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REMEDIATION IN CHALLENGING ENVIRONMENTS: PRELIMINARY NUMERICAL SIMULATION AND MEASUREMENT OF UNFROZEN WATER CONTENT FOR AN OUTDOOR PILOT-SCALE BIOPILE IN COLD CLIMATE

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Abstract: Cold-adapted bacteria are able to remain metabolically active in petroleum hydrocarbon-contaminated soils at low temperatures, and thus have been the basis for bioremediation efforts at cold-region sites. Recent studies have consistently reported significant microbial activity in partially frozen and frozen habitats, including in soils, sea ice cores and even at the interface between ice and water. Unfrozen liquid water in freezing and frozen soils is likely prerequisite for extended microbial activity. Predicting the presence and retention of unfrozen liquid water in cold site soils can be useful for planning, managing and implementing bioremediation for petroleum-contaminated soils at remote northern sites. However, available numerical simulation tools for predicting soil water content have not been extensively considered in bioremediation research for cold sites. For this research, a preliminary study was performed to calibrate a TEMP/W model for predicting soil temperatures and unfrozen water content in field-aged, petroleum-contaminated, clayey soils from outdoor pilot-scale biopiles exposed to winter temperatures of Saskatoon, Saskatchewan (Canada). The simulation of unfrozen water content in the biopiles subjected to representative winter temperatures was conducted using TEMP/W. The preliminary study predicted that significant quantities of unfrozen water remain available in the biopile during the seasonal transitional and winter periods. By comparing the simulated and measured unfrozen water data for the site soils, this study conservatively predicted an abundance of unfrozen water in the site soils during the winter season.

1 Introduction

Petroleum hydrocarbons are one of the most frequently identified contaminants in Canada, including at northern sites, mainly due to intensified anthropogenic activities and associated impacts. Bioremediation is often considered a cost-effective and less-destructive remediation technology for petroleum-contaminated soils at cold sites (Snape et al. 2008). The potential to enhance hydrocarbon biodegradation in cold site soils by stimulating cold-adapted hydrocarbon-degrading bacteria has been frequently reported over the last ten years (Whyte et al. 2001). More recently, microbial activity extended to sub-temperatures in freezing and frozen soils has been reported, implying that unfrozen liquid water content plays a critical role for maintaining metabolic activity of microbial survivors when temperatures are near or below the freezing-depression point of freezing and frozen soils (Panikov et al. 2006). Temperatures alone cannot explain the unique adaptations of microorganisms in freezing soils, where microbial habitats are subjected to multiple stresses. For example, Deming (2002) proposed an ecophysiological group, *eutectophiles*, to designate unique microorganisms that take advantage of soil phase changes at the water-ice interface. The microbial habitat of eutectophiles at the water-ice interface is influenced by a combination of factors including temperature, solute concentrations, and the physical state of the water.

It has been frequently observed that changes in unfrozen water availability is significantly correlated with the seasonal onset and inactivation of microbial activity in freezing and frozen soils (Chang et al. 2011). Rivkina et al. (2000) reported that microbial activity is correlated with the thickness of unfrozen water films in freezing soils. Similarly, Panikov et al. (2006) indicated that CO_2 evolution in freezing soils is related to changes in unfrozen water content. However, these prior studies are small lab-scale experiments using uncontaminated soils.

Some low-temperature studies have considered field-aged, petroleum hydrocarbon-contaminated sub-Arctic soils. Significant in-situ soil gas concentrations (CO_2 and O_2) were measured at a sub-Arctic site in Norway to estimate microbial respiration in the active and permafrost layers of oil-contaminated soils during a seasonal transition period and winter (Rike et al. 2003; 2005). Chang et al. (2011) observed a significant correlation between temporal changes in unfrozen water content and apparent microbial respiration activity (CO_2 and O_2) in soils subjected to varying site-representative freeze/thaw temperatures in an indoor, pilot-scale biodegradation experiment. However, that study was conducted in a laboratory by mimicking site temperatures using a temperature-programmable cold room.

On the other hand, the relationship between unfrozen water content and physical soil properties has been studied (Andersland and Ladanyi 2004). Empirical equations and predictive numerical soil thermal models are currently available to estimate unfrozen water content in various types of unsaturated soils (e.g., TEMP/W). Yet, a comparison of predicted unfrozen water content over time and measured unfrozen water data obtained for an outdoor biopile of field-aged petroleum-contaminated soils has rarely been reported.

The objective of this study is to compare simulated unfrozen water content with measured unfrozen water content in field-aged petroleum hydrocarbon-contaminated soils during seasonal freezing in an outdoor pilot-scale biopile installed in Saskatoon, Saskatchewan (SK), Canada. This preliminary study calibrated the numerical simulation tools and associated input parameters specifc to the site soils. This study is particularly important for planinng and managing practices for contaminated site remediation at remote cold sites, where only short summers are allowed for active site monitoring and soil treatment.

2 Materials and methods

2.1 Site soil

The site soils are field-aged, petroleum hydrocarbon-contaminated clayey soils. TPH concentrations were determined using the Canada-Wide Standard for Petroleum Hydrocarbons (CWS PHC) in Soil - Tier 1 Method. Briefly, wet soil samples (10 g) were placed in a cellulose extraction thimble (Gerhardt GmbH & Co. KG, Germany) with a surrogate standard (o-terphenyl; Sigma Aldrich Canada) for estimating hydrocarbon extraction efficiencies. For hydrocarbon analyses, approximately 150 mL of a 50:50 hexane/acetone (v/v) solvent was used for hydrocarbon extraction from the soil samples by automatic Soxhlet extraction (Gerhardt Soxtherm, Germany). Extract solutions were filtered through a column containing silica gel and sodium sulfate to remove polar compounds before 20 mL of a 50:50 hexane/ dichloromethane (DCM) solvent mixture was passed through the same column. The extracts obtained after the silica gel cleanup were concentrated by a nitrogen gas blow-down concentrator. The final volumes of concentrated extracts were measured. Hydrocarbons in the concentrated extract solutions were analyzed using gas chromatography (7890A, Agilent with J&W DB-1HT capillary column) with a flame ionization detector (FID).

2.2 Viable hydrocarbon degraders

For microbial enumeration, 10 g of site soils were added to 95 mL of phosphate buffer solution (PBS). Serial soil dilutions (10^{-1} to 10^{-5}) were prepared after a 30-min homogenization of the soils in the PBS solution. 0.1-mL aliquots of the soil dilutions were spread onto Bushnell Haas (BH) agar plates (0.2 g $MgSO_4$, 0.02 g $CaCl_2$, 1 g KH_2PO_4, 1 g K_2HPO_4, 1 g NH_4NO_3, 0.05 g $FeCl_3$ and 20 g agar in 1 L distilled water; Sigma Aldrich Canada). 0.1 mL of filter-sterilized diesel was added onto the plates as the sole source of carbon. Plates were incubated at 17 °C for 9 days. Colony forming units (CFU) were counted after the incubation.

2.3 Outdoor biopile construction

Prior to winter, a set of pilot-scale biopiles was constructed in September and October, 2015, at an outdoor soil remediation facility (PINTER & Associates) in Saskatoon. The size of the biopiles is approximately 2 m long, by 2 m wide and 1 m high. Approximately 3.2 tons of contaminated soils were used for each biopile. A drainage layer (gravel and collection pipes) was installed at the bottom of each biopile. Soil gas collection tubes were embedded in the biopile. Soil gases (CO_2 and O_2) were monitored using MX6i multi gas detectors (Industrial scientific, USA). Two sets of real-time soil temperature and water content sensors (5TM, Decagon devices, USA), along with a data logger (EM50, Decagon devices, USA), were installed in the top (at 90 cm) and bottom (at 10 cm) layers of the outdoor biopile. Soil temperature and water content in the biopile were monitored every six hours.

2.4 Preliminary simulation of soil temperatures and unfrozen water content

Soil temperature and unfrozen water content were simulated using TEMP/W (Geo-slope International Ltd.). An air temperature profile was constructed based on 10 years of historical air temperature data for Saskatoon (Environment Canada). The outside air temperature profile was then imported into TEMP/W to predict temperatures and water content in the soils subjected to seasonal freezing conditions. The simulated data were compared to the measured data.

3 Results and discussion

3.1 Biostimulation potential prior to the biopile experiment

Microcosm experiments were conducted with nutrient-amended and unamended soils, and viable hydrocarbon degraders were enumerated and compared. A C:N ratio of 100:1 was used for the site soil microcosms and the enumeration of viable hydrocarbon-degrading bacteria. As shown in Fig. 1, significant biostimulation potential was indicated in the nutrient-amended site soils by large populations of viable diesel-degrading bacteria (2.2×10^4 CFU/ g) compared to in the unamended soils (4.5×10^3 CFU/ g), based on the preliminary soil microcosm testing. The difference was statistically significant with $p < 0.05$ (t-test, GraphPad).

For further adjustment of the nutrient dosage, a range of C:N ratios from 100:0.5 to 100:2 were tested. These nutrients were applied in soil microcosms with 100 g soils, while soil respiration activity (CO_2 and O_2) was monitored. As shown in Fig. 2, the site soil readily responded to the different nutrient amendments. CO_2 production and O_2 consumption were significant greater in the nutrient-amended site soils compared to the unamended soils. Of the nutrient amendments tested, a C:N ratio of 100:0.8 exhibited the highest CO_2 production and O_2 consumption, based on the early response of the microcosm to the nutrient-amendment within 48 hours. The C:N ratio of 100:0.8 was used during the biopile setup for biostimulation.

It is important to indicate the presence of viable indigenous bacteria capable of degrading target hydrocarbon fractions (diesel fractions in this study), as well as determine favorable nutrient amendments, prior to installation of large-scale biopiles, in order to achieve successful bioremediation in practice. In particular, cold region sites have a short seasonal window for active soil treatment and field logistics are a concern. Characterizing the favourable soil conditions for stimulating indigenous hydrocarbon degraders is prerequisite. Changes in soil gas are a useful indicator, and soil gas monitoring (CO_2 production and O_2 consumption) has been widely employed to estimate microbial enhancement during bioremediation (Chang and Ghoshal 2014). Soil gases are monitored to demonstrate microbial response during biodegradation (Walworth et al. 2013; Akbari and Ghoshal 2015).

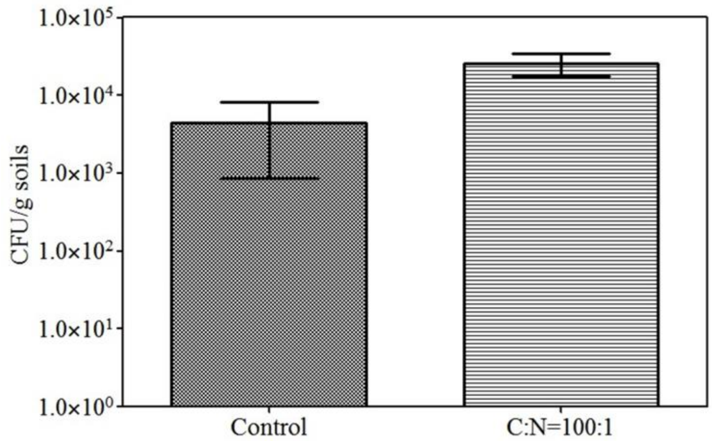

Figure 1: The microbial enumeration of hydrocarbon-degrading bacteria from the nutrient-amended soils with a C:N ratio of 100:1 and from unamended site soils. Enumeration was performed using diesel-spiked Bushnell Hass plates at 25 °C (Error bar: standard error)

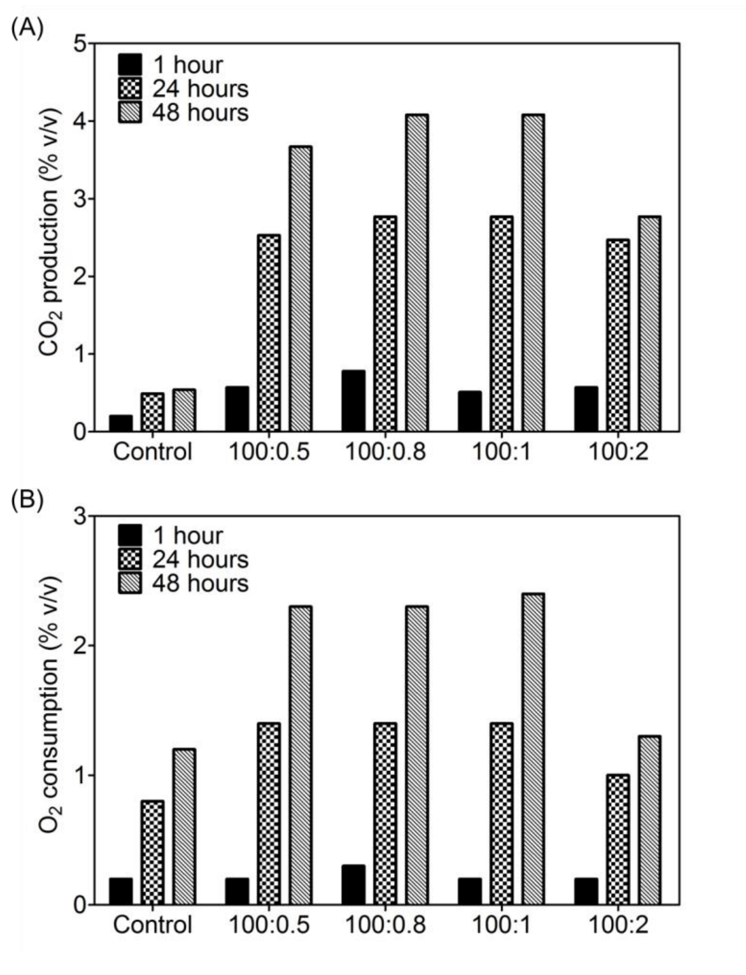

Figure 2: Soil CO_2 production (A) and O_2 consumption (B) in the site soils in response to different C:N ratios in the nutrient amendment.

3.2 Preliminary calibration of TEMP/W model

Prior to the field biopile experiment, temporal changes in the content and distribution of unfrozen water in the biopile were predicted using the historical temperatures (10-year data) and the TEMP/W model. The field biopile was directly exposed to ambient temperature conditions and snow cover. However, the simulation did not consider the effect of snow cover and wind. The highest, average and the lowest ambient temperature profiles constructed from historical data were used for the simulations, producing a range of unfrozen water content profiles as a result. In the present study, the unamended biopile was considered first for as a baseline study.

As shown in Fig. 3, the distributions of simulated unfrozen water content in the biopile during seasonal freezing is illustrated. Significant quantities of unfrozen water could be available in the bottom layers of the biopiles until early November, implying that soil conditions could accommodate microbial populations as long as other soil parameters, such as oxygen and nutrient diffusion, do not limit microbial activity. Although free unfrozen water is limited beginning in the middle of November, small amounts of unfrozen water were still measureable in microsites in the middle of November.

The predicted soil temperatures, based on the highest, average and lowest ambient temperature profiles constructed using historical climate data, were generated and compared with the measured soil temperatures from the biopiles in the field. As shown in Fig. 4, the measured soil temperatures are closer to the soil temperatures corresponding to the 10-year average soil temperature scenario. However, the measured soil temperatures were slightly higher than soil temperatures simulated using the 10-year average ambient temperatures of the site. On-site soil temperatures in the biopile (unamended) remained near 0 °C and fluctuated between 0 and -5 °C during winter. The soils were not completely frozen until January of the following year (2016). In reality, unfrozen liquid water content did not decrease during the period in which the biopile soil temperature was below 0 °C, but were not lower than the typical freezing-depression point of clayey soils (around -5 °C). This result implies that the biopile soils may exhibit the metabolic activity of cold-adapted microorganisms, even though the kinetics of microbial activity are slowed due to the low temperature. In the middle of November, the simulation using 10-year average temperatures indicated the depletion of unfrozen water content. However, measured unfrozen water content from the biopile is closer to the simulated unfrozen water content that used the highest soil temperature scenario.

The on-site climate conditions (e.g., snow cover) and soil properties (e.g., clay content) seem to influence the retention of unfrozen water. The simulation of soil temperatures and unfrozen water content prior to the field biopile implementation provided indications of temporal changes in unfrozen water availability over time during a freezing period. Currently, more sensitive analyses of the effects of a variety of parameters are being conducted to produce better results. In addition, the on-site data for microbial respiration activity and hydrocarbon biodegradation in the biopiles are being obtained, which will further highlight the implications of this study's findings for planning and management of bioremediation for petroleum-contaminated soils in cold climates. The present study provides a framework for investigating the feasibility extended bioremediation during seasonal freezing through the prediction of soil temperatures and unfrozen water content in field-aged petroleum hydrocarbon-contaminated soils.

4 Summary and future studies

This preliminary study indicated sufficient unfrozen water availability during freezing in both simulated and measured soil data. In general, existing numerical tools for predicting temporal changes in the distributions of soil temperatures and unfrozen water contents are available and applicable to contaminated soils in pilot-scale biopiles. The significant retention of unfrozen water, which is likely required for maintaining microbial activity in partially frozen and frozen soils, was observed in both the simulation and measurements of unfrozen water content in the testing biopile. With future investigations of microbial activity, soil properties and on-site climate conditions, the simulation study may produce more accurate results. The current study implies the feasibility of predicting soil temperatures and unfrozen water availability using available numerical tools, which has particularly important implications for the planning and management of contaminated site remediation in remote and cold regions.

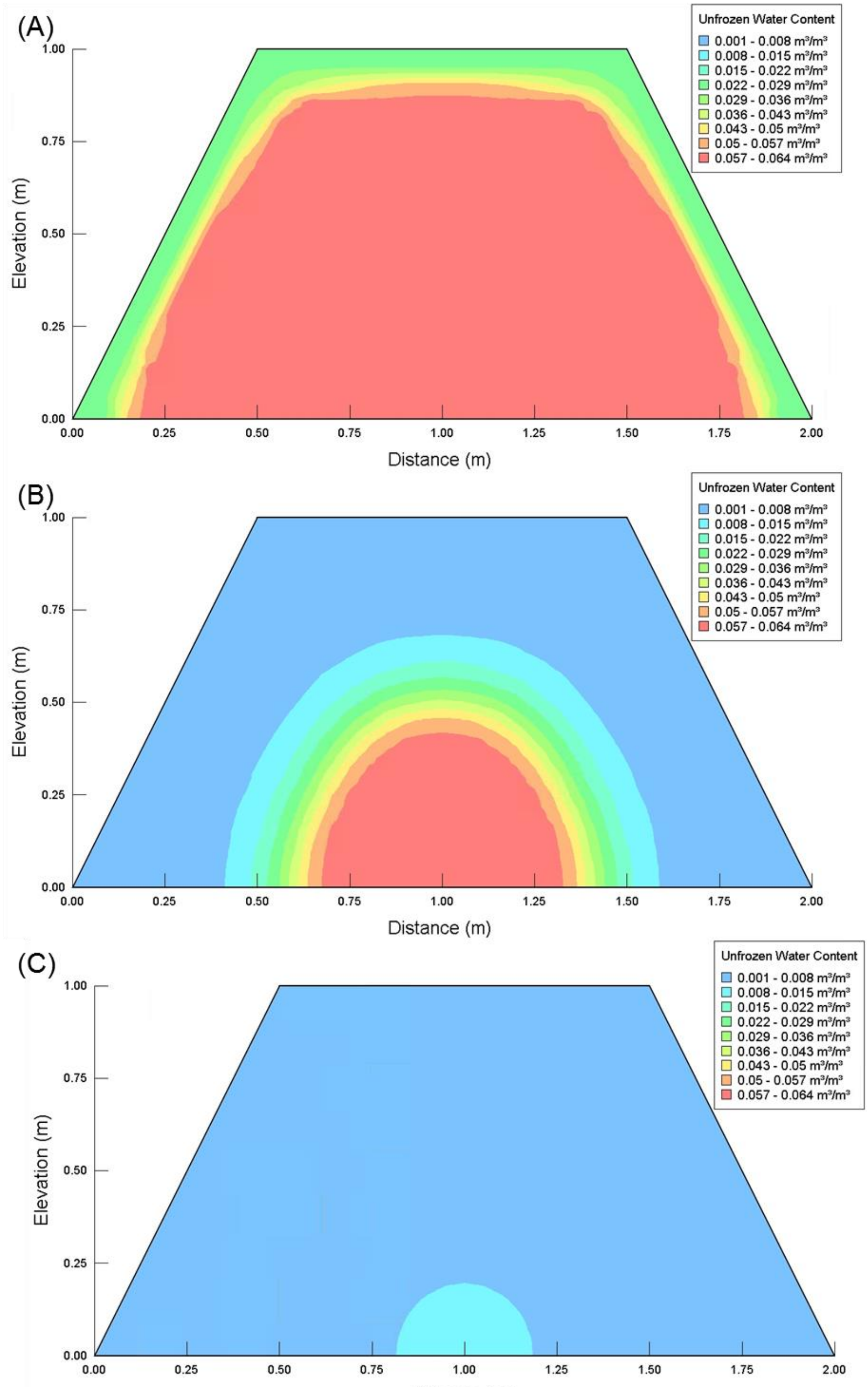

Figure 3: Results of the preliminary calibration of the TEMP/W model. The contour maps show simulated unfrozen water distributions at the end of October (A), in early November (B) and in the middle of November (C).

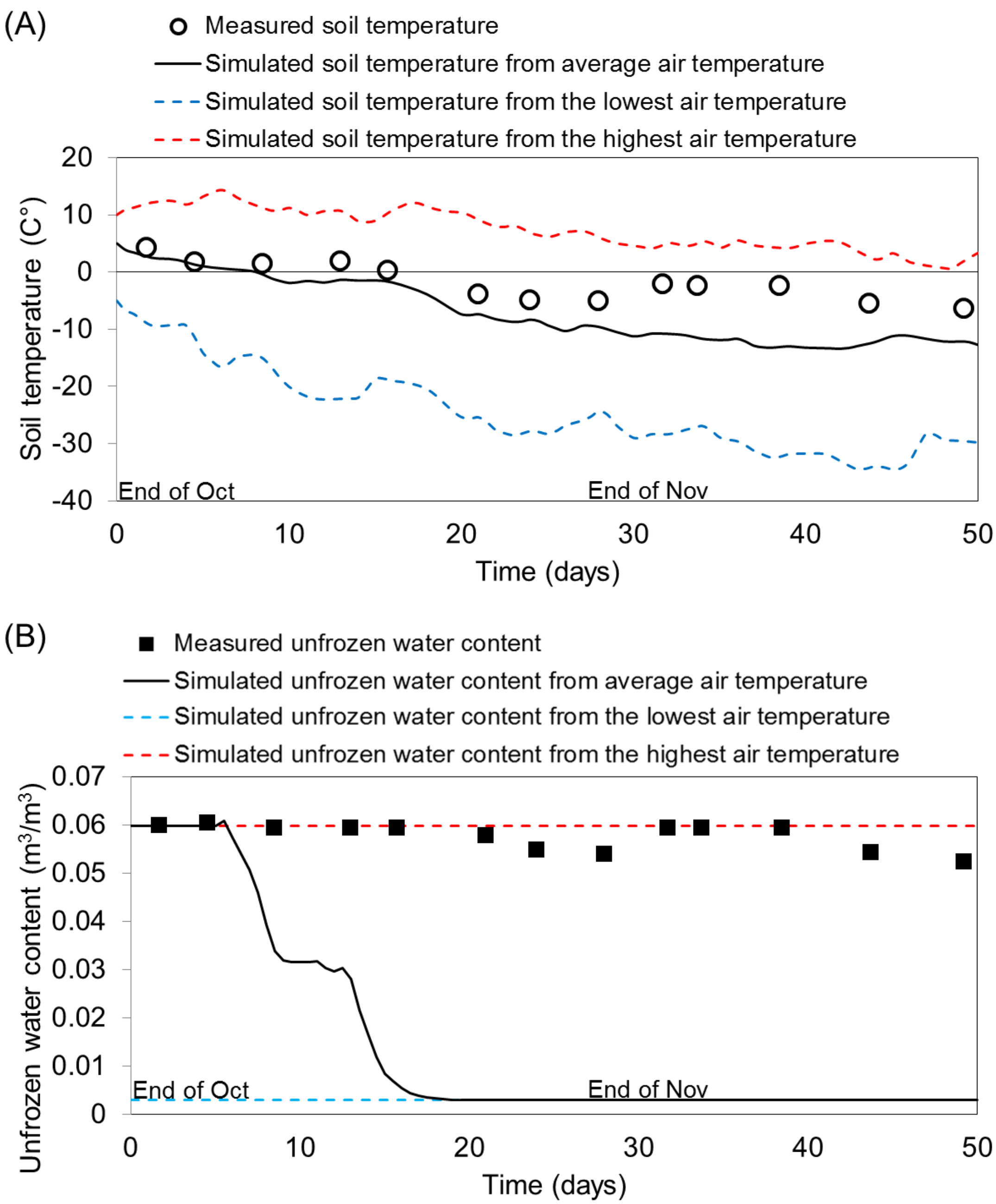

Figure 4: The preliminary comparison of the simulated data with the measured data (soil temperature and unfrozen water measurements from the end of October and November). The measured unfrozen water contents were obtained from a preliminary dummy biopile without the soil treatment and plastic cover. The plots show (A) soil temperatures and (B) unfrozen water content.

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