Influence of temperature on solute release from organic horizons in Siberian permafrost terrain

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Abstract
Solutes released from organic horizons in Siberian permafrost affected soils have a significant role for organic carbon sequestration by sorption onto mineral soils and for plant nutrition. Since ground temperature influences the solutes released through degradation of organic matter, organic carbon and major plant nutrients in water extracts of organic horizons under various temperature conditions ranging from -20 to 550°C were determined. Solutes release of the frozen sample was greater than those from the incubated samples at 25°C. The solution pH of the frozen sample was also lower due to dissociation of released organic acids. Destruction of plant tissue and microbial cell death and lysis by freezing probably increases solute concentrations. Heating the organic horizon samples up to 180°C drastically increased solutes release concurrent with low pH values. Thermal denaturation of organic materials can promote organic C solubilisation and cation and anion productions. Temperatures over 250°C made organic materials insoluble, resulting in less release of solutes and neutral pH values. Carbonization of organic materials in the temperature range between 250 and 550°C increases char products and hydrophobicity, resulting in less solute release. Seasonal freeze-thaw cycles and heating by forest fires strongly control dynamics of biogenic elements in the Siberian permafrost terrain.

Key Words
Permafrost, dissolved organic matter (dom), forest fire, Siberia, biodegradation

Introduction

Thick organic horizons are not only great carbon sinks (Prokushkin *et al.,* 2006) but also sources of biogenic elements through their biodegradation. High concentration of dissolved organic carbons (DOC) released from organic horizons can the retained by mineral soils by sorption processes (Kawahigashi *et al.,* 2006), enabling the soils in this region to be the greatest terrestrial carbon sink. Release of bases, N and P from the organic horizons probably contribute to net primary production in the taiga forest, and is also responsible for river water chemistry especially in the spring melt season (Pokrovsky *et al*., 2005). The greatest concentrations of solutes were probably produced through a freeze-thaw process in the organic horizon during winter to spring. Central Siberia has little rain fall and relatively high air temperature in summer, resulting in dry soil. The drying process of the organic horizons can also increase solute release after rewetting (Kawahigashi *et al*., 2008).

A high temperature ignition frequently attacks the organic horizons in central Siberia when forest fires have occurred. Usually ground fires with a low intensity of burning run on the forest floor, resulting in partial combustion of organic horizons. The heating conditions drastically change physical and chemical properties of organic horizons, affecting solutes released and composition.

The aim of this study is evaluation of solutes release using organic horizon samples prepared at a wide range of temperatures from frozen to igniting temperatures.

Methods

Sampling site

The study site was a mature Larch forest in the Kochechum River watershed (central Evenkia, Russia, 64° N, 100° E). The forest was 105 years old after the previous forest fire. Permafrost was found at 40 cm depth from the mineral soil surface. The permafrost table in the region prevents soil water percolation and drainage, keeping the soil moist, despite low precipitation of around 350mm in a year. The soil was classified as Oxyaquic Cryosol (WRB system) derived from the Siberian Basalt. The organic horizon consisting of Oi, Oe and Oa horizons had a 15 cm thickness due to the slow microbial decomposition under low soil temperature. Forest fires have often happened in this area. The forest fire in this region is a ground fire due to the low density of trees in the forest, affecting thickness and properties of organic horizons by burning (Ito 2005). Organic horizon samples were collected from the mature forest and the burned forest stands two months after the latest forest fire.

Sample preparation

Cubic samples composed of a 10 cm square bottom with a depth of the horizon were cut out from an organic horizon using a knife carefully taking care of contamination of minerals. Living mosses or lichens covering the organic horizons were removed from the samples for following experiments. After bringing back samples kept in an insulating bag, subsamples were kept in a deep freezer (-20°C). A subsample from the deep freezer was left in an incubator at 25°C keeping the field moisture for two weeks. Frozen subsamples after melting at the ambient temperature were kept in an oven set at 65°C for 4 days to completely desiccate the field moisture. The dried subsample were kept at 105°C in an oven for 24 hours and the other dried samples were kept in a muffle furnace for 15 minutes at 180, 250, 350, 430, 550°C, respectively. These nine subsamples prepared at different temperature were used for further experiments.

Water extraction and chemical analyses

Solutes from the organic horizons samples were extracted with ten fold amounts of water (W/V), taking into account the field soil moisture, at 25 °C for 24 hours without shaking. The same extraction was conducted for the frozen sample (-20°C) after defrost. After the extraction, pH values were measured immediately using a glass electrode. Extracts were obtained by filtration using 0.2 □m cellulose acetate membranes (Millipore Co Ltd, Tokyo). Filtrates were diluted with ultra-pure water to suitable concentration range taking into account analytical detection limits. Nitrate, chloride, fluoride, sulfuric and phosphoric anions were determined by injection of the diluted solutions into an ion chromatograph (Compact IC-761; Methorhom, Herisau, Switzerland). Base cations were determined by atomic absorption spectrometry (Z-5000; Hitachi, Hi-Tech, Tokyo, Japan). Total and inorganic carbon in the soil solutions were determined using a Shimadzu TOC-5000 analyzer (Shimadzu, Kyoto, Japan). Dissolved organic carbon (DOC) was calculated by subtracting inorganic carbon from total carbon.

Results and Discussion

Weight losses of the samples were not significant below 25 °C. Water vapour loss and organic matter combustion decreased the sample weight significantly at 65°C and 250°C respectively. Almost 60% of bulk samples were finally lost by an oxidative combustion at 550°C. Figure 1 A indicated the change in pH of the extract from each temperature sample. pH values were low around 4 at -20, 65, 105 and 180 °C. The solution pH was high at 25°C incubation. With increasing the heating temperature between 180 and 350°C, pH increased drastically, reaching pH 7. pH at the burned site was 5.17, indicating relatively higher pH compared to those of unburned samples incubated below 25 °C. An increasing trend of pH along with heating temperature has been confirmed by Prokushkin *et al.* (2007) using same Siberian organic horizons.

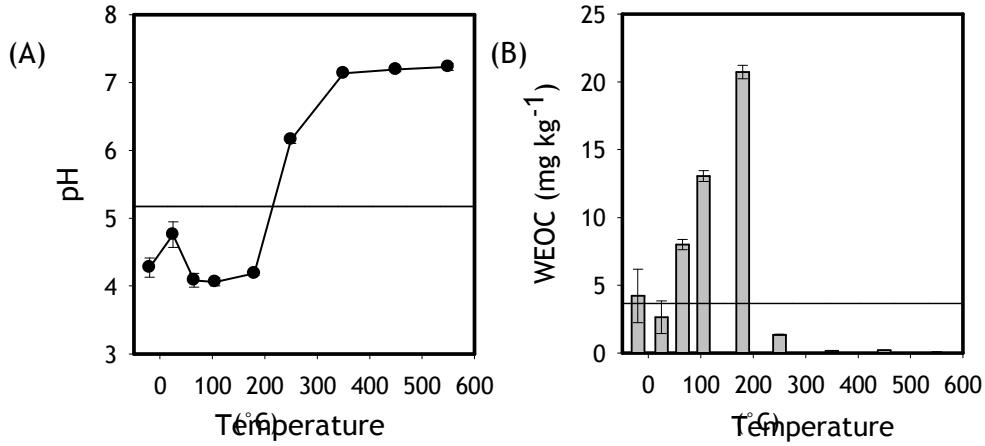

Figure 1. Changes in solution pH (A) and water extractable organic carbons (WEOC) (B) after incubation or oxidative combustion. The line in both figures indicates the values for an organic horizon sample obtained from the burned site 2 months after the latest forest fire which occurred in 2005.

Figure 1B showed WEOC (mg kg^{-1}) content of organic horizons. The temperature dependent of WEOC seems to be reciprocal to pH changes. Released protons from dissociated organic acids can decrease pH of the solution. Frozen samples release greater amount of WEOC compared to the incubated samples at 25°C. Biodegradation of WEOC at 25 °C probably decreased WEOC extracted. On the other hand, freezing promoted WEOC release probably due to plant tissue destruction, microbial death and cell lysis. Heating from 65 to 180°C increased WEOC almost twice to five times as compared to that at the 25°C incubation. Organic substances composed of plant tissues released through organic matter decomposition during the range of heating. Drying below 105 °C could also chemically denature organic horizons and contribute to the WEOC production. Water soluble organic C comprised a very small amount for samples heated over 250 °C that showed high water repellence. Organic horizons under the latest burned forest site released WEOC equivalent to the frozen unburned sample, indicating that physical-chemical properties of the burned organic materials had probably biologically changed after the forest fire.

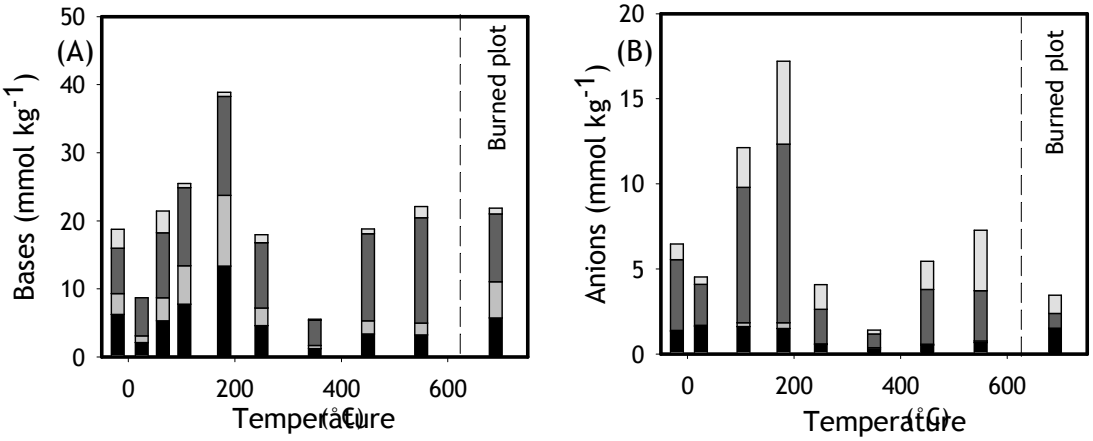

Figure 2. Changes in base cation content (A) and anion contents (B) in water extracts from organic horizons after incubation or oxidative combustions. Colour density of each bar indicate Ca, Mg, K and Na for bases and Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-} for anions from bottom to top. Bar of the right side is cation and anion contents from the burned site 2 months after the latest forest fire that occurred in 2005.

Sum of released base cations and anions are shown in Figure 2. Both temperature dependencies were similar. Frozen samples released greater amount of cations and anions as compared to the sample incubated at 25 °C. The higher the temperature up to 180°C is, the soluble ions. The lowest contents of released ions were observed at 350°C the same as for WEOC. The higher heating temperatures of 450 and 550 °C made more water soluble K and SO_4 than at 350°C. Potassium was the dominant soluble cation in all samples followed by Ca. In the anion compositions phosphate was dominant. Anions were always deficient to total charge of cations, indicating compensation by organic anions for the deficit (Nambu and Yonebayashi, 1999). The compositions of cations and anions in the solute from the 2005 burned site were different from laboratory burned samples (up to 250°C heating). Other field factors such as microbial activity, solar radiation, moisture and so on can chemically change burned organic materials in the field after the forest fire.

Conclusion

The organic horizons changed their solute release potential depending on temperature. Freezing promoted solute release probably due to destruction of plant tissues and microbial cell lysis. Despite drastic increase in solute production by the drying process up to 105 °C, the compositions of cations and anions were not largely different from those of frozen and 25 °C incubated samples. Incomplete combustion of organic materials at 180 °C enabled the greatest release of solutes. However, the high concentration of solutes can be easily flushed out by ground surface water flow, especially in early spring, because the composition and soluble organic C at the burned site was almost equivalent to the samples without heating. The ion composition and organic C release changed with heating over 250°C. Charcoal was formed under high temperature heating, making the carbon solubility of burned organic materials lower. On the other hand, potassium and sulphuric ions increased at the higher heating temperature. Potassium being abundant in larch leaves was easily released by the decomposition of litter under high temperature combustion. Ambient temperature of the organic horizons in the Siberian forest influences the physical and chemical properties of organic horizons, controlling the dynamics of biogenic elements in the Siberian permafrost ecosystems.

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