博士論文の要約

Application of TOT and BPCA methods to the reconstruction of past biomass burning from sediment archives

（熱光透過法およびベンゼンポリカルボン酸法を応用した堆積物記録からの過去のバイオマス燃焼復元）

北海道大学　大学院環境科学院
地球圏科学専攻
芦　松　（Lu Song）

Abstract

Behavior of black carbon (BC) is crucial for the earth's surface environment because it could cause global warming by absorbing sunlight in the atmosphere. BC is originated from incomplete combustion of biomass or fossil fuels. Robustness of BC to degradation in the natural environment (in soils or sediment) enables us to use BC as a proxy to study the frequency and burning temperatures of past wildfire events. Controlling factors for burning temperature has not been evaluated well.

Objective of this study is to understand factors controlling the thermal/optical/chemical/size characters of BC in relation to the variabilities of burning temperature, provenance and aging as well as the vegetation in the hinterland. For these purposes, BC was quantified as elemental carbon (EC) in coarse (>2 μm) and fine (<2 μm) fractions of sediment samples using a thermal optical transmittance (TOT) method, and their burning temperatures were estimated for bulk samples through measurement of composition of benzene polycarboxylic acids (BPCAs), molecular markers of fire residues, determined with high performance liquid chromatography (HPLC). Selected plants were experimentally charred to obtain standard charcoal samples, which were served as model BC materials to calibrate BPCA compositions to the pyrolysis treatment temperature.

Size dependencies of EC contents and thermal properties were compared with the contents and composition of BPCAs to examine the influences of sources, transport pathways, and burning temperatures of BCs contained in these sediment archives. The author also compared the thermal characteristics of BC determined by TOT method and BPCA compositions in order to verify the methods determining the amount and composition of BC in sediment archives.

1. Introduction

1.1. Environmental significance of black carbon

Black Carbon (BC) is the main solid product of fires, which is widely derived from biomass burning and fossil fuel combustion, such as agriculture, forest fires, and industrial production. The color of BC allows them to absorb radiant energy and potentially affects the climate. BC and minerals are combined to form stable particles, so that BC can be stored for long periods in environments.

1.2. Definition of Black Carbon (BC)

BC is a part of the various combustion residues, whose range of structures is often described as a continuum from partially charred plant materials that still retain their physical structure, to charcoal, soot, and ultimately graphite.

1.3. BC transportation from fire center to sediment

As a constituent of sediments, the diameter of the BC particles may retain the information of the fire source or the transport history of the particles. Various processes of BC deposition would be explained by the size of potential charcoal source areas, human activities, biological disturbances, atmospheric factors, and mechanical constraints. Previous studies have shown that micro charcoal comes from a wider area, while macro charcoal comes from local fire. However, there are very few data on BC concentration and particle sizes from marine sediment.

1.4. Detection and quantification of BC

Thermal optical transmittance analyses (TOT) has been widely used to quantify the BC content in aerosol samples, which could provide reasonable estimates of BC content in sediments. Referring to the previous research results, elemental carbon (EC) could be defined as the high-temperature component of the analyses, whereas organic carbon (OC) was the low-temperature component of the analyses. The benzene polycarboxylic acids (BPCA) method is another quantitative approach which could provide thermal characteristics of BC. This method has been also used to quantify the BC content in soil samples.

1.5. Forest fire temperature

Based on the type of biomass fuel and the location of the fire, the main pyrolysis temperature are concentrated on 350 °C, 550 °C and 850 °C. Ordinary temperatures in biomass burning are approximately 500 ~ 600 ℃, whereas canopy fires can be much hotter (> 800 ℃), and root smoldering can be much lower (< 400 ℃). Although the physical properties of charcoal from different biomass sources are similar, there are differences in thermal properties. Studies on BC from different plant sources are limited.

1.5. Objectives

1) Evaluation of the consistency between TOT and BPCA methods for BC quantification
2) Confirmation of BPCA applicability as a molecular thermometer to various plants collected in east Asia
3) Examination of the aging effect on old sediment archives (> 1 Million years)
4) Reconstruction of biomass burning magnitude, temperature, and fine BC emission in the east Asian region of the past.

2. Sediment cores

2.1. Site U1423 of the Japan Sea

Integrated Ocean Drilling Program (IODP) Expedition (Exp.) 346 Site U1423 is located in the eastern part of the Japan Basin at 41°41.95'N, 139°4.98'E, and was recovered from a 1785 m water depth. The sediment cores taken from Site U1423 extend from the Holocene to the early Pliocene and are dominated by clay, silty clay, and diatom ooze. Because the resolution of the initial age model is not high and one of the control points is ambiguous, the age model for U1423 was also revised. U1424 is located at the southeastern margin of the Japan Basin at 40°11.40′N, 138°13.90′E and is close to Site U1423. Both sites are under the influence of the first branch of the TWC. At Site U1424, GRA and NGR were tuned onto the LR04 benthic oxygen isotope stratigraphy by Tada et al. (2018). We projected this "U1424_LR04 tuned age" to Site U1423 based on the inter-site correlation using dark - light cycles from 0 to 75 m CCSF-D_Patched. From 75 m to 127 m CCSF-D_Patched, the GRA density of Site U1423 was directly tuned onto the LR04 oxygen isotope stratigraphy. The 109 samples between 0 and 200 m CCSF-D_Patched were collected for this study, which covered the last 4.3 Myr.

2.2. Wakasa Bay KR15-10 Sites WB6 & 8

Site WB6 is located in the Wakasa Basin at east of Wakasa sea knoll chain (36°54.2898’N, 135°10.5428’E), with its water depth of around 845 m. Site WB8 is located at the flat sea floor in the Oki Trough (36°54.2898N’, 135°10.5428’E), which is a ENE-WSW oriented bathymetric depression in the southern Japan Sea, with its water depth of 1738 m.

2.3. Lake Suigetsu SG-12

Lake Suigetsu is one of the Mikata Five Lakes located in the southern part of the Fukui Prefecture in central Japan. A short gravity core named SG12-LM3 with a length of approximately 25 cm was recovered from the central part of Lake Suigetsu using a Limnos core sampler on July 6, 2012. The accurate high resolution age model is based on radionuclide concentration and varve counts. The 118 data of elemental carbon (EC) concentration in the coarse (>2 μm) and fine (<2 μm) fraction for SG12 core covering the last 15 kyr were cited from Nakai (2016MS). The 15 samples out of these 118 samples between 0 and 16 m were selected for BPCA analysis in this study.

3. Methods

3.1. Thermal optical transmittance (TOT) measurement

The samples were dispersed in milli-Q water and separated into <2 μm (fine fraction) and >2 μm (coarse fraction) by the repeated settling method. The analysis was conducted using a Semi-Continuous OCEC Carbon Aerosol Analyzer manufactured by Sunset Laboratory at the Institute of Low Temperature Science, Hokkaido University. This apparatus is equipped with a thermal optical transmittance (TOT) system that uses a highly sensitive analytical method for determining the contents of EC. Analytical errors were introduced during the determination of carbon amount and the distinction of OC and EC.

3.2. Benzene polycarboxylic acids (BPCA) measurement

BPCAs contained in about 0.5 mg of finely powdered bulk sample were extracted using 0.5 ml HNO3 (65%) followed by solid phase extraction and re-dissolution in mobile phase A (Dittmar, 2008). BPCAs were analyzed with a Agilent HPLC system (Agilent 1260), equipped with an auto sampler, sample and column coolers, and the photodiode array absorbance detector (absorbance spectra (190–640 nm)). Quantification operated with Agilent Open LAB CDS ChemStation software. Only the peaks of pyromellitic acid (1,2,4,5-B4CA) were quantified as B4CA. We quantified total BC concentration of the samples as BPCA sum, all the BPCA concentration data was calculated without using the conversion factor 2.27 or even higher 4.5.

4. BPCA methods used as molecular thermometers

4.1. Preparation of standard charcoal

Confirmation of BPCA applicability to molecular thermometers to various plants collected in potential charcoal source area (PCSA). Therefore, this study selected five different plants to quantify their thermal properties, including four Japanese native plants and one Arctic tundra plant. Such a combination of plant species are intended to compare the thermal characteristics of the coarse BC produced by the local fire in the Japanese archipelago with the thermal characteristics of the BC of the remote fire. Wood / leaves-charcoal were produced from plants chips by combustion at 240 ℃ in the muffle furnace followed by pyrolysis under nitrogen gas flow at the temperatures of 350, 550, and 850 ℃ for 1 hour.

4.2. B6CA in standard charcoal

We quantified total BC concentration of the standard pyrolysis charcoal as BPCA sum. B5CA and B6CA are majority of BPCA sum at any time. Regardless of plant species or parts, relationship between B6CA (%) and pyrolysis temperature is consistent. The strong positive correlation between B6CA and pyrolysis temperature suggests that temperature is a first-order control on B6CA (%). Therefore, we recommend to use the B6CA (%) as a proxy of biomass burning temperature in the past.

5. Comparison between TOT and BPCA methods

We provide TOT and BPCA analyses to assess their ability to quantitatively record BC content in various sediments. When the BC concentration is high, the results of the two methods show relatively large differences. BPCA could be mainly extracted from fine EC. BPCA results show that the effect of carbonation on fine EC may be very limited. Fine particles of BC can be transported away from fire center and they have a larger specific surface area. A larger specific surface area can increase the efficiency of nitric acid oxidation, and BPCA has a higher yield. Namely, charcoal / soot ratio may control the EC / BPCA sum, and previous studies using the BPCA method may have underestimated the BC content in the sample (soil or sediment). Significant aging effect or diagenetic decomposition of BPCAs did not occur, and the BPCA method may be more sensitive to aged samples. For long-term aging sediment samples, the BPCA method can be used to quantify the BC content better than the TOT method. The effect of aging on B6CA (%) was not significant, this also means pyrolysis temperature of BC could be estimated from B6CA (%).

6. Application to sediment archives

6.1. Application to surface marine sediment

The surface sediments from Wakasa Bay show very low concentration of BPCA and EC, despite this, the far away from land site (WB8) is have a higher concentration of BPCA and EC than the close to land site (WB6). The thermal characteristics indicate that the combustion temperature of BC at WB6 is much lower than WB8. Unlike Lake Suigetsu's stable immersion environment, Japan Sea's submarine terrain has a large depth variation over very short distances, and the water flow rate is much faster than Lake Suigetsu. This also explains the low content of fine EC in the sediments of Wakasa Bay and U1423. This phenomenon at surface marine sediment may be explained by the differentiation of BC during transport due to particle diameter. There is another possibility that the BCs of WB6 and WB8 are from different fire center areas.

6.2. Application to deep marine sediment

EC in the coarse (> 2 μm) fraction are 5-10 times higher than those in the fine (< 2 μm) fraction. The content of coarse EC is steady in Subunit IIB (>3.0 Ma), whereas the contents of BPCA sum and fine EC shows significant fluctuations in the same subunit. The BPCA sum content showed two frequent biomass burnings at 2.3 Ma and 3.7 Ma, but the total EC content showed very limited biomass burning at those intervals.

Fine EC content varies independently from coarse EC content, which suggests a remote origin of fine EC. Taking into account the fact that the fine particles could be transported over long distances as aerosols, unusually high contents of fine EC suggest contributions from remote fires. Therefore, fine EC and Asian dust could have similar transport processes. Based on modern aerosol research and high-resolution variations in aeolian dust research, eastern and northwest China and Mongolia could be sources of fine EC. Strong westerly winds can carry large amounts of fine particulate matter over long distances and could finally deposit them in the Japan Sea. Considering that the main BPCA is derived from fine EC, it is possible that remote fires are very frequent at 2.3 Ma and 3.7 Ma.

The maxima events in fine EC / coarse EC occurred during interglacial intervals. In interglacial stages, large-scale terrestrial vegetation could provide ample loads of fuel and higher chances for ignition events, where lightning might be a main ignition trigger. When precipitation exceeded a threshold, it may suppressed or promoted fires. Such large-scale biomass burning at a remote fire site could have served as a fine EC supply for Site U1423.

Under normal circumstances, the amount of coarse EC is much higher than that for fine EC. Changes in wind strength could significantly affect fine EC flux. Therefore, these exceptionally high fine EC contents suggest a special condition of enhanced winds during particular glacial stages. The wind strength or direction during glacial stages could also affect the change in charcoal deposition. Although the fine EC concentration increased during those particular glacial phases, it does not necessarily mean that the biomass burning or fuel load had increased. The strong winds could have carried land-deposited EC particles into the ocean.

The total pollen number was a proxy for the volume of terrestrial vegetation that could be a major part of biomass fuel load for fires. A larger biomass or high biomass fuel load could be a first-order control on coarse EC supply. The relationship between total number of pollen and fine EC content shows no significant correlation. Data based on total pollen number shows that high values for volume of terrestrial vegetation occur in interglacial periods. And the fire temperature estimated from B6CA (%) indicate that they have frequent high temperature fire events in interglacial periods, while the low temperature fire events in glacial periods.

With a longer time scale and a wider range of sources, the biomass fuel loads controls changes in fire temperature. High-temperature paleofires occurred more frequently during interglacial stages in Northern Asia. Because the burning at high temperatures with high level of biomass fuel loads is difficult in a cold and dry environment, the sizes of biomass fuel loads during glacial times might have been very small and were insufficient for large-scale biomass burning or high-temperature burning.

6.3. Application to lake sediment

The younger sediments from Lake Suigetsu (SG12) have high concentration of BPCA and EC. BPCA sum and Fine EC was dominated during the early stage (15~10 ka), and coarse EC increased during the later stage (10~0 ka). The high coarse EC content at 4 ka may be derived from increased human activity. The high concentration of BPCA sum and fine EC in the early stage (15~10 ka) benefited from the supply of remote fires, which was the high fuel load at the remote fire point at that time.

The fire temperature estimated from B6CA (%) indicate that they have frequent high temperature fire events in EASM strong periods, while the low temperature fire events in EASM weak periods. When EASM is strong, East Asia is warm and humid, and the fuel load is relatively high, which is more conducive to high-temperature fire events. The fact that long-term continuous precipitation induced frequent local flood events that inhibited high-temperature fire events. Extremely high precipitation will inhibit the occurrence of local fires, which is also reflected in the reduction of coarse EC concentration. This tendency is consistent with the situation at U1423, which means that the fuel load and the wildfire temperature are positively correlated.

7. Conclusions

In this study, the author compared the thermal characteristics of TOT and BPCA methods, constructed a molecular thermometer using various plants collected in east Asia, examine the aging effect, and, then, reconstructed the biomass burning magnitude / temperature for various sediment archives.

7-1 TOT and BPCA methods could quantifies changes in BC content although it turned out that BPCA could be mainly originated from fine EC.

7-2 B6CA% could be used as "molecular thermometers" for east Asian plants as well.

7-3 An aging effect are not significant for BPCA and fine EC in old sediment archives.

7-4 The volume of terrestrial plants (fuel loads) could be a main controlling factor of fire intensity, which affected the burning temperature.