

Article **Hydrothermal Changes and Physicochemical Characteristics of Subtropical Subalpine Soils under Freezing and Thawing**

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Abstract: The soil column samples were collected for indoor simulated freeze-thaw experiments to monitor the soil hydrothermal dynamics and measure the basic physicochemical properties to research the effects of freeze-thaw on the hydrothermal process of peat bog soil and its relationship with physicochemical properties. The results indicate that in the initial phase of freezing-thawing, soil water content decreases and soil temperature changes, respectively. Unfrozen water content in soil in the stable freezing period decreases sharply. Compared with the freezing period, the fluctuation of soil moisture rate during thawing is more moderate with the temperature change. Soil ammonium nitrogen content decreases with decreasing soil temperature and is significantly positively correlated with soil water content after freeze-thaw, while total phosphorus, fast-acting phosphorus, total nitrogen and nitrate have no significant correlation with soil temperature and soil moisture content after freeze-thaw.

Keywords: freeze and thaw; hydrothermal process; soil characteristics; subtropical subalpine; peatland; soil temperature; soil moisture

1. Introduction

The soil freeze-thaw cycle is a repeated freeze-thaw process caused by diurnal or seasonal heat changes and is formed at a certain depth in the topsoil, and this phenomenon commonly occurs in high-latitude or high-altitude areas [\[1\]](#page-8-0). Soil freezing and thawing result in frequent phase changes in soil water, and consequently changes the thermal conditions and soil characteristics. During the soil freezing period, part of the liquid water transforms into solid ice. When the water content of soil is low, the potential of soil matrix declines [\[2\]](#page-8-1). Driven by the soil substrate potential gradient, the soil liquid water keeps moving towards the freezing front, resulting in a peak in soil water content at the freezing front of the soil [\[3\]](#page-9-0). The soil freezing front moves deeper gradually, forming a temperature gradient in the vertical profile of the soil [\[4\]](#page-9-1). Then, heat is transferred from a high temperature to a low temperature by this gradient force, and finally a complex waterheat exchange interface is formed [\[5\]](#page-9-2). In the thaw period, the solid water accumulated on the frozen front of the soil was transformed into liquid water [\[6\]](#page-9-3). Driven by gravitational gradient, water accumulation occurred in the vertical profile of soil [\[7\]](#page-9-4).

Seasonal freezing and thawing can alter soil moisture characteristics [\[6\]](#page-9-3). Many studies have shown that soil temperature affects water transport in freezing-thawing soils [\[8\]](#page-9-5). Soil freezing-thawing will promote the movement of soil moisture and move the unfrozen region to the frozen region [\[9\]](#page-9-6). At the freezing front of the soil, the oxygen content at the freeze-thaw interface is relatively low due to water migration and aggregation [\[10\]](#page-9-7), which accelerates the denitrification of microorganisms and causes the loss of nitrogen in a certain area [\[11\]](#page-9-8). The freeze-thaw cycle strengthens the water release which makes it easy for nutrients to accelerate the mineralization and nitrification rate of organic matter in the soil [\[12\]](#page-9-9). The freeze-thaw effect causes the death of a large number of microorganisms and the release of microbial nitrogen, which generates a large amount of nitrate and increases

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the nitrogen content in the soil [\[13\]](#page-9-10). Soil nitrogen content also changes as freeze-thaw dynamics change [\[14\]](#page-9-11). The effect of the soil freeze-thaw cycle will alter the physical properties of the soil, reduce the degree of compactness of soil aggregates, and the size of soil particles becomes smaller [\[15\]](#page-9-12), which will release soil ammonium nitrogen. Freeze-thaw alternation causes the release of phosphorus from soil solid phase to soil water, including the mineralization of organic phosphorus, etc. [\[16\]](#page-9-13).

Most existing studies focused on freeze-thaw dynamics limited in the area with a severe degree of freezing, such as Inner Mongolia, Qinghai-Tibetan Plateau, Hokkaido and the Rocky Mountain Region, USA [\[17–](#page-9-14)[20\]](#page-9-15). The freezing-thawing characteristics of this region are different from those of permafrost regions [\[21\]](#page-9-16). Due to the specificity of alpine peat bog soils, soil water and heat transfer characteristics under seasonal freeze-thaw conditions are unclear [\[22\]](#page-9-17). For low-latitude subtropical alpine peat bog areas, the peat accumulation rate is high due to the low temperature and wet environment all year round, and the freeze-thaw cycle caused by the diurnal and seasonal temperature difference will change the soil hydrothermal process, which makes the peat soil release a large amount of $CO₂$ when melting, thus affecting the regional microclimate. Therefore, the present study elucidates the effect of freeze-thaw action on hydrothermal processes in alpine peat bog soils.

Mid-to low-latitude subtropical subalpine peat wetland, unlike soil under severe freezing conditions, has unique hydrothermal processes due to the high rainfall and large diurnal temperature difference in subtropical mountainous areas. Seasonal freeze-thaw characteristics of subtropical high-elevation peat bogs differ significantly from those at higher latitudes [\[23\]](#page-9-18). The seasonal permafrost soil freezing and thawing process shows the characteristics of unidirectional freezing; seasonal freezing and thawing processes usually occur in early winter, from the surface layer of the soil freezing at night, to the daytime melting of the daily freezing and thawing cycle. With the decline in the average daily temperature, the freezing layer continues to deepen, reaching the maximum depth in early spring [\[24\]](#page-9-19). After that, due to the gradual warming of the temperature, the surface layer again appears. In the daily freezing and thawing cycle, the melting layer continues to deepen, while the lower interface of permafrost begins to melt slightly later than the surface layer; with the passage of time, the upper and lower melting fronts meet, and the soil is melted through [\[25\]](#page-9-20). However, in perennial permafrost areas, freeze-thaw alternation occurs mainly in the near-surface layer of permafrost, which is a seasonal thawing layer (thawing of permafrost with mean the average temperature is below $0^{\circ}C$), where soil thawing is unidirectional [\[26\]](#page-9-21). However, ground freezing is bidirectional, starting simultaneously from the ground and active layer bottom [\[27\]](#page-9-22). In subtropical high altitude rapid warming areas, seasonal freeze-thaw and freeze-thaw cycling processes occur frequently, soil cohesion decreases, porosity increases [\[28\]](#page-9-23), which may change soil hydrothermal process [\[29\]](#page-9-24). Previous studies have mostly focused on perennial permafrost regions or high-altitude seasonal freeze-thaw regions. Subtropical alpine regions have different climatic conditions than other cold regions. Previous studies have shown that in permafrost areas, the soil water content decreases at the beginning of freeze-thaw and the soil temperature changes rapidly. However, it is not clear whether the soil freeze-thaw processes in subtropical subalpine regions are consistent with those in cold regions.

Due to the key role of subtropical high-altitude peat bogs in regional climate change and the specificity of seasonal freeze-thaw processes under high-altitude conditions, the effects of freeze-thaw processes on soil hydrothermal and physicochemical in subtropical high-altitude peat bogs need to be further explored. The aims of the current study were: (1) to assess soil hydrothermal interactions under freeze-thaw, and (2) to assess the relationship between soil moisture and soil properties after freezing and thawing.

2. Materials and Methods

2.1. Study Area

The study was conducted in the Hundred Thousand Ancient Fields (HTAF), located in southwestern Hunan Province, central China (Figure [1\)](#page-2-0) [\[30\]](#page-9-25). It is in the mid-subtropical monsoon humid climate zone. The local average annual temperature is about 12–13 ◦C, and the average annual rainfall is 1800 mm. HTAF is a rare alpine marsh wetland in southern China. It is the headwaters of the Yuan and Pearl River, which eventually drains into Dongting Lake and is important for protecting the ecological security of Dongting Lake. It is also an important migratory corridor for migratory birds on the East Asia—Australasia flyway. HTAF is one of the few subtropical subalpine peat bog seasonal permafrost areas worldwide, with important implications for regional microclimate change.

Figure 1. Location of the study area. (**a**) Permafrost distribution area in China; (**b**) Location of the study site in Hunan Province, China; (**c**) Location of soil column A, B, C at the study site.

2.2. Experimental Method and Soil Collection

Samples were collected using peat column samplers at three selected sampling sites in the Hunan Nanshan Hundred Thousand Ancient Fields peat bog in October 2020, and the collected peat soil columns were cut according to the soil occurrence layer and peatland thickness. The division of soil column depth is shown in Table [1.](#page-2-1) The 12 soil samples were saved in 8 plastic bags and frozen. The sampling points in this study are evenly distributed within the study area and provide a good representation of the study area as a whole.

Soil samples were wrapped with filter paper around and at the bottom of each layer to reduce the exchange of water vapor with the outside world, and the soil samples were wrapped and put into the artificial climate chamber to start the freeze-thaw simulation experiment (Figure [2\)](#page-3-0). Soil hydrothermal changes were measured using a soil multiparameter recorder at each change in incubation temperature.

Figure 2. Soil samples.

2.3. Soil Analysis

Determination of soil total nitrogen, total phosphorus and nitrate nitrogen content by UV spectrophotometry. Soil fast-acting phosphorus content was determined by the sodium bicarbonate method. Measurement of soil ammonium nitrogen content was performed by the photometric method.

2.4. Statistical Analysis

Differences in soil hydrothermal process and soil characteristics were calculated with a Student's t-test in SPSS 13.0 (IBM, Armonk, NY, USA). The associations between soil hydrothermal process and soil characteristics were discussed with Pearson's correlation coefficient. The statistical inferences discussed below were analyzed using a significance level of *p* < 0.01.

3. Results

3.1. Changes of Soil Temperature

Figure [3](#page-4-0) gives information about soil temperature dynamics with incubation temperature for soil columns. We set the initial incubation temperature of the soil samples to 0° C. We raised the temperature by 5 °C every 4 h and lowered it to -10 °C for 8 h when the incubation temperature reached 15 ◦C. The trend of temperature change in different soil columns at each soil depth is generally the same; for soil column A, with the increase in incubation temperature, the temperature of soil at 50 cm depth and 120 cm depth increased, and the soil temperature reached 12.9 \degree C and 18.3 \degree C at the incubation temperature of 15 ◦C; the temperature of soil at 150 cm depth decreased at the incubation temperature of 5 ◦C to 10 ◦C, and decreased by 9.3 ◦C. Compared with the soil at 50 cm and 100 cm depth, the soil temperature at 150 cm depth changed more drastically. For soil column B, the soil temperature at the 50 cm depth was highest at an incubation temperature of 5 $°C$, with a maximum soil temperature of 20.4 $°C$. The soil temperature at the 150 cm depth changed most dramatically at an incubation temperature of 10 \degree C, with a soil temperature increase of 4.7 \degree C. For soil column B, the temperature of soil at the 50 cm depth was highest at an incubation temperature of 5 °C and the maximum soil temperature is 20.4 °C. For soil column C, the soil temperature increased with increasing incubation temperature at 50 cm, 150 cm, 200 cm and 250 cm, with the highest soil temperature at an incubation temperature of 15 ◦C. The soil temperature at 100 cm depth decreased at an incubation temperature of 0 \degree C and 5 \degree C, with the highest soil temperature of 16 \degree C at an incubation temperature of 0° C.

Figure 3. Soil temperature changes at different depths.

3.2. Changes of Soil Moisture

Figure [4](#page-5-0) shows the characteristics of soil water content of soil columns A, B and C from top to bottom with the change in incubation temperature. As can be seen from Figure [4,](#page-5-0) for soil column A, the soil water content at 50 cm depth was highest at the incubation temperature of 5 ◦C and lowest at −10 ◦C, and the soil moisture content was 29% and 18.3%, respectively; the soil water content at 100 cm depth presented a downward trend and then increased with the increasing incubation temperature, and the incubation temperature varied most drastically between 5 and 10 $\mathrm{^{\circ}C}$, and the soil water content increased by 16.7%. The water content of soil at 150 cm depth was highest at 10 °C and lowest at 0 °C, 16.4% and 2.5%, respectively. For soil column B, the soil water content at 50 cm depth did not have a significant variation when the incubation temperature rose. The soil moisture content at 100 cm depth was the highest at the incubation temperature of 0 \degree C, reaching 11.6%. With the increase in culture temperature, it shows a decreasing trend. The 150 cm depth soil water content was the highest at the incubation temperature of 0 ◦C and the lowest at the temperature of $-10\degree C$, and the soil water content was 2.7%, 11.4%, and $-10\degree C$, respectively. For soil column C, except for the depth of 50 cm, the soil water content at all depths showed a trend of increasing and then decreasing with the increase in incubation temperature. The soil moisture content at 150 cm depth showed the greatest variation, and it at all five depths was the lowest at the incubation temperature of -10° C.

Figure 4. Soil water content changes at different depths.

3.3. Soil Physicochemical Properties Changes

We measured the properties of the soil at different depths in three soil columns with a total of 12 sample points. From Table [2,](#page-5-1) it can be seen that the pH variation in the collected soil samples ranged from 4.20 to 4.86, which is acidic soil. The contents of total phosphorus, fast-acting phosphorus, total nitrogen and ammonium nitrogen in all three soil columns decreased with increasing soil depth, and the nitrate-nitrogen contents in soil column A and column C were the highest at 100 cm depth, 11.71 mg kg⁻¹ and 11.92 mg kg⁻¹, respectively. The range of total soil phosphorus was 0.94–2.93 mg kg⁻¹. Total phosphorus content was highest at soil column A of 50 cm depth and lowest at 250 cm depth in soil column C. The range of total nitrogen was 13.03–19.84 mg kg⁻¹. As with total phosphorus, total N content was also lowest at a depth of 250 cm in soil column C. Soil ammonium nitrogen content was highest at 50 cm depth in soil column C and lowest at 150 cm depth in soil column B. The content was 11.78 mg kg⁻¹ and 7.89 mg kg⁻¹.

4. Discussion

4.1. Hydrothermal Dynamic Changes

In this study, the freeze-thaw cycle period was delineated according to the experimental control temperature, and the freeze-thaw cycle process was divided into the initial freezing stage, stable freezing stage and thawing period, with incubation temperatures of 0–5 ◦C, −15–0 ◦C and 5–15 ◦C, respectively. We used indoor simulation to precisely control the incubation temperature with different freeze-thaw stages. During the beginning freezing stage, as the incubation temperature was reduced, the soil started to freeze and formed a temperature gradient, and some water condensed into ice [\[30\]](#page-9-25). At the same time, the unfrozen water content decreased, the water potential of the frozen layer of soil decreased, the soil suction increased, and the water potential of the non-frozen layer of soil increased relatively. Meanwhile, a gradient of unfrozen water content (soil water potential gradient) was formed, in which water flowed from the area of high soil water potential to that of low soil water potential [\[31\]](#page-10-0). During the stable freeze period, as soil temperature decreased, more soil liquid water was converted to solid ice and soil volumetric water content decreased. Compared with the stable freezing stage, the fluctuation of soil moisture content with soil temperature during the thawing period was relatively flat, which is mainly due to the potential heat release of phase transition from the phase change in moisture that makes the soil temperature gradient smaller [\[32\]](#page-10-1). From the above analysis, it is clear that temperature leads to moisture migration and phase change. On the contrary, soil water has a certain influence on temperature change as well [\[33\]](#page-10-2).

Studies in the Daxinganling Mountains have shown large changes in soil hydrothermal dynamics [\[34\]](#page-10-3). This may be due to the lower coverage resulting in the groundwater and heat exchange. At the same time, soil is also greatly affected by other factors including temperature, light and rainfall [\[35\]](#page-10-4). Soil hydrothermal dynamics in the Songnen Plain [\[2\]](#page-8-1), Loess Plateau [\[36\]](#page-10-5) and the Beiluhe area [\[4\]](#page-9-1) were relatively similar during freeze-thaw, and soil water content increased during thawing. This may be due to melting snow that seeps into the soil and increases its water content [\[37\]](#page-10-6). On the contrary, the soil water content decreased at the melting stage in this study, which may be due to the constraints of indoor conditions, not simulating natural rainfall to supplement precipitation and not considering soil water movement in the vertical direction. Comprehensive existing studies found that soil hydrothermal changes during the freeze-thaw period are greatly influenced by soil properties and the environment of the study area, and the change patterns are different (Figure [5\)](#page-6-0).

Figure 5. Characteristics of soil hydrothermal changes in different study areas.

4.2. Correlation Analysis of Soil Characteristics with Hydrothermal Changes

Due to the high water content of the soil in the area we are researching, it is difficult to collect soil samples under unfrozen conditions, and the amount of soil samples collected in this study are small enough to support multiple simulated freeze-thaw experiments, so only the physicochemical properties of soil samples after freeze-thaw cycles were measured, and the effect of soil physicochemical properties on hydrothermal changes after freeze-thaw action was analyzed. The results showed that soil ammonium nitrogen content after freezethaw decreases with increasing soil temperature, and soil water content was significantly correlated with ammonium nitrogen content (Table [3\)](#page-7-0). On the contrary, it was suggested that the soil ammonium N content was basically stable under different moisture conditions, i.e., ammonium N fixation was greater than nitrification when the soil was full of moisture and denitrification was stronger [\[38\]](#page-10-7). The reasons for the different results may be related to factors such as different study subjects and soil types, and the mechanisms need to be further investigated. In addition, this study found no correlation between the change in soil moisture and physicochemical properties during the initial and stable freezing periods. This is completely different from the thawing period. It shows that soil hydrothermal during the initial freezing period is not a direct determinant of soil property changes.

Table 3. Correlation of soil physical and chemical properties with soil temperature and moisture content after freeze-thaw.

Total soil phosphorus, fast-acting phosphorus, total nitrogen and nitrate were positively correlated with soil heat and soil moisture content, but none of them were significant (Table [3\)](#page-7-0). Some studies showed that the effect of water content on the release of phosphorus from frozen soils was more significant; the release of phosphorus from soils with high water content was higher, while the release of phosphorus from soils with medium and low water content was relatively low [\[38\]](#page-10-7). However, it also indicates that freeze-thaw has little effect on the phosphorus release capacity of soils with higher water content, but can significantly enhance the phosphorus release capacity of soils with lower water content [\[39\]](#page-10-8), and the changes in soil phosphorus are mainly due to periodic freeze-thaws that alter the supply of organic state phosphorus from dead soil microorganisms and plant residues [\[40\]](#page-10-9). Only one freeze-thaw cycle was conducted in this study, thus it may result in no significant change in soil agglomerate size and stability, and the soil surface area did not provide more adsorption sites for phosphorus adsorption. In addition, this study found that ambient temperature was the main extrinsic factor affecting soil freezing and thawing. Changes in soil moisture content due to freeze-thaw temperature are intrinsic to the freezethaw mechanism. Changes in soil water content not only cause direct physical damage to microorganisms, but also further induce ecological niche differentiation in microbial distribution. This has complex effects on microbial abundance, community composition and diversity, and these changes are likely to further affect their mediated nutrient element cycling functions.

Unlike other ecosystem types, the most abundant functional group of patchouliproducing microorganisms in the subtropical subalpine region is Acidobacteria, which are well adapted to nutrient-poor and acidic conditions. HTAF is a typical subtropical subalpine rainfed poor nutrient swamp with peat moss as the absolute dominant species. It has been shown that the relative percentages of Nitrospirae are high in nutrient-poor

swamps, and the lack of nitrogen nutrients makes microbial nitrogen fixation in subtropical subalpine peatlands very dependent on atmospheric nitrogen deposition processes [\[41\]](#page-10-10), Nitrospirae is able to oxidize ammonia to nitrite and thus further oxidize it to nitrate that can be used by plants. Although the anaerobic microbial activity of peat soils are inhibited in the frozen state, studies have shown that microorganisms are still active in the frozen state at $-16\degree C$ and will still play a degrading role as long as unfrozen water is present [\[42\]](#page-10-11). The total and organic nitrogen content of the soil is mainly derived from the freeze-thaw alteration of soil microorganisms [\[43\]](#page-10-12). In general, the higher the water content of the soil, the greater the effect of ice crystals formed during the freezing process on soil microorganisms [\[44\]](#page-10-13).

In this study, we found that soil ammonium nitrogen content was significantly correlated with soil water content during the thawing period. Previous studies have shown that differences in soil hydrothermal conditions and basic physicochemical properties can significantly influence the effect of freeze-thaw cycles on N_2O emissions. Therefore, soil physicochemical properties change significantly with water content during the thawing period compared to the initial freezing period and the stable freezing period. This affects the soil nitrogen cycle and may increase greenhouse gas emissions. Therefore, measures such as raising the groundwater level are recommended to mitigate greenhouse gas emissions during the melting period in subalpine soils.

5. Conclusions

- (1) In subtropical subalpine areas, the trends of soil temperature and water content change differently at different freeze-thaw stages, and change more slowly during the thawing period.
- (2) During the initial freeze-thaw period, soil hydrothermal trends in the subtropical subalpine region are consistent with those in the seasonal permafrost and permafrost zones.
- (3) Soil hydrothermal and physicochemical properties are intrinsically linked differently at different freeze-thaw stages. The soil ammonia nitrogen content positively correlated with soil water content after freeze-thaw. Total phosphorus, fast-acting phosphorus, total nitrogen and nitrate nitrogen showed no significant correlation with soil heat and soil moisture content after freeze-thaw.

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