

主論文の要約

学位論文題目:

Determination of the chemical structures of atmospheric organic aerosols and their light-absorption and fluorescence properties based on solvent extraction

(溶媒抽出に基づく大気有機エアロゾルの化学構造及び光吸収・蛍光特性の決定)

所属: 大学院環境学研究科 地球環境科学専攻

氏名: CHEN Qingcai

Summary

Organic compounds constitute a large fraction of aerosols in the atmosphere. Their presence influences on the properties of the aerosols, thereby affects the role of aerosols in climate and human health. Characterization of the chemical structures of organics is important for understanding their sources and properties. However, the entire structural characteristics of the organic aerosol components remains poorly characterized to date because they are comprised of a wide variety of compounds. Brown carbon in organic aerosols has an ability to absorb light at visible and near-ultraviolet (UV) wavelengths. Brown carbon therefore potentially plays important roles in photo-initiated reactions of organic aerosols and thus in the macroscopic-scale radiative balance of the Earth. Characterization of brown carbon is important to gain insight into their source and formation processes, and to examine the estimates of the direct radiative effect by brown carbon in model simulations.

This study applied fractionation methods for organic aerosol components according to their solubility and polarity using solvent extraction and solid phase extraction (SPE) methods, in order to understand the chemical-structural characteristics and optical properties of complex organic aerosol mixtures. This approach makes it possible to characterize different organic components with multiple analytical techniques and thus to understand the relationship between the chemical-structural characteristics of organic aerosols and their properties. Based on this method, this study aimed at revealing the followings: (1) the chemical structures of total organic matter in total suspended particulates (TSP) collected in the city of Nagoya in summer/early autumn and winter; (2) the light-absorption and fluorescence properties of total organic matter in the TSP samples; (3) the chemical structures and light-absorption of water-insoluble organic mixtures (WISOM) in the submicron aerosols ($PM_{0.95}$) collected in Nagoya; and (4) the light-absorption and fluorescence properties of water-soluble organic matter (WSOM) in $PM_{0.95}$ collected in urban, forest and marine environments (Nagoya, Kii Peninsula, and the tropical Eastern Pacific).

For the first and second objectives, a combination of solvent extraction and reverse-phase SPE was used to extract and fractionate organic compounds with different polarities in the TSP samples (WSOM, WISOM, two fractions of humic-like substances, showing neutral and acidic behavior (HULIS-n and HULIS-a, respectively), and the remaining highly-polar part of WSOM). Their chemical structures and optical properties were obtained from the high-resolution aerosol mass spectra (HR-AMS spectra), soft ionization mass spectra, Fourier transform infrared (FT-IR) spectra, UV-visible absorption spectra and the excitation-emission matrices (EEMs). Nearly total aerosol organics were collected from the urban TSP filter samples using multiple solvent extractions (water, methanol and a mixture of methanol and dichloromethane) and separation using an Oasis HLB column. Then the mass fractions,

elemental composition, average molecular weights, mass fractions of chemical functional groups, and the optical characteristics (i.e., MAE, Å, fluorescence efficiency and relative contribution of the fluorescence components) of the organic components respective fractions were determined. The WISOM and HULIS-n, the less polar fractions of the organics, accounted for large fractions both of the masses (mean: 70%) and the total light-absorption (mean: 84% at 400 nm) of the total organics in the urban TSP. Correlation analyses between their optical characteristics and chemical structures indicate that organic compounds with oxygen and nitrogen atoms may contribute largely to the total light absorption and fluorescence of the organic aerosol components.

For the third objective, the WISOM in the urban PM_{0.95} were fractionated to six sub-fractions using solvent extraction and normal-phase SPE. The structural and light-absorption characteristics of these sub-fractions were then determined using multiple analytical techniques including HR-AMS and FT-IR analyses. The characteristic compounds in the six sub-fractions of WISOM in the PM_{0.95} samples were aliphatic hydrocarbons, phthalic acid esters, aliphatic nitrates and esters, esters, alcohols, ethers and ketones, phenols and quinones, and carboxylic acids and carboxylate esters. The MAEs of relatively more polar organic fractions were much higher than those of relatively low and non-polar organic fractions. The high MAE values of organics may associate with compounds containing aromatic structures and heteroatomic functional groups (containing oxygen and/or nitrogen atoms) and compounds with high molecular weights.

For the fourth objective, chemical-structural and optical characteristics of WSOM in urban, forest and marine PM_{0.95} samples were investigated based on EEMs and HR-AMS spectra. The origins of water-soluble brown carbon were inferred from the signatures in the HR-AMS spectra and EEMs, and from hierarchical cluster analysis and backward air mass trajectory

analysis. The results show that fluorescence components in the HULIS and protein-like organic matter are ubiquitous classes of water-soluble chromophores in different types of aerosols, and their relative abundances are highly variable depending on locations and time periods. The results indicate the differences of their origins and formation processes. The EEM components of HULIS-1 and HULIS-2 were associated with highly and less-oxygenated structures, respectively. Whereas HULIS-1 was ubiquitous in water-soluble chromophores in different environments, HULIS-2 was abundant only in terrestrial aerosols.

The analytical methods used in this study provided quantitative information on the chemical-structural and optical characteristics of atmospheric organic aerosol components from low- to high-polar compounds, which comprised the total organic matter. Application of this approach to the characterization of other types of aerosols in different environments may provide further insights into the concentrations, structural characteristics, sources and formation processes. The obtained values of MAE and \tilde{A} can be used as inputs for atmospheric radiative models and can be used to examine the estimates of the direct radiative effect by brown carbon in model simulations. The results from the correlation analysis of the light-absorption and fluorescence properties of organic matters against their chemical structural characteristics are useful for understanding the reaction pathways that lead to the formation/loss of chromophores and for further classification and source identification of brown carbon.