective remediation strategy that uses chemical reagents to enhance precipitation of heavy metals. The success of this technique depends upon how well the contaminated soils are accessed, which is usually hindered by soils of low permeability. Application of chemical reagents after several freeze–thaw cycles during winter may increase the effectiveness of the remediation process.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Design of the experimental setup (Figure S1), details of treatment steps (Figure S2), metal mobilization in a duplicate core (Figure S3), mobilization of the colloidal fraction of metals (Figure S4), pH of the effluent and quantity of colloids, cesium, and strontium mobilized in each cycle (Table S1), and mineralogical and elemental characterizations of colloids (Tables S2 and S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [mohantys@stanford.edu](mailto:mohantys@stanford.edu).

### Present Address

<sup>‡</sup>Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305, United States.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors thank the U.S. Department of Energy Environmental Science and Management Program for supporting this research under Grant DOE-FG02-08ER64639. The authors thank Timothy Dittrich and Mark Serravezza (University of Colorado Boulder) and Tonia Melhorn and Philip Jardine (Oak Ridge National Laboratory) for assistance during sampling of soil cores from Oak Ridge, TN. The authors acknowledge the support of Dennis D. Eberl at the U.S. Geological Survey, Boulder, CO, for analysis of the soil minerals and colloids by XRD. Sabre Duren provided comments that improved the paper. The authors thank the reviewers for their comments, which have improved the paper.

## ■ REFERENCES

- (1) Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averyt, K.; Tignor, M.; Miller, H. *Climate Change 2007: The Physical Science Basis: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: New York, 2007; p 996.
- (2) Henry, H. A. L. Climate change and soil freezing dynamics: Historical trends and projected changes. *Clim. Change* **2008**, *87* (3–4), 421–434.
- (3) Dagesse, D. Effect of freeze-drying on soil aggregate stability. *Soil Sci. Soc. Am. J.* **2011**, *75* (6), 2111–2121.
- (4) Van Klaveren, R. W.; McCool, D. K. Freeze–thaw and water tension effects on soil detachment. *Soil Sci. Soc. Am. J.* **2010**, *74* (4), 1327–1338.
- (5) Koponen, H. T.; Martikainen, P. J. Soil water content and freezing temperature affect freeze–thaw related N<sub>2</sub>O production in organic soil. *Nutr. Cycling Agroecosyst.* **2004**, *69* (3), 213–219.
- (6) Fitzhugh, R. D.; Driscoll, C. T.; Groffman, P. M.; Tierney, G. L.; Fahey, T. J.; Hardy, J. P. Effects of soil freezing disturbance on soil solution nitrogen, phosphorus, and carbon chemistry in a northern hardwood ecosystem. *Biogeochemistry* **2001**, *56* (2), 215–238.
- (7) Feng, X. J.; Nielsen, L. L.; Simpson, M. J. Responses of soil organic matter and microorganisms to freeze–thaw cycles. *Soil Biol. Biochem.* **2007**, *39* (8), 2027–2037.
- (8) Oztas, T.; Fayetorbay, F. Effect of freezing and thawing processes on soil aggregate stability. *Catena* **2003**, *52* (1), 1–8.
- (9) Lehrsch, G.; Sojka, R.; Carter, D.; Jolley, P. Freezing effects on aggregate stability affected by texture, mineralogy, and organic matter. *Soil Sci. Soc. Am. J.* **1991**, *55*, 1401–1406.
- (10) Bergendahl, J.; Grasso, D. Colloid generation during batch leaching tests: Mechanics of disaggregation. *Colloids Surf., A* **1998**, *135* (1–3), 193–205.
- (11) DeNovio, N. M.; Saiers, J. E.; Ryan, J. N. Colloid movement in unsaturated porous media: Recent advances and future directions. *Vadose Zone J.* **2004**, *3* (2), 338–351.
- (12) U.S. Department of Energy (DOE). *Environmental Remediation Sciences Program Strategic Plan*; Office of Biological and Environmental Research, U.S. DOE: Washington, D.C., 2006.
- (13) Saiers, J. E.; Lenhart, J. J. Colloid mobilization and transport within unsaturated porous media under transient-flow conditions. *Water Resour. Res.* **2003**, DOI: 10.1029/2002WR001370.
- (14) Cheng, T.; Saiers, J. E. Colloid-facilitated transport of cesium in vadose-zone sediments: The importance of flow transients. *Environ. Sci. Technol.* **2010**, *44* (19), 7443–7449.
- (15) Majdalani, S.; Michel, E.; Di-Pietro, L.; Angulo-Jaramillo, R. Effects of wetting and drying cycles on in situ soil particle mobilization. *Eur. J. Soil Sci.* **2008**, *59* (2), 147–155.
- (16) Zhuang, J.; McCarthy, J. F.; Tyner, J. S.; Perfect, E.; Flury, M. In situ colloid mobilization in Hanford sediments under unsaturated transient flow conditions: Effect of irrigation pattern. *Environ. Sci. Technol.* **2007**, *41* (9), 3199–3204.
- (17) Cheng, T.; Saiers, J. E. Mobilization and transport of in situ colloids during drainage and imbibition of partially saturated sediments. *Water Resour. Res.* **2009**, DOI: 10.1029/2008WR007494.
- (18) Michel, E.; Majdalani, S.; Di-Pietro, L. How differential capillary stresses promote particle mobilization in macroporous soils: A novel conceptual model. *Vadose Zone J.* **2010**, *9* (2), 307–316.
- (19) Kim, W. H.; Daniel, D. E. Effects of freezing on hydraulic conductivity of compacted clay. *J. Geotech. Eng.* **1992**, *118* (7), 1083–1097.
- (20) Safadoust, A.; Mahboubi, A. A.; Mosaddeghi, M. R.; Gharabaghi, B.; Unc, A.; Voroney, P.; Heydari, A. Effect of regenerated soil structure on unsaturated transport of *Escherichia coli* and bromide. *J. Hydrol.* **2012**, *430–431*, 80–90.
- (21) Watanabe, K.; Flury, M. Capillary bundle model of hydraulic conductivity for frozen soil. *Water Resour. Res.* **2008**, DOI: 10.1029/2008WR007012.
- (22) Luxmoore, R. J.; Abner, C. H. *Field Facilities for Subsurface Transport Research*; U.S. Department of Energy (DOE): Washington, D.C., 1987.
- (23) Jardine, P. M.; Jacobs, G. K.; Wilson, G. V. Unsaturated transport processes in undisturbed heterogeneous porous media: I. Inorganic contaminants. *Soil Sci. Soc. Am. J.* **1993**, *57* (4), 945–953.
- (24) Mohanty, S. Colloid-facilitated transport of cations in an unsaturated fractured soil under transient condition. Ph.D. Thesis, University of Colorado Boulder, Boulder, CO, 2011.
- (25) Serne, R. J.; Zachara, J. M.; Burke, D. *Chemical Information on Tank Supernatants, Cs Adsorption from Tank Liquids onto Hanford Sediments, and Field Observations of Cs Migration from Past Tank Leaks*; Pacific Northwest National Laboratory (PNNL): Richland, WA, 1998.
- (26) Luxmoore, R. J.; Jardine, P. M.; Wilson, G. V.; Jones, J. R.; Zelazny, L. W. Physical and chemical controls of preferred path flow through a forested hillslope. *Geoderma* **1990**, *46* (1–3), 139–154.



- (27) Taber, S. The mechanics of frost heaving. *J. Geol.* **1930**, *38* (4), 303–317.
- (28) Kvaerno, S. H.; Oygarden, L. The influence of freeze–thaw cycles and soil moisture on aggregate stability of three soils in Norway. *Catena* **2006**, *67* (3), 175–182.
- (29) Taber, S. Frost heaving. *J. Geol.* **1929**, *37* (5), 428–461.
- (30) Jardine, P. M.; Jacobs, G. K.; Wilson, G. V. Unsaturated transport processes in undisturbed heterogeneous porous media. 1. Inorganic contaminants. *Soil Sci. Soc. Am. J.* **1993**, *57* (4), 945–953.
- (31) Reedy, O. C.; Jardine, P. M.; Wilson, G. V.; Selim, H. M. Quantifying the diffusive mass transfer of nonreactive solutes in columns of fractured saprolite using flow interruption. *Soil Sci. Soc. Am. J.* **1996**, *60* (5), 1376–1384.
- (32) Dietzel, M. Impact of cyclic freezing on precipitation of silica in Me–SiO<sub>2</sub>–H<sub>2</sub>O systems and geochemical implications for cryosoils and -sediments. *Chem. Geol.* **2005**, *216* (1–2), 79–88.
- (33) Turner, N. B.; Ryan, J. N.; Sayers, J. E. Effect of desorption kinetics on colloid-facilitated transport of contaminants: Cesium, strontium, and illite colloids. *Water Resour. Res.* **2006**, DOI: 10.1029/2006WR004972.
- (34) Chen, G.; Flury, M.; Harsh, J. B.; Lichtner, P. C. Colloid-facilitated transport of cesium in variably saturated Hanford sediments. *Environ. Sci. Technol.* **2005**, *39* (10), 3435–3442.
- (35) Litaor, M. I.; Barth, G.; Zika, E. M.; Litus, G.; Moffitt, J.; Daniels, H. The behavior of radionuclides in the soils of Rocky Flats, Colorado. *J. Environ. Radioact.* **1998**, *38* (1), 17–46.
- (36) Niven, R. K.; Singh, K. Mobilization and rupture of LNAPL ganglia during freeze–thaw: Two-dimensional cell experiments. *Environ. Sci. Technol.* **2008**, *42* (15), 5467–5472.