Aerosol Properties and Air Pollutants over Higashi-Osaka

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Abstract

The relationship is examined between aerosol properties obtained from radiometry with AERONET and the particulate mass simultaneously measured with a new instrument (SPM-613D). The AERONET site has been set up at Higashi-Osaka since 2002 to make measurements for understanding the characteristic features of the urban atmosphere. It is found that the SPM measurements classified as fine particles (PM2.5), coarse particles (TSP/PM10), and optical black carbon (OBC) are very useful for determining the dominating of particle size and air quality. There was a strong correlation between the SPM concentrations and aerosol properties (AOT/AI), which indicates that aerosol characteristics can be estimated from SPM data, and vice versa.

Keywords: Atmospheric aerosols, Air pollutants, PM2.5, SPM, OBC

1. Introduction

Multi-spectral photometers CE-318-2, (Cimel Electronique) was set up for an AERONET site at Higashi-Osaka in 2002. This instrument has four observing channels for photometry whose central wavelengths are 0.44, 0.67, 0.87 and 1.02 μm, and polarimetric facilities at 0.87 μm. The radiometer was calibrated using a standard AERONET procedure [1].

Higashi-Osaka (which is on the east side of Osaka) is, along with Osaka, Kobe and Kyoto, one of the industrial cities comprising the so-called Keihanshin Industrial Zone. Referring to Fig.1, our Osaka site is located between Osaka bay and the Ikoma mountains. Anthropogenic aerosols produced by industries are mixed with oceanic aerosols transported from Osaka bay and trapped near this site, which explains why this city is famous for its heavy air pollution. The aerosol properties here are especially complicated due to this mixing of anthropogenic and natural compounds.

The concentrations of suspended particulate matter (SPM) at ground level have been compiled for 10 years in Japan. It is difficult to relate SPM data directly to aerosol properties, but SPM data approximately represents the mass concentration of atmospheric particles at the surface. In other words, air pollutants could bear some relations to the emission and transportation of aerosols. In order to elucidate the correlation between aerosol properties and concentrations of in-situ atmospheric particles at the surface, a new instrument (SPM-613D, Kimoto Electric;

Fig.1) began taking measurements of SPM concentrations as TSP (total suspended particulates), PM10 (<≈ 10μm), PM2.5 (<≈2.5μm), and OBC (optical black carbon) on March 15, 2004 at the AERONET/Osaka site. In addition, the results of the aerosol sampling executed by using the PCI sampler (Tokyo Dyrec corporation) are shown.

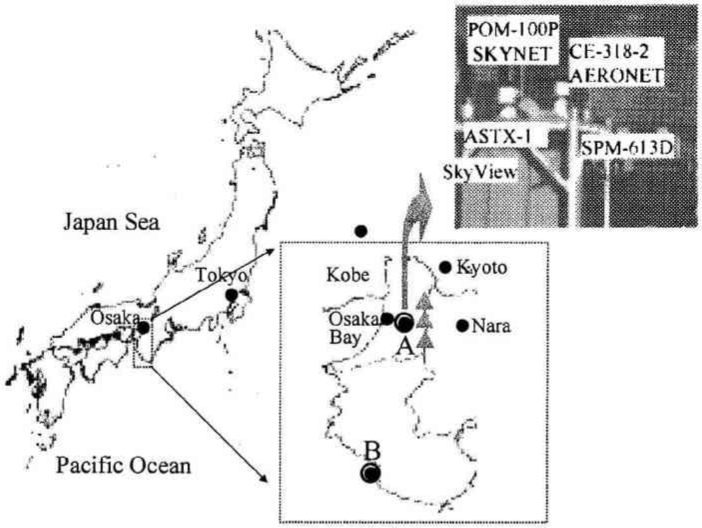

Fig.1: Geographical position of AERONET sites in Japan. A and B correspond to Osaka and Shirahama, respectively. The triangles show the Ikoma mountains. The image shows the instruments for measuring atmospheric aerosols at the Osaka site set up on the roof of university building (about 30m above the ground and about 50m above sea level).

2. Radiometry of aerosols

The column aerosol optical thickness (AOT: τ_λ) is an important aerosol parameter that is measured by direct sun photometry of the sun. The Ångström exponent (α) is calculated from the spectrum tendency of AOT as

$$\alpha = -\ln(\tau_{\lambda 1}/\tau_{\lambda 2}) \ / \ \ln(\lambda_1/\lambda_2), \qquad (1)$$

where wavelengths λ_1 and λ_2 correspond to the central wavelengths of two observing channels. The values of α are closely related to the aerosol size. The aerosol index (AI), a good indicator of the dominance of anthropogenic particles, is defined as

$$AI = AOT \cdot \alpha. \qquad (2)$$

Other aerosol properties, such as the size distribution, complex refractive index, and single scattering albedo, are retrieved based on the AERONET standard inversion method [2, 3].

Figure 2 shows the AOT(0.87μm), and the α for all days for which measurements are available from 15 March to 20 November, 2004, at Osaka. The dotted line at 0.2 and dashed line at 0.3 in the AOT(0.87μm)-panel, and the solid line at α=1.0 in the other panel are referred to below. The dashed line denotes the reference value for the discrimination of dust events. Each labeled shaded region represents an aerosol event, which defined as an unusually heavy aerosol loading, namely AOT(0.87μm) > ~0.3 as indicated by the dashed line.

It can be seen that there were fourteen such events during the period shown. The complicated features of aerosols at Osaka are demonstrated in Fig.2. Events- a, -b, -c, -d and -f are typical dust events with high

AOT and low α, but rather high values of α are evident in events-e, -g –h, -i, -j, -k, -l, -m and -o. The events since May are all the same.

Figure 2 shows that the aerosol properties over Osaka can be roughly divided into three types: (1) an ordinary Osaka aerosol whose AOT(0.87 μm) is less than 0.2, (2) one with large values of AOT and α; (i.e., AOT(0.87 μm) > 0.2 and α > ~1.0), indicating the dominance of anthropogenic aerosols, and (3) large coarse dust for which AOT(0.87 μm) > 0.2 and α < 1.0 [1].

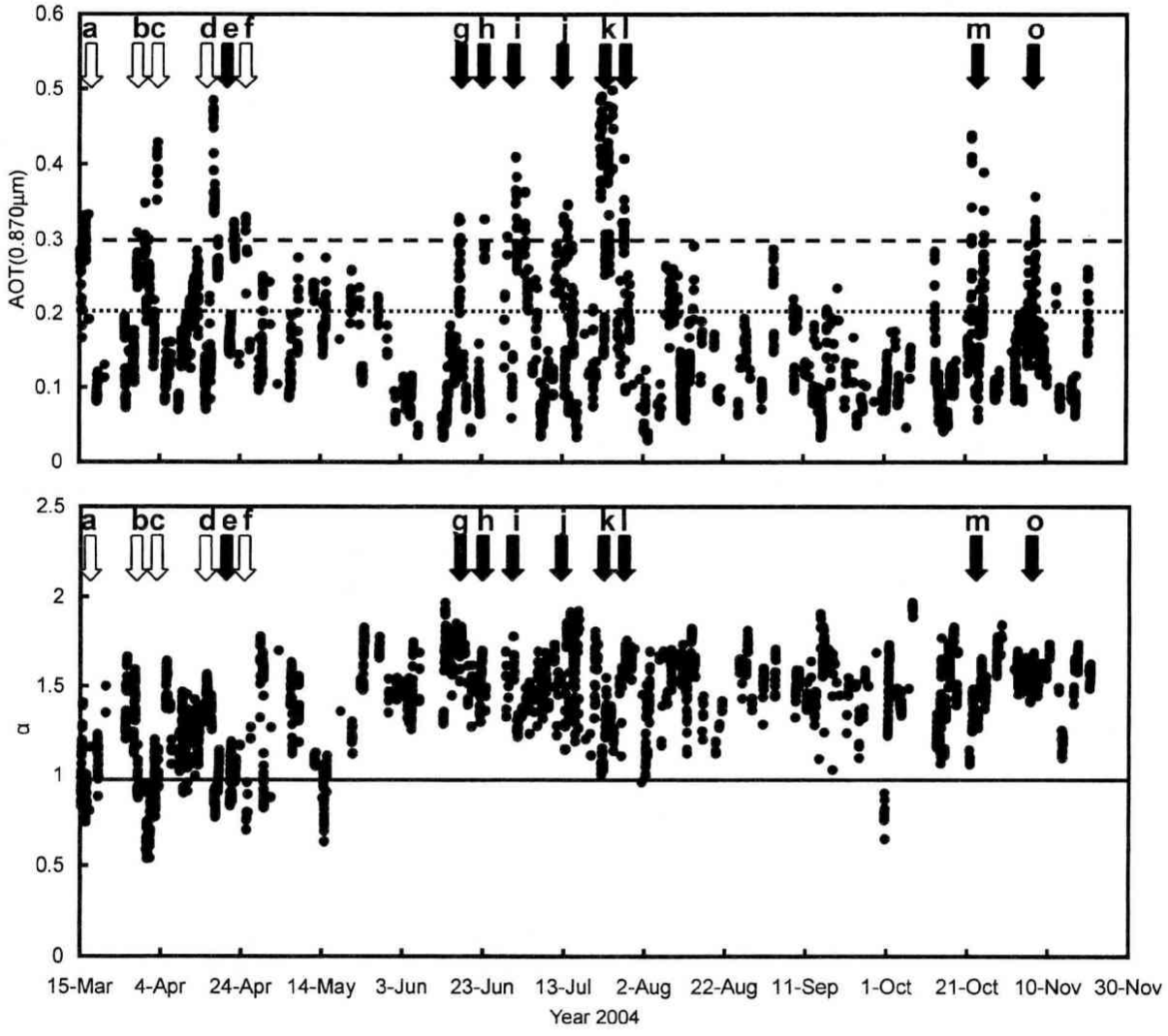

Fig.2: Radiometric data of aerosols from 15 March to 20 November in 2004 at Osaka. AOT(0.87μm), and α are shown in the upper and lower panels respectively. The dotted and dashed lines indicating in AOT(0.87μm) values of 0.2 and 0.3, and the solid line for α=1.0 are discussed in the text. The labeled shaded regions represent aerosol events with AOT(0.87μm) > ~0.3.

3. Sampling of SPM over Osaka

The synthetic monitoring system of aerosols is necessary to be available for the quick change of aerosol properties. The system is able to obtain the various observational data that are collected in Higashi-Osaka. The observational results of AERONET instruments are transmitted from the transmission antenna of the each observational point to the geo-stationary satellite, and then retransmitted to the appropriate ground receiving station at NASA/GSFC. After that, the analysis results are shown on AERONET web page (http://aeronet.gsfc.nasa.gov/) with the near real-time [4].

We introduced the instrument for monitoring of the sky condition is named Sky View: PSV-100 (PREDE CO.,LTD, Fig.1). A photograph of the sky is taken with CCD camera for every fixed time. It is the equipment automatically saved to the HDD of a personal computer. The atmospheric data from various instruments are accumulated from day to day in Kinki University. However, the data-user is not able to use the data easily. The transfer system of observed data is needed to examine a correlation between SPM concentrations and aerosol properties. Here, the system for forwarding SPM and Sky View data (shown in Fig.6), and that for drawing graphs of that has been developed. The SPM and Sky View data are accumulated to a personal computer (Windows PC) that is established in the rooftop. The windows PC has been installed the FTP server. Furthermore, it is possible that the on-campus data server (Linux PC) acquires data from control PC by arranging communication environment using the LAN cable for an outdoor setting. The application (the Borne Shell program) is prepared to the data server, to obtain the file of observational data automatically. The acquisition of the data is carried out every 10 minutes. Also, this application writes out the message of success, or failure of data acquisition in a log file. After that, the present situation is grasped.

These series of action is automated by the control using cron jobs of Unix system. In the case of SPM data, the server uploads the text file of the CSV format. After that, the data-user is able to download the file from web page. The graph is drawn automatically from present data simultaneously, and is displayed to web page with the GIF format. Furthermore, image of Sky View is automatically displayed every 5 minutes.

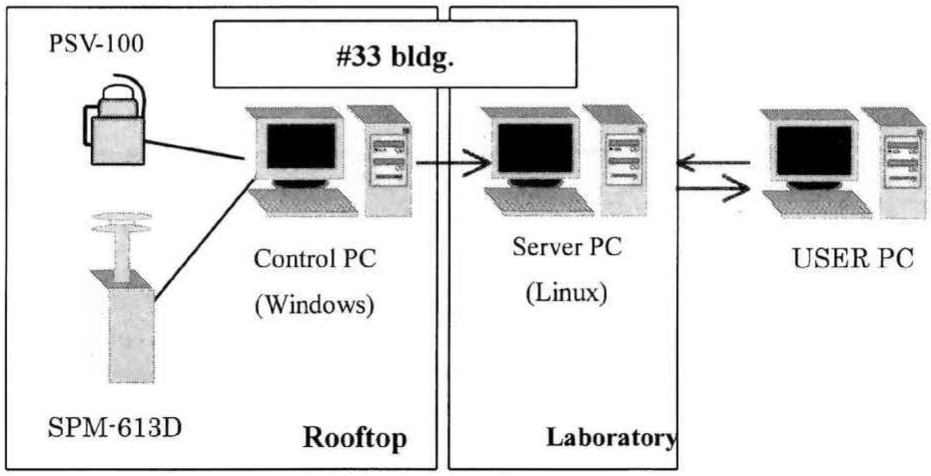

Fig.6: The outline of the synthetic aerosols monitoring system.

The SPM concentrations at ground level have been compiled in Japan under AEROS, which is controlled by the Ministry of Environment in Japan. Various elements of air pollutants such as SO_2, NO, NO_2, CO, Ox, NMHC, and CH_4 are measured along with SPM there. The concentration of SPM correlates with the column AOT [5, 6], indicating that anthropogenic aerosol particles dominate the air over urban cities due to local emissions such as from diesel vehicles and, chemical industries [7]. It is also well known that small atmospheric particles play an important role in human health and climate change [8].

The new SPM-613D instrument makes it possible to determine the relationship between aerosol properties and the particulate mass, since it can separate the contributions of fine particles (PM2.5), coarse particles (PM10/TSP), and OBC. A replaceable Teflon tape filter is used to collect particles entering into the tip of SPM-613D, and ICP-MASS analysis is employed for extraction. The mass concentrations of PM2.5 and PM10/TSP are measured using the beta gauge method. TSP is only measured for the yellow sand season. The OBC is measured by optical density. SPM-613D provides continuous data.

Figure 3 shows the measurements of PM2.5 and coarse mode particles (named PMc hereafter, derived from the difference between PM10/TSP and PM2.5), during the same period as Fig.2. High concentrations of PMc occurred simultaneously with the radiometric aerosol events in Fig. 2, as indicated by the letters. The coincidence of the temporal variation of SPM with that of the column AOT confirms previous work [Smirnov et al. 2000]. Other high concentration events, -(i.e. u: March 24-26, v: April 10-13, w: May 6-9 and x: May 11-13 and y: Sep 2-3, are only evident in Fig.3, because the SPM sampler works continuously, even on cloudy/rainy days, while radiometry is only available during daytime on a clear day. These data also indicate that several dust events occurred at Osaka during spring of 2004. It is of interest to mention that the dust events appear with approximate periodic of 4 days, and are attributable to soil dust transported from China on westerly winds. During the period shown, the air pressure system typically changed every 4 days.

Figure 3 indicates that the concentration of PM2.5 is almost equal to that of PMc even during dust events, except for events- b, -c and -f. On the other hand, the high concentration events of PM2.5 increase since May. Especially, the density is low in summer though that is high in winter. The U.S. Environmental Protection Agency defines the 24-hour averaged PM2.5 concentration as the air quality index (AQI): from nearly zero in a very clean atmosphere to about 500 in very hazy conditions. The AQI at the Osaka site is occasionally larger than 65.5 μgm^{-3}, which means not good for health [9].

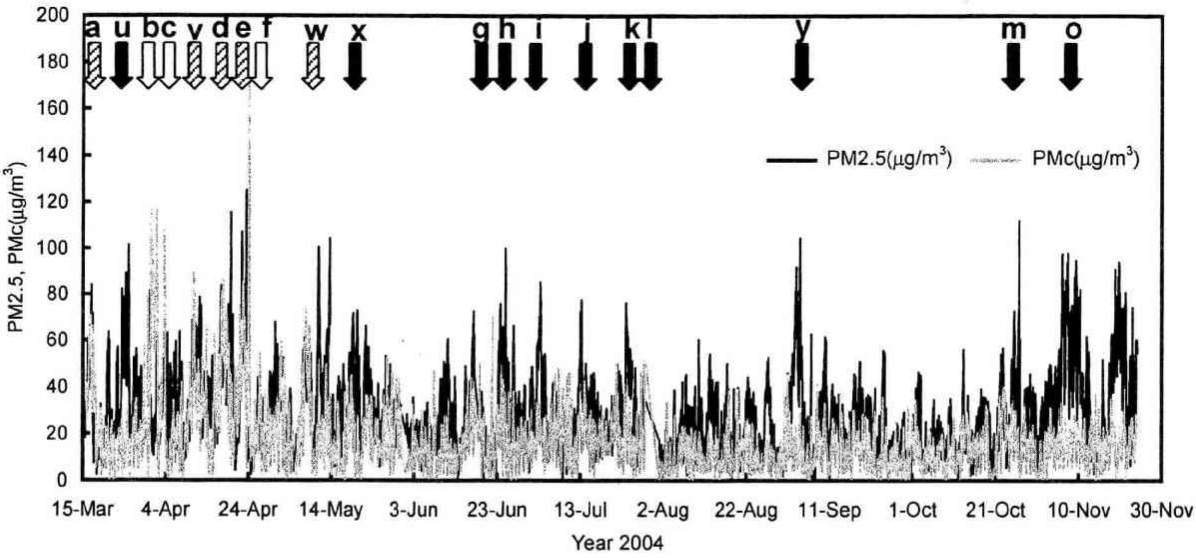

Fig.3: Measurements of PM2.5 (black curves) and coarse particles PMc (gray curves) from 15 March to 20 November, 2004 at Osaka. Anomalous heavy loading of SPM is indicated, where events-a ~ -o correspond to the radiometric aerosol events in Fig.2.

4. Seasonal changes of the element in the atmospheric aerosols

Atmospheric aerosols were collected with quartz filters (Pallflex corporation, New York, USA) on PCI sampler at constant flow rate of 20dm^3/min from the roof of our university building. Aerosol sampling was carried out for 7 days in one month from April 2002 to March 2003. After filtration, the filter was replaced in a Teflon beaker and 10 ml of 60% nitric acid solution (ultra fine grade) was added. The beaker was warmed at 160 °C for 1 hour on a hot plate. After cooling, 1 ml of 70% perchloric acid solution was added and warmed at 180°C for 1 hour. After cooling, the filter removed from a beaker, the solusion was concentrated to 1ml and then it removed a 20 ml volumetric flask and dilute exactly to the mark with deionized water. The concentrations of major and minor elements in the aerosols were determined by ICP-AES Optima 3300DV (PerkinElmer Co. Ltd.).

Seasonal changes of Al, Ca, Fe, Mg and K from April 2002 to March around Kinki University are shown in Fig. 4. Seasonal changes of Cu, Mn, Pb, V and Zn are shown in Fig.5. Correlation coefficients in bilateral elements in the coarse particles of >10μm, 2.5-10μm and fine particles <2.5μm are shown in Tables 1-3, respectively.

Seasonal change of Al in coarse particles of >10 μm was similar to those Ca, Fe and K. Table 1 shows that Al has a good correlation with Ca, K and Fe. It is considered that the coarse particles in the urban areas are supplied from resuspension of industrial dust and soil, Suspension of soil, biological and ocean spray, and major constituent was Si, Al, Fe and Na [10]. Tomiyasu et al (1996) shows that source apportionment of individual airborne particle by using electron probe microanalyzer, deduced emission sources of cluster include Al, Si, Ca and Fe are mineral dust and tire dust emitted from friction between road surface and tire of vehicle [11]. According to the correlation coefficient, Al has the same source as Ca, K and Fe. Seasonal changes of the elements of <2.5 μm without V are similar to each other (Table 3). The fine particles of <2.5 μm are emitted from primary anthropogenic and secondary particle. Primary particles in the urban areas

are almost emitted from the vehicle as black carbon of diesel exhaust particle (DEP). According to the correlation coefficient, the elements of <2.5 μm supplied from same pollution source such as DEP. Vanadium exhibits a roughly cyclic pattern with a maximum in June and August. Such a trend is obtained in the urban air in the South of Saitama [12]. It is suggested that V came from the volatilization of petroleum oil in storage and its burning as a fuel.

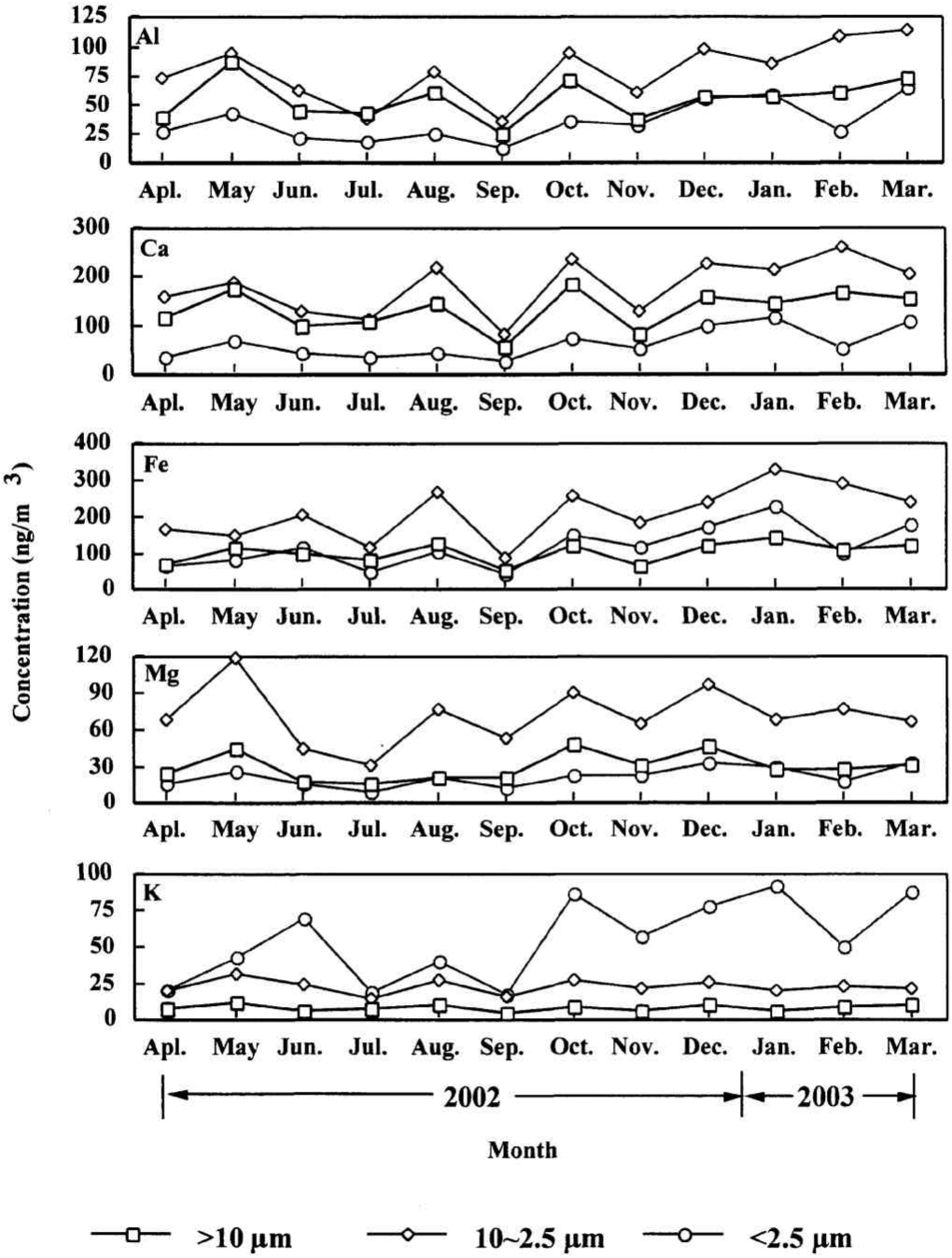

Fig.4: Seasonal changes of aluminum, calcium, iron, magnesium and potassium in the atmospheric aerosols around Kinki University from April to March 2003.

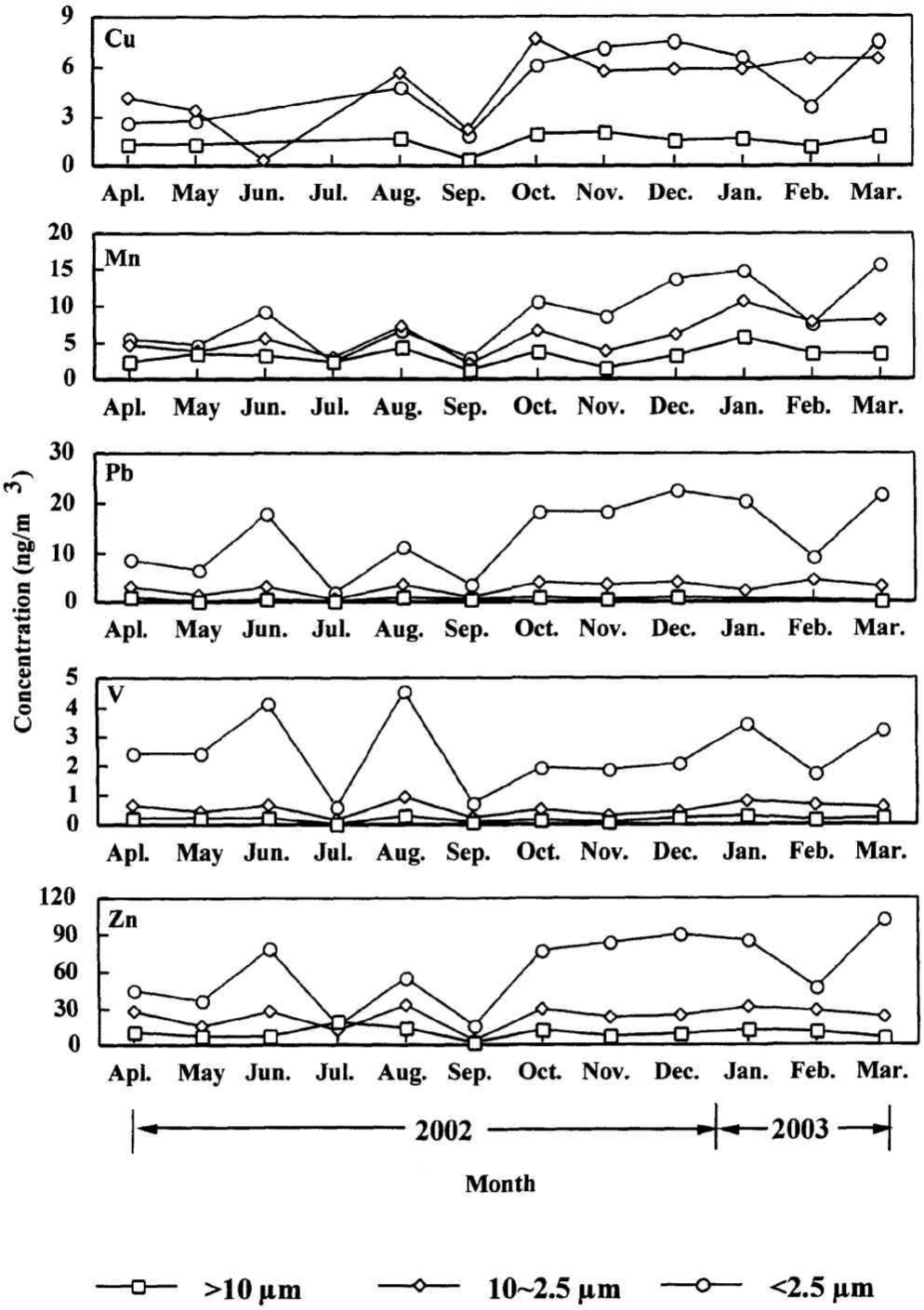

Fig.5: Seasonal changes of copper, manganese, lead, vanadium and zinc in the atmospheric aerosols around Kinki University from April to March 2003.

Table 1 Correlation coefficients in bilateral elements in the coarse particles of >10 μm. (in 2003)

	Al	Ca	Fe	Mg	K	Cu	Mn	Pb	V	Zn
Al	1.00	—	—	—	—	—	—	—	—	—
Ca	**0.90**	1.00	—	—	—	—	—	—	—	—
Fe	**0.79**	**0.84**	1.00	—	—	—	—	—	—	—
Mg	0.63	0.64	0.43	1.00	—	—	—	—	—	—
K	**0.84**	**0.78**	0.62	0.64	1.00	—	—	—	—	—
Cu	0.42	0.43	0.48	0.39	0.28	1.00	—	—	—	—
Mn	0.61	0.69	**0.93**	0.19	0.39	0.40	1.00	—	—	—
Pb	-0.17	0.13	0.12	0.18	-0.02	0.04	0.21	1.00	—	—
V	0.53	0.55	**0.73**	0.31	0.54	0.33	**0.76**	0.11	1.00	—
Zn	0.11	0.31	0.29	-0.14	0.09	0.55	0.41	0.11	0.07	1.00

Table 2 Correlation coefficients in bilateral elements in the coarse particles of 2.5-10 μm.(in 2003)

	Al	Ca	Fe	Mg	K	Cu	Mn	Pb	V	Zn
Al	1.00	—	—	—	—	—	—	—	—	—
Ca	**0.90**	1.00	—	—	—	—	—	—	—	—
Fe	**0.71**	**0.84**	1.00	—	—	—	—	—	—	—
Mg	0.70	0.65	0.32	1.00	—	—	—	—	—	—
K	0.61	0.59	0.35	**0.82**	1.00	—	—	—	—	—
Cu	0.65	**0.72**	0.63	0.41	0.11	1.00	—	—	—	—
Mn	0.69	**0.77**	**0.95**	0.24	0.23	0.55	1.00	—	—	—
Pb	0.62	0.64	0.68	0.34	0.43	0.54	0.52	1.00	—	—
V	0.51	0.58	**0.73**	0.31	0.42	0.17	**0.73**	0.58	1.00	—
Zn	0.55	0.68	**0.86**	0.24	0.40	0.44	**0.77**	**0.79**	**0.83**	1.00

Table 3 Correlation coefficients in bilateral elements in the fine particles of <2.5 μm.(in 2003)

	Al	Ca	Fe	Mg	K	Cu	Mn	Pb	V	Zn
Al	1.00	—	—	—	—	—	—	—	—	—
Ca	**0.97**	1.00	—	—	—	—	—	—	—	—
Fe	**0.88**	**0.93**	1.00	—	—	—	—	—	—	—
Mg	**0.93**	**0.91**	**0.83**	1.00	—	—	—	—	—	—
K	**0.79**	**0.86**	**0.94**	**0.75**	1.00	—	—	—	—	—
Cu	**0.76**	**0.77**	**0.87**	**0.78**	**0.87**	1.00	—	—	—	—
Mn	**0.88**	**0.91**	**0.97**	**0.84**	**0.93**	**0.90**	1.00	—	—	—
Pb	**0.74**	**0.76**	**0.89**	**0.74**	**0.91**	**0.98**	**0.93**	1.00	—	—
V	0.35	0.33	0.49	0.40	0.46	0.35	0.48	0.51	1.00	—
Zn	**0.77**	**0.77**	**0.88**	**0.77**	**0.91**	**0.98**	**0.94**	**0.99**	0.56	1.00

5. Relationship between aerosols and SPM

The SPM-613D measurements indicate the dominance of fine anthropogenic (PM2.5) and coarse (PMc) particles over Osaka during the dust events (except for events -b, -c and -f). Furthermore, PM2.5 data are larger than PMc in events-u, –x, -g –h, -i, -j, -k, -l, -m and -o. This feature is also clearly shown by the aerosol size derived from the radiometry of AERONET.

The scatter grams in Fig.7 of PM2.5 against AOT(0.87μm) and AI show clear correlations. The correlation coefficient is 0.58 for AI, and 0.60 for AOT. Furthermore, the value rises except the dust events. The value is 0.59 for AI, and 0.61 for AOT.

Chemical analysis of the Teflon tape filter used in the SPM-613D combined with the obtained OBC data reveal the compound elements of particulate matter. These results all indicate that the high-level anthropogenic particles in the air over the Osaka site. It is well known the air quality of Osaka site is very poor, and our results indicate that the local air quality is influenced not only by local emissions from sources as diesel vehicles and, chemical industries, but also by large scale climatic condition such as dust particles coming from continental desert areas.

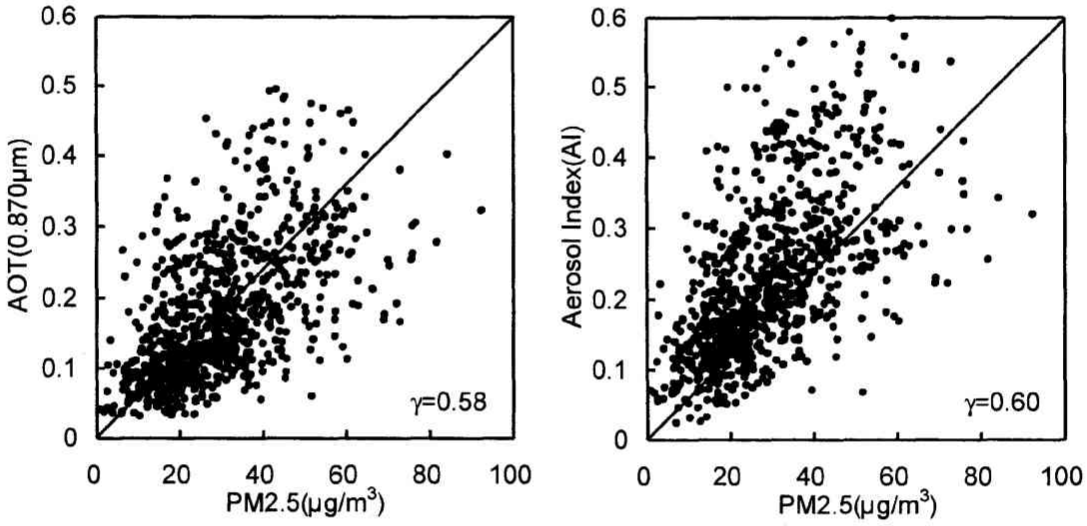

Fig.7: Scattergrams of PM2.5 against AOT(0.87μm) / aerosol index (AI).

6. Conclusions

We have examined the relationship between the aerosol properties derived from radiometry and the particulate mass simultaneously obtained with the new SPM-613D instrument. Strong correlations were found between the SPM concentrations and the AOT(0.87μm)/ and AI values. SPM measurements allow the dominate particle size to be determined (i.e. PM2.5, TSP/PM10, or BOC). Combining radiometric aerosol information and the surface-level particulate mass is useful when studying air quality and aerosol properties. For example, the linear correlation between SPM and AI (or AOT) allows the aerosol properties to be estimated from SPM data in areas without an AERONET site, on cloudy/rainy days, or at night. Alternatively, satellite-derived aerosol information is useful for indicating air quality in a global scale.

Chemical analysis of the SPM-613D measurements will help determine the aerosol composition.

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References

[1] Sano,I. Mukai, S. Okada, Y. Holben, B.N. Ohta, S and Takamura,T (2003), Optical properties of aerosols during APEX and ACE-Asia experiments, *J. Geophys.Res.*, **108**, 8649, doi:10.1029/2002JD003263.

[2] Dubovik,O., Smirnov, A., Holben, King, M.D., Kaufman, Y.J., Ech, T.F. and Slutsker, I. (2000),Accuracy assessments of aerosol optical properties retrieved from AERONET sun and sky-radiaometric measurements, *J. Geophys.Res.*, **105**, 9791-0806.

[3] Dubovik,O. and King, M.D.(2000), A flexible inversion algorithm for retrieval of aerosols optical properties from sun and sky radiance measurements, *J. Geophys.Res.*, **105**, 20673-20696.

[4] Holben, B.N., T.F. Eck, I. Slutsker, D. Tanré, J.P. Buis, A. Setzer, E. Vermote, J.A. Reagan, Y. Kaufman, T. Nakajima, F. Lavenu, I. Jankowiak, and A. Smirnov, AERONET - A federated instrument network and data archive for aerosol characterization, *Rem. Sens. Environ.*, **66**, 1–16, 1998.

[5] Goloub, P., Deuze, J.L., Herman, M.,Marchand, A., Tanre, D., Chiapello, I., Roger, B.,Singh, R.P. (2000), Aerosol Remote Sensing Over Land From The Spaceborne Polarimeter POLDER, *Proc. IRS2000*,115-116.

[6] Smirnov, A., Holben B.N., Savoie, D., Prospero, J.M., Kaufmann, Y.J. Tanre, D., Eck, T.F. and Slutsker, I.S. (2000), Relationship between column aerosol optical thickness and in situ ground based dust concentrations over Barbados, *Geophys. Res. Letter,* **27**, 1643-1646.

[7] Wang, J. and Christopher, S.A. (2003), Intercomparison between satellite-derived aerosol optical thickness and PM2.5 mass: Implications for air quality studies, *Geophys. Res. Letter,* **30**, 2095, doi:10.1029/2003GL018174.

[8] Balasubramanian, R., Qian, W.-B., Decesan, S. Facchini, M.C. and Fuzzi, S. (2003), Comprehensive characterization of PM2.5 aerosols in Singapore, *J. Geophys.Res.*, **108**, 4523,doi:10,1029/2002JD002517.

[9] Eck, T.F., Holben, B.N.Reid, J.S., Dubovik,O., Smirnov, A., O'neill, N.T., Slutsker, I. and Kinne, S. (1999), Wavelength dependence of the optical depth of biomass burning, urban, and desert dust aerosols, modal, *J. Geophys.Res.*, **104**, no.D24, pp.31,333-31,349.

[10] Kasahara, M. (2002), The present state and future assignments of air pollution by particulate matter -The measuring of innovation of PM2.5-, *J. Jpn. Soc. Atmos. Environ.*, **37**(2), 96-107(in Japanese).

[11] Tomiyasu, B., Arai, N., Koyama, H., Liu, G., Owari, M., and Nihei, Y. (1996), Source apportionment of individual airborne particle in underground center by using electron probe microanalyzer, *Chem. Soc. Jpn.*, 500-507 (in Japanese with English abstract).

[12] Sensui, Y. and Tomura, K. (2001), Temperature effects on the concentration of Cl and Br and seasonal behavior of several elements in urban air in the south of Saitama, Japan, *J. Soc. Atoms. Environ.*, 185-194.