C-051 Studies on the Processes of Transport and Transformation of Aerosols and Their Precursors from Asian Continent (Abstract of the Final Report)

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[Abstract]

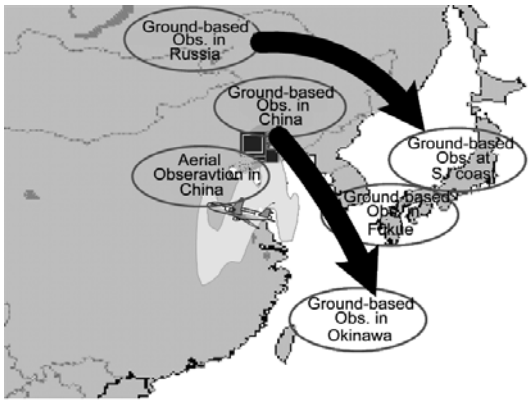
In this project it was achieved to carry out aerial and ground-based observations of atmospheric pollutants and aerosols in China. Simultaneous ground-based observations at down wind areas such as Fukue, Cape Hedo, Okinawa, and Ogasawara were also performed. According to those observations along the stream line of Asian monsoon, it also became possible to analyze the transformation of atmospheric pollutants on the way of long-range transport over the East China Sea. Difference in chemical composition was mainly due to air mass history and chemical reaction during long range transport. Chemical transformation was investigated by Lagrangian methods. For the air mass traveling to Hedo via Fukue, we have shown that increase of sulfate and decrease of SO_2 is quantitatively correspondent. As for particulate nitrate, the longer the transport time from the continent was, the more the nitrate in coarse particles was found.

Model simulation pointed out that the contribution of continental emission to the deposition of pollutants originated in the East Asia was much higher than that believed before. The relationship between continental emission source area and down wind receptor area became much more distinct and clearly grasped. This project has demonstrated necessity to investigate the effects of the long-range transported atmospheric pollutants on ecosystem and human health in order to work out effective measures against such transboundary environmental problems.

1. Introduction

East Asia is an important area in which a vast amount of atmospheric aerosols and their precursors are emitted. Atmospheric aerosols are deeply related to global warming as well as acid rain. However, the chemical composition of aerosols is very complicated and the spatial and temporal distribution of atmospheric aerosols is quite variable; there still remain unknown and/or uncertain problems. There is urgent necessity to analyze and to evaluate the impacts of aerosols from this area on the atmospheric environment of not only northwest Pacific but whole northern

hemisphere.



2. Research Objective

This research subject is composed of 6 sub-subjects. They are all aiming at one of three targets: (I) observations along the transport pass of pollutants, China ~ the East China Sea ~ Okinawa, (II) observations along the transport pass of pollutants, Siberia ~ the Sea of Japan ~ Honshu, Japan, (III) model analyses of the transport of aerosols form Northern Eurasia, China, and South-Southeast Asia. As for (I) a large scale intensive experiment was carried out in April, 2006.

The target areas of this study are China, Fukue, and Okinawa, which are a large emission source of air pollutants in the East Asia, the course ground of air masses transported, and the downstream receptor, respectively, as illustrated in the figure above. Long range transport of air pollutants and their chemical transformation should be investigated. For this purpose, aerial and ground-based observations of air pollutants in China, and ground-based observations in Fukue, Okinawa, as well as in Ogasawara were carried out to clarify the processes of aerosol formation, transport, and removal. In such a manner, so to say, Lagrangian analyses of atmospheric pollutants and aerosols were performed. Chemical transformation of ionic species and carbonaceous compounds was investigated during the experiment. The data obtained on the way of air-mass-transport were input to the simulation model and the large scale air pollution in the East Asia was studied as a whole in order to make it possible to propose measures against the large scale air pollution in this area.

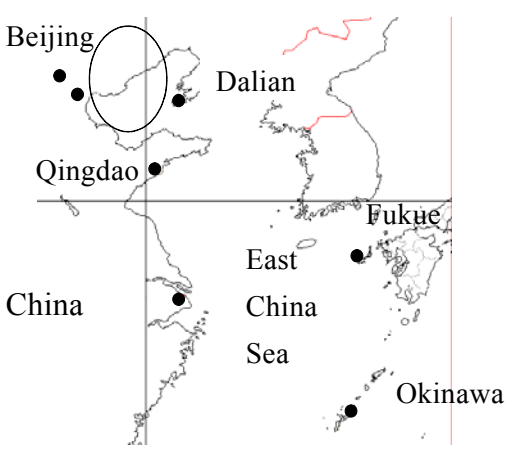
3. Results and Discussion

This project was composed of 6 sub-subjects. Results of each sub-subject are as follows.

(1) Studies on the distribution and transport of air pollutants and aerosols by ground-based and aerial observations

In this sub-subject following three studies were done: (i) aerial observation and ground-based observation around Beijing, China as well as ground-based observations in Fukue and Okinawa for collecting data along the transport pass of pollutants from China to Okinawa via the East China Sea; (ii) ground-based observations at Maki, Niigata Pref. seeking for data along the transport pass of pollutants from Siberia through the Sea of Japan to Honshu, Japan; and (iii) preparation of simulation models and utilization of them to analyze the distributions and transports of pollutants from East Asia.

(i) Yun-12 air plane (a reciprocal airplane of twin-engine) was employed for the aerial observation of atmospheric pollutants over the main land China. Instruments installed on board were an ozone monitor, a NOx monitor, an SO_2 monitor, a CO monitor, a PM10 sampler, and a PM2.5 sampler. Meteorological parameters were recorded on board. Eight observation flights were made around Beijing-Tianjin area (area surrounded by the oval in the figure below). Air masses strongly affected



by yellow sand dust were observed. Aerosols with high concentration of Ca^{2+} as a basic component were observed, which were different from usual ammonium rich aerosols over coastal area of central east China or northeast China.

In November 2005, both polluted air mass and dust storm (yellow sand) were observed at CHAAMS (Cape Hedo Atmosphere and Aerosol Monitoring Station in Okinawa) almost simultaneously. In the former half of the high aerosol loading period, sulfate, ammonium and organics were major species. In latter half, dust was dominant according to the TEOM and LIDAR measurements. Anthropogenic aerosol reached CHAAMS slightly before dust storm and this was the same phenomenon as was observed at Nagasaki and Fukue.

Measurements by an aerosol mass spectrometer (AMS) showed that sulfate was higher than organics in Cape Hedo, while organics were higher than sulfate in Fukue, indicating that aerosol chemical compositions were different in southern part from northern part in East China Sea. Collection efficiency for the AMS was found to be unity at Cape Hedo, where sulfate is major species. Difference in chemical composition was mainly due to air mass history and chemical reaction during long range transport. Chemical transformation was investigated by Lagrangian methods. For the air mass traveling to Hedo via Fukue, we have shown that increase of sulfate and decrease of SO_2 is quantitatively accounted for by comparing Hedo data with those in Fukue. The longer the transport time from the continent was, the more the nitrate in coarse particles was found.

Fourteen Polycyclic aromatic hydrocarbons (PAHs) in aerosols, collected at Cape Hedo, between 2005 and 2007, were identified with gas chromatography-mass spectrometry. The total concentrations of PAHs were 0.01-23.5 (av. 1.85) ng m^{-3}. The average value measured at Cape Hedo was lower than those measured previously in Chinese cities (~117 ng m^{-3}), but was higher than that measured at Chichi-Jima Island in the Pacific (0.11 ng m^{-3}). The average of benzo[a]pyrene to benzo[e]pyrene ratio was 0.48 during winter and spring seasons and was lower than those measured in Chinese cities (~0.85), showing that PAHs observed at Cape Hedo were aged by the photochemical reactions proceeding during long-range transport. These results indicate that the pollutants transported from the Continent by the monsoon contribute to PAHs observed at Cape Hedo.

Environmental impacts by trans-boundary aerosols were evaluated utilizing networked lidars which are continuously operated in East Asian region. Seasonal variation of the height of boundary (mixing) layer was examined by statistical analysis on the lidar data. The lowest boundary layer height was detected in summer. That means that the humid lower atmosphere reaches saturation height easily and cloud is formed in the lower height. This situation prevents vertical mixing up to higher altitude in summer. Several specific aerosol events were analyzed intensively. In May 2007 Asian dust particles were detected during the severe photochemical oxidant event occurred in

Western Japan. These phenomena suggest that a heterogeneous reaction on Asian dust particles contributed to the promotion of photochemical reaction. A carbonaceous aerosol layer was detected in the upper troposphere in June 2007. The optical properties of this layer indicated this layer consisted of small and non-spherical particles. The origin of these aerosols was forest fires in Eurasian continent, and the optical depth of this layer was 0.67, a value not negligible in the local radiation budget.

(ii) We conducted daily collection of gaseous and particulate compounds as well as chemical analysis of them to clarify the temporal distribution of air pollutants in the coastal area of the Sea of Japan. Seasonal variation of sulfur dioxide was small. The concentration of non-sea-salt component was high in summer and was low in winter. Monthly averaged concentration of non-sea-salt component was low in December due to the heavier snowfall compared to normal years. A similar situation was observed in July due to the concentrated heavy rainfall. Ammonium was transported with incorporation of non-sea-salt sulfate as judged from the observational results that the concentration variations of ammonium and non-sea-salt sulfate were strongly correlated and the maximum daily averaged concentrations of both the ionic species were recorded on the same day. We compared the averaged concentrations of chemical components by wind field. Non-sea-salt sulfate, nitrate, ammonium and sulfur dioxide concentrations were the highest when the air mass traveled from China and Korean peninsula. As for nitric acid and ammonia, the concentrations were the highest when the air mass traveled over surrounding areas of Japan. The concentrations of gaseous components were dependent on nearby sources because the residence time is short. On the other hand, particulate matter was dependent on long range transport because particles are formed from the gaseous component by photochemical reactions during the transport.

(iii) The Community Multi-scale Air Quality modeling system (CMAQ) coupled with the Regional Atmospheric Modeling System (RAMS) was used to analyze (1) the dynamics of Elemental Carbon (EC) in East Asia during spring 2001, (2) the impact of Chinese megacity emissions on regional air pollution episode in Kyushu area during winter and (3) the contribution of transboundary pollution to the acid deposition over Japan.

1) The CMAQ/RAMS was used to analyze the dynamics of EC in East Asia during spring 2001. The model reproduces the fundamental features of the EC concentrations measured around Japan. In Japan, the contributions of domestic emissions to the surface EC concentrations are 46 %, whereas the contributions of emission from China are relatively high (37 %).

2) The total contribution from the emission sources in Beijing and Shanghai areas during half a month in February, 1999, is 18% for SO_x and 12% for NO_y in the western Japan. The CMAQ can reproduce the fundamental features of the temporal variations of observed SO_x and NO_y concentrations at Fukue and over the East China Sea.

3) Two-nested models, whose horizontal resolution is 80 km in East Asia and 20 km around Japanese Islands, can reproduce the fine structure in spatial distribution of acid deposition over Japan. The model simulation showed that the contribution of transboundary pollution to the acid deposition over Japan is 70%, 64%, and 58% for SO_x, NO_y, and NH_x, respectively, in January.

(2) Observations of tracers (CO, VOC) of biomass aerosols in Okinawa and elucidation of transport processes

We analyzed long term data of surface ozone and carbon monoxide observed at Hedo Okinawa Observatory from 2002 through 2007. On the basis of trajectory analysis, we classified the air masses according to the location of their origins as Chinese continent (C), Korean Peninsula (K), Japan (J), and Oceanic (O). Averaged concentrations in C and K air masses are essentially the same with each other but that in J is systematically lower than those in either C or K. This fact is explained as the dilution by oceanic air which contains lower pollutants. VOC data were obtained by the campaign conducted from March to May 2004. The isomer fraction of pentanes was used to locate the origin of the air masses containing those hydrocarbons. From long term VOC canister measurements, the seasonal variation in the concentration of saturated hydrocarbons such as ethane was analyzed. The variation is explained in terms of OH seasonality and switching of air mass from continental to oceanic. C_2Cl_4 is demonstrated to be a potential index of industrial activity, because very high correlation between C_2Cl_4 and CO has been obtained.

(3) Studies on the temporal variation of aerosol characteristics at Fukue, Okinawa, and Ogasawara Islands and the evaluation of direct radiative forcing

Characteristics, transport pattern, chemical transformation, and the climatic effect of aerosols flying out from Asian continent have been studied at Ogasawara Island, Japan, which is located at the most downwind side in observational stations deployed in this project. A real-time sulfate monitor (TECO, 5020SPA) installed at Ogasawara observation site in 2005 has been calibrated 48-hr filter samples during the intensive monitoring campaign in 2007 spring.

The concentration of SO_4 showed a synchronized variation with that of particulate black carbon, but the ratio of these species had different values among the transport events. A transport event on April 9-10, 2007, exhibited large SO_4 /black carbon ratio, suggesting the aged particles in the state of high SO_2 oxidation ratio. While, the high concentrations on April 16-17, 2007, were transported with the passage of cold-front over the islands. At Cape Hedo, the mass ratio of SO_4 /black carbon was stable and low (~7) just after the front passage, while at Ogasawara Island, the ratio increased to double (~18) of Cape Hedo, suggesting the additional oxidation of SO_2 to form sulfate during the transport. At the same time, at Cape Hedo station, a low-pressure type cascade impactor sampling was conducted during 2006 and 2007 spring intensive measurement periods to measure size-segregated aerosol composition. NIES operated AMS simultaneously during that period. The submicron mode of SO_4 resided in unexpectedly large sizes (0.5–0.7μm in aerodynamic or vacuum diameter) both by LPI and AMS measurements. The observed mode was similar to that found by Hering and Friedlander (1982) for sulfur aerosols in Los Angeles, which is referred to as the “droplet mode”.

This result implies that the so called “global model” of aerosol characteristics that has been used in the prediction of aerosol radiative forcing may lead to an erroneous estimation at least over the Asia-Pacific region.

(4) Observations of air pollutants and aerosols in a large emission source area in China

The measurements of EC in fine particulate matter were made at hourly intervals from 25

November 2005 through 31 October 2006 at Peking University in Beijing, China using a Sunset Laboratory's semi-continuous carbon analyzer. CO and CO_2 were also measured simultaneously. EC concentrations generally decreased with increase in the wind speeds, indicating the importance of dilution by vertical mixing and horizontal transport in controlling their near surface concentrations. For this reason, we focused on the data in the condition of weak wind speed (2 m s^{-1}). EC and CO were well correlated throughout the measurement period due to a similarity in sources. CO and CO_2 were also well correlated in autumn and winter, indicating that both CO and CO_2 are good tracers of EC. CO and CO_2 with EC were introduced as a useful parameter to detect those emissions, because those ratios are not affected by dilution in the atmosphere.

The average EC concentrations for each season ranged between about 6 and 8 μg m^{-3}. CO showed minimum values of about 0.8 ppmv in spring-summer and maximum of about 1.6 ppmv in winter. Slightly higher EC concentrations were identified in fall and winter, while severely elevated CO concentration in winter occurred by domestic combustion for heating. CO_2 in summer showed the lowest level (423 ppmv) related to the vegetative activities. Investigation of diurnal cycles in EC measurements over the entire study period revealed that EC concentrations showed a consistent diurnal behavior, characterized by not a typical pattern of rush hour peaks occurring in the morning or evening but a noticeable pattern of nocturnal elevated EC concentration. CO showed a similar diurnal pattern with EC. In the case of CO_2, the concentrations decrease during the daytime, and show the lowest level in summer because of take-up by photosynthesis.

The ΔEC/ΔCO ratios showed a similar diurnal pattern with EC, increasing at night and peaking to the maximum values during the nighttime after the midnight, because of increasing inflow of diesel trucks into the city after 2200 LT under the traffic policy in Beijing. This is supported by strong dependency of the nocturnal ΔEC/ΔCO ratios on the ambient temperatures. This suggests that diesel exhaust is the dominant local source of EC emissions. The diurnal pattern of $\Delta EC/\Delta CO_2$ ratios also underwent similar cycles with higher nocturnal values in summer and fall related to the increase of the EC emissions. During the winter periods, however, the diurnal pattern of ΔEC/ΔCO ratio was different from that in other seasons, because large amounts of coal in winter were consumed in Beijing due to residential heating causing extremely high CO concentrations. An interesting finding was that no weekend effect was indicated for all measured species in Beijing. In addition, the diurnal patterns of the ΔEC/ΔCO ratios did not change between weekdays and weekends.

Our observed surface concentrations of EC, CO, and CO_2 were compared with the emission inventory data proposed by Streets *et al*., [2003] to estimate the emission rates using their correlation relationships. The results of this comparison reveal the possibility of overestimation in EC and CO emission rates estimated by Streets *et al*., [2003] around Beijing region.

(5) Model studies on the transport of aerosols from South or Southeast Asia to Japan via China and chemical processes

A global scale aerosol transport/chemistry/deposition model has been developed and validated with use of observation data in China and Japan for March 1 to 31, 2001. The model was applied to evaluate relative contribution of both anthropogenic and natural emission sources to aerosol

concentration in the cities in China and Japan. For one month of March in 2001, the calculated results were compared with TSP (Total Suspended Particulates) concentrations at observation sites in China and with PM10 at Tokyo and Osaka in Japan. The calculation acceptably well reproduced the observations, showing different relative importance of soil dust emission, biomass fire emission, and anthropogenic emissions in urban areas in China and Japan. For example, extremely high PM concentration episodes in Beijing and northern cities are highly associated with soil dust storm in spring season, while anthropogenic emission is rather important in Shanghai area. In southwestern China city such as Kunming, biomass fire emission can be significant. In Tokyo and Osaka, soil dust just occasionally affects PM10 concentration, and anthropogenic emissions are always a dominant factor.

As an example of tropical mega-cities, air pollution transport/chemistry, influenced by characteristic local winds, in Jakarta has been numerically investigated for the first time. Characteristics of land/sea breeze in Jakarta were clarified both in dry and wet seasons. In dry season, sea breeze develops everyday in Jakarta area, but its extent is always suppressed by the synoptic scale southeasterly which blows over and flows around the southern mountains in western Java. Thus air pollutants discharged in Jakarta do not deeply intrude inland with sea breeze in the daytime, but those move long over the Java Sea with enhanced land breeze at night and in the early morning. Hence photochemical smog reactions mainly proceed in the pollutants rich air mass over the Java Sea near the coast.

(6) Studies on the transport of pollutants from background area (Northern Eurasia) and their effects

In order to evaluate atmospheric environment quality in Russian East Siberia and Primorsky region, which are in transition area on long-range transportation of air pollutants, wet deposition, gas/aerosol concentration, lead concentration, and lead isotopic composition were determined at 3 sites (Irkutsk, Listvyanka, and Mondy) in East Siberia and 1 site (Primorskaya) in Primorsky region.

Annual average of pH in wet deposition ranged from 4.62 through 5.53 for three years. Precipitation was acidified mainly by sulfuric acid and neutralized by calcium aerosol and ammonia gas. Wet deposition of major components in precipitation varied with season being large in summer and small in winter depending on the variation of precipitation amount. SO_2 gas concentration was the highest in Irkutsk. HNO_3 and NH_3 concentrations were fluctuated for every year at every site. Mondy was the cleanest sites among the four sites in the concentration of aerosols. The composition of acidic components in precipitations was almost similar to that in aerosols. The concentrations of lead at 4 sites were lower than those in the previous year. Those monitoring results and analytical procedures may be useful for establishing numerical model and evaluating EANET data.

In order to make a common understanding of model performance and uncertainties in Asia, a model intercomparison study on long-range transport and deposition of air pollutants has been carried out since 1998. In 2007, the project yielded 9 scientific papers which have been prepared by participants in MICS-Asia Phase 2 project.

A workshop for this study was held at International Institute for Applied System Analysis (IIASA, Austria) on 18-19 February 2008, in order to review the recent activities on modeling and emission inventories and to discuss the concrete items to be investigated in Phase 3 in accordance with the interest and progress of each participant. According to the discussion, it was decided that 5 topics would be considered as Phase 3 activities.

Major Publications

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