



Effects of heating on composition, degree of darkness, and stacking nanostructure of soil humic acids



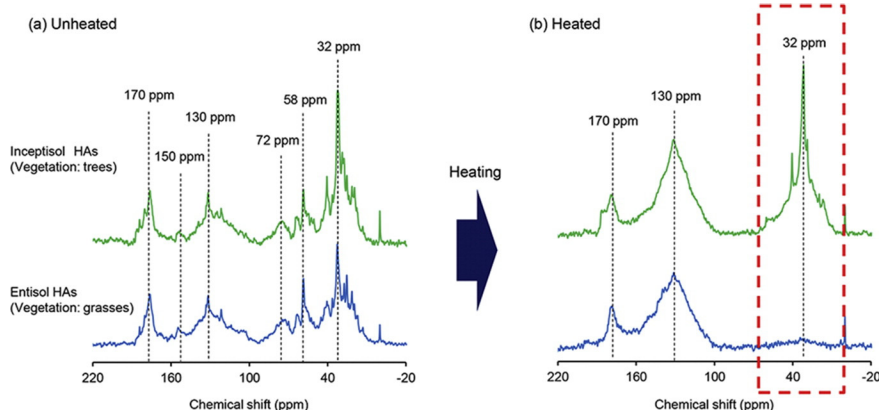
Naoya Katsumi *, Koyo Yonebayashi, Masanori Okazaki

Faculty of Bioresources and Environmental Sciences, Ishikawa Prefectural University, 1-308 Suematsu, Nonouchi, Ishikawa 921-8836, Japan

HIGHLIGHTS

- Darkness of humic acids increased with increasing heating time and temperature.
- Aromatic carbon content increased during darkening.
- Carbon and nitrogen stable isotope ratios of humic acids increased during heating.
- A stacking aromatic nanostructure developed during heating.
- Heat-induced changes in humic acid chemical structure depended on the source plant.

GRAPHICAL ABSTRACT



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ABSTRACT

Wildfires and prescribed burning can affect both the quality and the quantity of organic matter in soils. In this study, we investigated qualitative and quantitative changes of soil humic substances in two different soils (an Entisol from a paddy field and an Inceptisol from a cedar forest) under several controlled heating conditions. Soil samples were heated in a muffle furnace at 200, 250, or 300 °C for 1, 3, 5, or 12 h. The humic acid and fulvic acid contents of the soil samples prior to and after heating were determined. The degree of darkness, elemental composition, carbon and nitrogen stable isotope ratios, ^{13}C nuclear magnetic resonance spectra, and X-ray diffraction patterns of humic acids extracted from the soils before and after heating were measured. The proportion of humic acids in total carbon decreased with increasing heating time at high temperature (300 °C), but increased with increasing heating time at ≤ 250 °C. The degree of darkness of the humic acids increased with increasing heating time and temperature. During darkening, the H/C atomic ratios, the proportion of aromatic C, and the carbon and nitrogen stable isotope ratios increased, whereas the proportions of alkyl C and O-alkyl C decreased. X-ray diffraction analysis verified that a stacking nanostructure developed by heating. Changes in the chemical structure of the humic acids from the heated soils depended on the type of soil. The major structural components of the humic acids from the heated Entisol were aromatic C and carboxylic C, whereas aliphatic C, aromatic C, and carboxylic C structural components were found in the humic acids from the heated Inceptisol. These results suggest that the heat-induced changes in the chemical structure of the humic acids depended on the source plant.

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Abbreviations: AIF, alkali-insoluble fraction; FA, fulvic acid; HA, humic acid; SOM, soil organic matter; TC, total carbon; TRG, Ishikawa Forest Experiment Station; YGU, Experimental Farm of Yamagata University.

* Corresponding author.

E-mail address: n-katsu@ishikawa-pu.ac.jp (N. Katsumi).

1. Introduction

Soil organic matter (SOM), the major component of soil, plays important roles in providing nutrients to plants, in pH buffering, and in interactions with heavy metals and persistent organic pollutants (Hillel, 2007). SOM can be separated into humic substances and nonhumic substances. Humic substances are dark heterogeneous mixtures of structurally complex, high-molecular-weight aromatic and aliphatic components bearing many acidic functional groups with various pK_a values and having a wide molecular weight distribution (Yonebayashi, 1997). Humic substances, which are the major constituents of environmental organic matter, are believed to be biochemically and chemically synthesized in the environment from biomass constituents and their metabolites (Stevenson, 1994). Humic substances can be operationally divided into three main fractions according to their solubility in acid and alkali: the fulvic acid (FA) fraction, which is alkali- and acid-soluble; the humic acid (HA) fraction, which is alkali-soluble and acid-insoluble; and the humin fraction, which is alkali- and acid-insoluble.

The progress of humification is evaluated on the basis of increases in the degree of darkness, particularly for HAs (Watanabe and Takada, 2006). The degree of darkness of HAs increases with increasing aromatic C content (including condensed aromatic components), with increasing carboxyl group content, and with decreasing O-alkyl C and alkyl C contents (Ikeya et al., 2007; Watanabe and Takada, 2006; Yonebayashi and Hattori, 1988). In addition, humification is associated with the development of a stacking nanostructure and with increases in C and nitrogen (N) stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$, respectively), and these changes have recently been observed by means of newly developed analytical methods (Katsumi et al., 2015, in press). As humification progresses, HAs become more structurally and chemically stable and thus highly resistant to biodegradation (Yanagi et al., 2003), and the residence time of highly humified HAs sometimes exceeds 10,000 years (Yamada, 1986).

Wildfires and prescribed burning dramatically alter C cycling and storage in the ecosystem (Wadle et al., 2003). Fire alters the physical, chemical, and biological properties of soil (DeBano, 2000; Hart et al., 2005); the most commonly reported effects of fire are qualitative and quantitative changes in SOM (González-Pérez et al., 2004; Knicker, 2007). SOM undergoes pyrolysis, charring, and oxidation during burning (Certini, 2005). The transformations of HAs and FAs during wildfires have been modeled and studied in detail in the laboratory by Almendros et al. (1990) and González-Villa and Almendros (2003). These investigators heated HAs or FAs at 350 °C for various durations and made the following observations: heating results in (1) increased aromatic C content owing to aromatization of carbohydrates, (2) removal of oxygen-containing functional groups, (3) formation of heterocyclic N compounds, (4) reduction in the chain length of alkyl compounds, and (5) decreases in the amounts of FAs and HAs accompanied by increases in the amounts of humins and black carbon. These changes lead to the formation of weakly colloidal organic substances with enhanced resistance to chemical and biological degradation (Knicker et al., 2005). Such recalcitrant substances are important because they determine the long-term SOM content and C-sequestration ability of soils (Egli et al., 2012).

Forest fires typically produce temperatures ranging from 200 to 400 °C in the region from the soil surface down to a few centimeters below the surface (Gimeno-García et al., 2004). However, previous laboratory studies of the effects of heating on soil humic substances (Almendros et al., 1990, 2003; González-Villa and Almendros, 2003) have been carried out only at 350 °C, and the effects of temperatures of <350 °C on the quantity and quality of humic substances are not clear. Furthermore, how soil type and vegetation affect the changes in HA chemical structure due to thermal denaturation is also largely unknown.

The objective of the present study was to examine how the properties of humic substances in two different soils hosting different vegetation (an Entisol from a paddy field and an Inceptisol from a coniferous forest) were affected by heating at temperatures ranging from relatively

low to high. We determined the effects of heating on the quantity and quality of soil humic substances by analyzing their composition and chemical structure by means of conventional methods, as well as by a new technique developed by Katsumi et al. (2015, in press).

2. Materials and methods

2.1. Soil samples and heating conditions

Samples were collected from the A horizon of two mineral soils, an Entisol and an Inceptisol, hosting different vegetation in Japan (Table 1). The Entisol was collected from a paddy field at the Experimental Farm of Yamagata University (YGU); this soil originated from the alluvial plain of the Akagawa and Mogami Rivers. This area has been used as a paddy field for at least 300 years. The Inceptisol was taken from a coniferous forest at the Ishikawa Forest Experiment Station (TRG), where planted Japanese cedar (*Cryptomeria japonica*) has been the predominant vegetation for the past 80 years after oak forest (*Quercus serrata*) for about 300 years. A 10-kg soil sample was collected from each of four points in the two study sites, and the four samples from each site were mixed well. The resulting mixed samples were air-dried and passed through a 2-mm-mesh sieve. Fine roots and litter were removed from the samples with tweezers.

For the heating experiments, a 50-g portion of each mixed soil sample was placed in a ceramic crucible with a lid, and the crucible was placed in a muffle furnace (FO300, Yamato Scientific Co., Tokyo, Japan) and heated in a controlled manner at 200, 250, or 300 °C for 1, 3, 5, or 12 h. Samples were introduced into the muffle furnace after it had reached the target temperature. At the end of the heating time, the sample was allowed to cool to room temperature (ca. 25 °C) in a desiccator, the weight loss of the sample was determined by comparing the sample weights before and after heating, and then the sample was mixed well.

The total carbon (TC) content of each heat-treated soil sample was determined in triplicate by dry combustion with an elemental analyzer (2400 Series II, Perkin-Elmer Japan, Yokohama, Japan).

2.2. Composition of humic substances and degree of darkness

The HA and FA contents of each soil sample before and after heating were determined; and we used the methods of Ikeya and Watanabe (2003) to determine the A_{600}/C values of the HAs, where A_{600} is the absorbance at 600 nm, and C is the concentration of organic C ($mg\ C\ mL^{-1}$). To obtain the HAs and FAs, 45 mL of 0.1 mol L^{-1} NaOH was added to a soil sample containing 150 mg of C, and the mixture was continuously shaken for 24 h at room temperature under a N_2 atmosphere. The suspension was centrifuged at 2000 g for 10 min and the supernatant filtered through a Whatman GF/B glass fiber filter (nominal pore size, 1.0 μm ; Whatman International, Maidstone, England). Fine-grained materials were removed by centrifugation of the filtrate at 20,000 g for 20 min. The supernatant was acidified to pH 1.5 with 4 mol L^{-1} H_2SO_4 and allowed to stand overnight. HAs and FAs were separated from each other by centrifugation of the resulting suspension at 2000 g for 10 min.

The organic carbon content of the FAs in the supernatant was determined with a total organic carbon analyzer (TOC- V_{CSH} , Shimadzu, Kyoto, Japan) under acidic conditions after bubbling with N_2 gas. The HAs were redissolved in 0.1 mol L^{-1} NaOH, and the absorbance at 600 nm was measured with a UV-vis spectrophotometer (UVmin-1240, Shimadzu). The HA solution was diluted with 0.7 mol L^{-1} KH_2PO_4 , and the organic carbon content was determined with a total organic carbon analyzer. The carbon content of the alkali-insoluble fraction (AIF) was calculated as the difference between the TC of the soil samples and carbon contents of the HAs and FAs.

Subsequently, the HA solution was purified as follows: 0.3 mol L^{-1} HF/0.1 mol L^{-1} HCl was added to the solution, and the mixture was stirred for 5 h at room temperature to dissolve fine-grained minerals.

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