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Changes in the mineral element compositions of soil colloidal matter caused by a controlled freeze-thaw event

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ABSTRACT

This study investigated the effects of a controlled freeze-thaw event on the mineral element compositions of colloidal matter in soil interstitial water. The experiment was designed to decouple the freeze-thaw effect from the warming effect by conducting sequential treatments. The temperate soil samples were incubated in a refrigerator at 2 °C for four weeks and compared with those frozen at − 20 °C in the second week and thawed at 2 °C for the following two weeks; this was done in order to study the freeze-thaw effect while minimizing the influence caused by warming. The soil samples incubated at 25 °C in the fourth week after two weeks of the freeze-thaw treatment were compared with the freeze-thaw treatment group to investigate the warming effect. The laser-induced breakdown spectroscopy (LIBS) technique was used to analyze the relative elemental concentrations in the soil colloidal matter (SCM), which was collected on nylon membrane filters. The six predominant mineral elements were classified into two groups based on their distinct trends in response to the treatment conditions. The type 1 element (Si, Mg, Al) contents were decreased both by the warming condition and by the freeze-thaw treatment, whereas the type 2 element (Fe, Ca, Ba) contents were decreased by the freeze-thaw treatment but increased by the warming condition. Only type 1 elements showed positive correlations with the amount of organic carbon. From the results of the elemental compositions in SCM, the effects of a freeze-thaw event can be contradictory depending on the thawing temperatures.

1. Introduction

Colloidal matter in soil is composed of ubiquitous soil constituents such as organic matter and clay minerals (Villholth, 1999), which closely interact with dissolved organic matter and metal ions in soil interstitial water (Grout et al., 1999; Pontoni et al., 2016). Colloidal matter is an intermediate substance that can transform into either dissolved or particulate matter depending on the environmental conditions (Aiken et al., 2011). He et al. (2016) illustrated the various geochemical processes of the dynamic exchange between dissolved and particulate organic matter, which involve particulate colloids as a heterogeneous counterpart. Although the sizes of soil colloidal matter (SCM) have been defined differently (ranging from 0.1 kDa to several micrometers), many results have agreed that SCM plays an important role in regulating the solubility and bioavailability of the organic compounds, metal ions, and other nutrients in soil interstitial water (Kepkay, 1994; Stordal et al., 1996; Aiken et al., 2011).

Freeze-thaw events are known to change soil aggregate stability (Zhao et al., 2009), the extent of which depends on the local moisture content (Starícka and Benoit, 1995). The physical disruption of soil aggregates during frosting events is known to involve the expansion of pore structures by the formation of ice crystals (Six et al., 2004) and micro-scale fractures (De Kock et al., 2015). In contrast, shrinkage of locally dry soil mass during frosting events can increase the soil aggregate stability (Six et al., 2004). A subsequent thawing process could also enhance the stability of wet soil aggregates by a cohesion process (Hinman and Bisal, 1968). Compared to soil aggregates that undergo such physical rearrangements, SCM (consisting of soil organic matter and clay) is more resistant to the structural changes induced by freeze-thaw events (Sillanpää and Webber, 1961). However, small changes in SCM in response to freeze-thaw events can notably influence the nutrient availability and microbial activities of the soil system (Aiken et al., 2011; Sharma et al., 2006).

Pokrovsky and Shirokova (2013) have demonstrated that the changes of SCM in response to environmental factors relate to the bioavailability of trace metals, which identify potential limiting micronutrients in the overlying water system. Mohanty et al. (2014) also reported that freeze-thaw cycles stimulated the release of SCM and

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resulted in increased dissolution of cesium and strontium into soil interstitial water. To determine the extent to which the element concentration and speciation will be affected by a controlled freeze-thaw event, we monitored the amounts of mineral elements in SCM and investigated the correlation between these elemental compositions and total organic carbon.

The effects of freeze-thaw events involve covariant factors, such as the temperature, physical disintegration of soil aggregates during phase transitions, and dissolution of solutes (Henry, 2007), which account for the difficulties in distinguishing the effects of the individual factors that are associated with biogeochemical changes in soil constituents. To understand the effects of individual factors, we adopted a minimum thawing temperature (2 °C) to minimize the warming effect during freeze-thaw events. This experimental setting should allow us to analyze the consequences of physical rearrangement of soil aggregates during a freeze-thaw event while limiting the influence of microbial activities associated with warm thawing conditions. The results from this experimental setting may reveal whether a freeze-thaw treatment itself would result in significant changes in the compositions of SCM (Martínez et al., 2003; Mohanty et al., 2014). Comparing samples with or without a subsequent warming condition may indicate the significance of a warming condition in an overall freeze-thaw event.

Henry (2007) has addressed the implications of climate change for the frequency and amplitude of freeze-thaw cycles, and thus on physico-chemical properties of soils. Therefore, understanding the effects of each factor associated with climate change on soil constituents are imperative to predict the changes in soil chemistry from various future climate scenarios. Among many factors, we focused on temperature condition during thawing. The objective of this study was to examine the significance of the freeze-thaw treatment a minimal warming condition on the mineral element compositions of soil colloidal matter (0.2–1.2 μm) and compare it with the warming effects, which can vary depending on various climatic conditions during a freeze-thaw event. The results of this study are expected to provide valuable information about the dynamic nature of SCM that is influenced by the freezing and thawing conditions.

2. Materials and methods

2.1. Study sites

The soil samples were collected on the 21st of January 2015 from a green area (37°34.015′ N, 126°56.907′ E) located 10 m from the laboratory. The top 10 cm of the surface horizon, consisting of sandy loam (ISO/CD 11277, sand 75.7%, silt 12.6%, clay 11.7%, USDA Soil Texture Classification, https://www.nrcs.usda.gov/) Regosols (IUSS Working Group WRB, 2015), was collected within an area of 1 m^2. *Pinus* species were planted more than 40 years at the sampling site. The monthly average temperatures in this region ranged from − 2.4 °C in January to 25.7 °C in August and the annual average rainfall was 1450 mm for the past 30 years (Korea Meteorological Administration (KMA), Korea). The initial moisture content of the soil was 14.3%, and the pH was 6.1–6.2 (Korea Ministry of Environment, 2009; ISO 11465:1993 & ISO 10390:2005). The air-dried soil samples were sent to the National Instrumentation Center for Environmental Management (http://nicem.snu.ac.kr) for the elemental analysis of C, H, and N (ISO 10694:1995 & ISO 13878:1998); the average elemental compositions of the triplicate samples were 1.19%, 0.38%, and 0.11%, respectively. The average ignition loss (US EPA, 1971) of the triplicate samples was 3.1%. The soil characterization results are summarized in Table 1.

2.2. Experimental design

The collected soil was immediately transferred to the lab, where the soil samples were homogeneously mixed and passed through a 2-mm sieve (Chen and Shrestha, 2012). The sieved soil was kept at 4 °C until the experiment began. The homogenized wet soils (160 g) were placed in 250-mL Nalgene centrifuge bottles, and 100 mL of deionized water was added. The lids of the bottles were loosely closed to prevent evaporation of the overlying water and to maintain atmospheric pressure in the headspace, regardless of gas consumption or production by soil microorganisms. All soil samples were incubated with overlying water throughout the experiment in order to avoid artifacts from aerobic respiration in the top soil layer during the freezing or thawing processes.

Table 1
The properties of the homogenized soil sample. All tests were done in triplicate.

Test name	Test results Average (± standard deviation)	Test methods
Soil texture	Sandy loam	ISO/CD 11277
WRB classification	Regosols	IUSS Working Group WRB, 2015
Moisture content	14.3 (± 0.2)%	ISO 11465:1993
pH	6.19 (± 0.05)%	ISO 10390:2005
Carbon content	1.19 (± 0.11)%	ISO 10694:1995
Hydrogen content	0.38 (± 0.01)%	ISO 13878:1998
Nitrogen content	0.11 (± 0.01)%	ISO 13878:1998
Ignition loss	3.1 (± 0.2)%	US EPA Method 160.4

Laboratory experiments were carried out in a freezer, a cold chamber, and a growth chamber, where the ambient temperatures were kept constant at − 20 °C, 2 °C, and 25 °C, respectively. A total of eight bottles were separated into four groups (i.e., the Tϕ group, control group, freeze-thaw treatment group, and warming treatment group), each group with 2 bottles were prepared as follows. The Tϕ group was incubated at 2 °C for one week to allow the soil to settle and to establish anoxic conditions (Lüdemann et al., 2000) in the soil media. The control group was incubated at 2 °C for four weeks and was compared with the freeze-thaw treatment group (FT → 2 °C group), which was kept under the same incubation conditions as the control group, with the exception that it was frozen at − 20 °C only in the second week (i.e., incubated at 2 °C in the first week followed by one week at − 20 °C and then two weeks at 2 °C). This freeze-thaw treatment group functioned as a control group for the subsequent warming treatment. The warming treatment group (FT → 25 °C group) was kept under the same incubation conditions as the freeze-thaw treatment group, with the exception that it underwent warming at 25 °C in the fourth week (i.e., incubated at 2 °C in the first week followed by changing the temperature to − 20 °C, 2 °C, and 25 °C in sequence).

2.3. Sample preparation

After four weeks of incubation (except for the Tϕ group, which was incubated for one week), the soil samples were centrifuged at 2000 rpm at 4 °C for 10 min to obtain the overlying water that contained SCM (Ulén, 2004). The supernatant was transferred into 100-mL acid-washed glass bottles and stored in a refrigerator at 2 °C until filtration. The filtration was conducted within 4 h after the centrifugation. The liquid sample was filtered by 1.2-μm Whatman GF/C™ glass fiber filters (GE Healthcare, UK), and the filtrate was filtered again by Whatman NY-TRAN 0.2-μm nylon blotting membranes to retrieve the colloidal matter. The first filtrate contained both colloidal (0.2–1.2 μm) and dissolved (< 0.2 μm) matter, and the second filtrate contained only dissolved matter. After each filtration process, 1 mL of the filtrate was sub-sampled and diluted with DI water to prepare 10 mL of the analyte for the total organic carbon (TOC) analysis. The sub-samples were stored in a refrigerator at 2 °C and then brought to room temperature right before analysis. The nylon membranes with colloidal matter were dried in a convection oven at 80 °C for 5 min and stored in a refrigerator at 2 °C until LIBS analysis.