B-8 Studies on the effects of organic aerosols on regional and global climate (Abstract of the Final Report)

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1. Introduction

In addition to the effects of green house gases effects of aerosol, ozone, SOx, and other species on global climate and the trends of their concentrations are important and urgent problems in the studies on global warming. Although aerosols, in particular, are known to have a significant impact on radiative forcing, which controls global as well as regional climate, the information about the effects of aerosols is yet very limited compared to that for green house gases. It is mostly due to the difficulty to fully understand the processes of emission, growth, transformation, transport, and deposition of aerosols in detail and to the complicated situation of radiative forcing caused by aerosols to be dependent on not only spatial distribution but also size, shape, and chemical composition. In order to make a precise estimation of future global warming it is necessary to precisely evaluate the radiative forcing caused by aerosols by taking into account the various conditions of aerosols. On the other hand, dense haze layer up to 3 km altitude was found, recently, covering a large area of south-southeast Asia; named as Asian Brown Clouds, Asia (ABC). This haze is mainly composed of sulfate, nitrate, organics, and black carbon. Carbonaceous aerosols were pointed out to reach even Japan on the basis of model analyses from Southeast Asia beyond China. Since such air pollution transported long range has a possibility to give various environmental impacts to many countries in East Asia, it is important to investigate from a point of view of global and/or regional scale and to look for the way to solve the problem.

2. Research Objectives

In order to make precise estimates of future global warming, amount of information about organic aerosols and its reliability are insufficient. Aerosols named ABC are mainly composed of organic compounds, whereas there are a lot of things remained unclear

concerning ABC aerosols. For example, formation mechanisms, spatial distribution, transport processes, and impacts on the climate change are not yet well investigated. Therefore, organic aerosols contained in ABC were set as an important target of this study. The objectives of this study are to elucidate the formation mechanisms for the aerosols covering south-southeast Asia, to clarify the spatial distribution and transport process, and to analyze the effects on the climate change.

3. Results and Discussion

(1)Studies on the transport and radiative forcing of organic aerosols

1. Model studies on the transport and distribution of aerosols in south-southeast Asia

In this sub-theme we have developed a model to estimate the global distribution of aerosols which have many kinds of sources such as anthropogenic and natural sources. The purpose of this modeling study is to clarify the large scale spatial distribution of aerosols which cover South-Southeast Asia and their transport processes.

Effect of aerosol particles on global warming, i.e. mainly cooling and, in certain situations, warming, is considered roughly in two aspects of "direct" and "indirect" influence on radiation balance in the atmosphere. Because of not simple relationships among nature of aerosol particle, such as size, chemical composition, etc., cloud microphysics, and atmospheric dynamical field, "correct" quantitative evaluation of the "indirect" effect is, in particular, difficult, and its result tends to have large uncertainty. To reduce this uncertainty partially, we are developing AGCTM (Aerosol Global scale Chemical Transport Model) which can explicitly describe source-receptor relations on various chemical species forming aerosol particles. By using the model, we have performed numerical simulation of transport/chemistry/deposition of aerosols and other chemical species during 20 Feb to 31 Mar in 2001 on the occasion of TRACE-P campaign. Performance of our AGCTM has been evaluated mainly by comparing the calculation results with TSP (Total Suspended Particulates) concentration at various observation sites all over China.

2. Studies on radiative forcing of organic aerosols

In order to investigate the climatic impact of Asian originated air pollutants over the North Pacific Ocean, atmospheric aerosols have been monitored at a site on a mountain (240 m m.s.l.) in Chichi-jima Island, Japan, located 1000 km south of the mainland Japan and about 1800 km east of the Asian coast. At the same time, aerosols were collected at 1100 m hill site in Jeju Island, Korea, and at the summit of Mt. Fuji, Japan.

Concentration of black carbon (BC) exhibited prominent seasonal variation, i.e., high in winter to spring and low in summer to early autumn. High concentration of BC is conveyed with the passage of cold fronts, which consists the intermittent transport over the region. The seasonal variation of single scattering albedo ω_o, which determines the aerosols' ability to cool/warm the earth, reflected that of black carbon (BC) aerosol concentration, showing low values (around 0.9 at 550 nm) in the high BC period during

winter-spring season, and high values (>0.98 at 550 nm) in the low BC period in summer. In the either period, values of ω_0 occasionally showed sudden decreases that correspond to the transport of polluted air mass. The chemical analysis procedures of Polycyclic Aromatic Hydrocarbons (PAHs) were improved so that the concentration in pg m^{-3} level typically found in aerosols at Chichi-jima Island can be determined. Concentration PAHs was high in winter period both in Jeju and in Chichi-jima Island. With he rations of the species of PAHs, organic aerosols originated from industrial sources and biomass-burnings were fractionated according to the season.

An intensive field campaign was conducted in the winter of 2004 to obtain detailed aerosol optical properties, aerosol vertical profile in the lower troposphere, vertical profile of relative humidity, and mass size distributions of aerosol components. During the intensive period, notable aerosol transport event accompanied by the cold front passage was observed. The comprehensive data set for the radiation transfer calculation was obtained for this transport phenomenon.

3. Transport and concentration distribution of carbon monoxide due to biomass burning

Steady observation has been carried out in the northern tip of Okinawa Main Island where the atmosphere is free from pollution due to the local human being activities such as carbon monoxide, ozone, and hydrocarbon. The purpose of the observation is to elucidate mechanism of long-range transport process from the Chinese continent. Carbon monoxide concentration was different for each air mass category: highest in the air mass from Chinese direction and second highest from Korean direction. On the other hand, ozone showed almost the same concentration for Chinese, Korean, and Japanese air mass categories during winter. In spring, ozone concentration is the highest in Korean category. To identify the origin of the polluted air, volatile organic carbons were analyzed. They showed different concentration change probably caused by the difference of their origin. More frequent measurements will help the identification of the origin of polluted air masses.

In order to get information about the dynamical behavior of carbon monoxide due to biomass burning in Asia, we set three sub-themes as 1. Analysis of long term observational data obtained at remote area in Japan, 2. Influence of Siberian forest fire, and 3. Oxidation capacity in maritime air. Obtained results are as follows. Seasonal variation of VOC concentrations in mid and higher latitude is determined in terms of OH field. Okinawa is well affected by the air pollution from the Continent except summer season. Especially sporadic high ozone and CO due to the emissions from the Continent were occasionally observed according to the passing the low pressures. VOC concentrations observed at remote islands are found to be controlled by mixing with background air in the Ocean. Judging from VOC and CO analysis, pollutants contain urban type air pollution rather than bio-fuel burning. Highly reactive VOCs are observed in mid Ocean due to biogenic activities. This finding suggests that DMS oxidation by OH radicals may be affected by reactive VOC emission in the Ocean.

(2) Studies on characterization of organic aerosols

1 . Observation studies of chemical characteristics of aerosols

In order to understand both concentration levels and chemical compositions of aerosols in East Asia, we measured aerosol at Fukue Island (128.5°E, 32.5°N), using an Aerosol Mass Spectrometer (AMS)[1] produced by Aerodyne Research Inc. The aerosol aerodynamic diameter was measured by a Time-of-Flight (TOF) measurement and chemical compositions are analyzed by a quadrupole mass spectrometer. A PM2.5 cyclone was used to cut off larger particles such as dust. From October 2003, aerosol measurements by the AMS began at Cape Hedo, Okinawa (129°E, 27°N) in order to monitor both concentration levels and chemical compositions of aerosols in East China Sea.

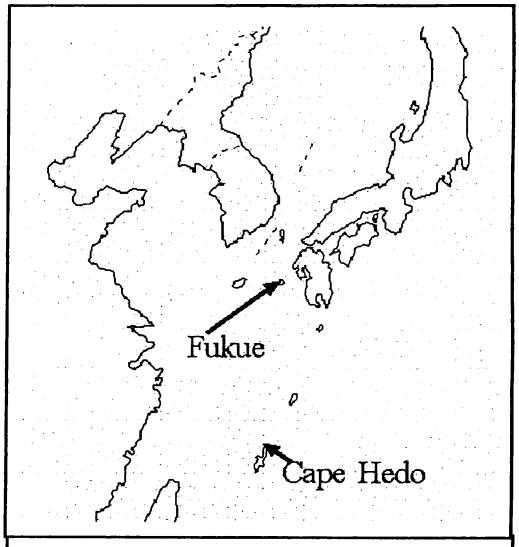

Fig.1: Monitoring sites on Fukue Island, Nagasaki Prefecture and at Cape Hedo, Okinawa Prefecture.

The AMS measurements at Fukue Island were carried out from March to May in 2003. Sulfate and organics are major chemical components and their average concentrations were 4.8 and 5.0 μg m^{-3}, respectively. On March 25-27, ammonium, sulfate and organic increased and high concentrations were kept for a few days. During these periods, size distributions of ammonium, sulfate and organic are very similar, indicating that these species were internally mixed. As for the inorganic species, the equivalent ratio of ammonium to sulfate was close to unity, suggesting that aerosol were neutralized. The concentrations of nitrate and chloride were low throughout the observation period. Mass spectra for organics were analyzed and m/z=44 (m/z; mass to charge ratio) was the one of the largest signals in organic species. High m/z=44 signal is considered to belong a carboxyl group, indicating that the oxidation of organic species were extensively occurred. Major species of oxygenated organics found in aerosols include oxo-, hydroxyl- and di-carboxylic acids and/or humic-like substances [2, 3]. Back trajectory analysis [4, 5] shows that the concentration of sulfate was high when the air mass arrived at Fukue Island from Chinese continent, and that the concentration of organics was high when the air mass arrived from Korea and Japan. In addition to m/z=44 signal, the signals of m/z=43 and 55 was detected, which belong to aldehyde and ketones [3]. These signals are considered to be a major signals observed at urban environment.

The concentration of organics are higher than sulfate at the northern East China Sea, that is, the coastal regions of southern Korea (Jeju Island) and West part of Japan (Fukue Island). Taking the extensive oxidation of organics in this region into account, it is expected that that oxidized organics are important for the cloud formation.

In May 2003, the high organics were observed. The average concentrations of

ammonium, nitrate, sulfate and organics were 4.7, 2.6, 12, 14 μg m^{-3}, respectively. Analysis of organics mass spectra shows that spectra patterns were similar to the Korean influenced period observed in April, indicating that the effect of the Siberian Forest Fire was little at Fukue Island.

The AMS measurements at Cape Hedo were carried out from October 2003. In the winter period, the high sulfate event was observed on December 19, when the weather condition was typical for winter, *ie*, high in west and low in east. The sulfate concentration was recorded to be 40 μg m^{-3}. Back trajectory analysis shows that the air mass arrived at northern China. The equivalent ratio of ammonium to sulfate was as low as 0.3, and sulfate was excessive to ammonium.

In the spring period of 2004, the integrated observation for CO, mercury and aerosol was conducted. The average concentrations of ammonium, nitrate, sulfate and organics were 2.1、0.17、7.2, 2.2 μg m^{-3}, respectively. Sulfate was the major species and the organics to sulfate ratio was lower than that observed at Fukue Island. Taking the low mixing ratio of SO_2 at Cape Hedo into account, sulfur compounds including SO_2 was oxidized during the long range transport from the Chinese continent. Mass spectra for organics were analyzed and m/z=44 was the one of the largest signals in organic species. The ratio of m/z=44 to organics was 0.2 at Cape Hedo, which is larger than the urban results (0.08) and the Fukue result (0.15), indicating that the extensive oxidation of organics was observed at Cape Hedo. This is probably due to the oxidation during the long range transport.

The mass ratio of CO to S was about 11 in China, which was estimated from the emission data [6], while the average ratio of CO to S is about 104 at Cape Hedo. This means that the CO/S ratio at CHO is about ten times larger than that at China, indicating that sulfur compounds are reduced to one tenth during the transport

The concentrations of each species are high in winter due to the air mass arriving from China, while those are low in summer due to the air mass arriving from the Pacific Ocean. The one- year measurements shows the clear seasonal dependence of aerosol mass concentration.

2. Study of spatial distribution and movement of aerosols using lidars

To illustrate three dimensional distributions of organic aerosols, continuous observations by automated two-wavelength dual-polarization lidars were conducted at Sri Samrong in Thailand and at Miyakojima in Okinawa. At Sri Samrong Observatory, backscatter intensity showed clear diurnal variations in the boundary layer during dry seasons. Typically at the beginning of dry seasons, thin aerosols were distributed near the surface. Gradually they went upward and total optical depth became larger toward the end of dry seasons. Time series of optical depth revealed large year-to-year variations. Optical properties of organic aerosols were characterized with two-wavelength observations. Depolarization ratio indicated that transported dust appeared at the end of dry seasons above boundary layer height. Optical properties suggested that both of

organic aerosols and dust were internally mixed over Thailand. In Miyakojima, slightly depolarized air masses were observed in the winter time. Chemical transport model CFORS also predicted that OC/BC frequently reached over Miyakojima. Horizontal distribution of OC/BC by CFORS suggests that organic aerosols originated from Southeast Asia cover southwest part of Japan.

3. Aerosol formation by reactions of unsaturated hydrocarbons with chemically reactive species

In order to examine the oxidation mechanisms of unsaturated hydrocarbons minutely, the direct products of the reactions of unsaturated hydrocarbons with hydroxy radical (OH), hydrogen atom (H), and oxygen atom (O) were examined by using a laser flash photolysis - photoionization mass spectrometry and laser induced fluorescence technique. The sample gas mixtures of propene and butenes with precursors of OH, H, and O flowed in the quasi-static reactor and were irradiated by an ArF or KrF excimer laser. Without the reactions with OH, radicals as the direct products were observed. The product yields for CH_3, C_2H_5, CH_2CHO, and CH_3CHCHO for the O + alkene reactions were obtained by comparing with calibrating reactions. At the results, a part of strongly depending on the total pressure and also less-depending part are found in the product yields. Those pressure dependences are due to the complex reaction scheme for the O + alkene reactions, that is, radical-radical dissociation channels via the stable intermediate formation by isomeriztion of H and the direct release channels of the product radicals with the displacement of O correspond to the pressure dependence and no dependence part, respectively.

Also, acetylene was used for a reactant with OH, which is representative of unsaturated hydrocarbons including triple bond. Only the m/e=42 signal was observed as a primary products and another signal was not found. The m/e=42 signal corresponds to ketene (CH_2CO), which was expected from the OH addition reaction to acetylene with successive reaction of H atom migration and elimination. We conclude that this reaction channel is dominant in the experimental condition of low-pressure region so that the reaction intermediate of OH + acetylene adduct (hydroxy vinyl radical, CH(OH)CH) may be important at the condition of high-pressure region.

On the other hand, vinyl radical (CH_2CH) radical is expected to have similar reactivity to hydroxy vinyl radical so that examining the vinyl radical oxidation process is still important for atmospheric chemistry. We found the vinoxy radical as a primary product from the reaction of vinyl radical with O_2 for the first time. The branching ratio of CH_2CHO + O channel from CH_2CH + O_2 reaction was obtained as $\phi \sim 0.2$ in the total pressures of 10-200 Torr at room temperature. So, we suppose that formation of the vinoxy-type radical unsaturated oxidation process should be considered in the atmospheric chemistry.

4. Research on the chemical composition of aerosol transported from East Asia

Filter sampling measurement, molecular-level analysis and atmospheric back trajectory were conjointly used to study the influence of atmospheric transportation from East Asia on the chemical components of organic aerosols at Okinawa Island. 19 polycyclic aromatic hydrocarbons (PAHs) and 20 monocarboxylic acids (MCAs) were analyzed in organic aerosols collected at Okinawa Island from March 6 to March 15, 2004 by using a HPLC-UV method and a newly-developed HPLC-ESIMS method, respectively. The detection of specific PAHs and diagnostic concentration ratios of PAHs indicated that PAHs had undergone long-range transportation from their combustion sources; The concentration distribution profile of MCAs showed that MCAs came from marine micro biotic sources and terrestrial organic matter with the former being the main source. Back trajectory analysis demonstrated that the source region of organic aerosols was East Asia; the transportation of the air mass from East Asia brought the PAHs pollutants and input the higher molecular weight MCAs (C_{20}-C_{31}) to the organic aerosols at Okinawa Island in spring.

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