Special Feature: Powertrain and Environment

Review

Air Quality and Vehicle Exhaust Impact

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ABSTRACT The impact of vehicle exhaust on ambient ultrafine particles was investigated from the aspect of nucleation, condensation, and evaporation processes at a roadside atmosphere. The ultrafine particles relationship to traffic environment, affect on the urban background and relationship with photochemical reaction, particle growth, and source contribution to particles was studied.

The behavior of ultrafine particles less than 100 nm in the roadside atmosphere has not been clarified because it involves unstable volatile components. Using a fast-response aerosol spectrometer capable of providing near instantaneous particle number concentration measurements in real-time, the behavior of ultrafine particles during one signal cycle became understood, and it was understood that the effect of condensation/evaporation processes is important, in addition to coagulation. The number concentration of ultrafine particles depends on the traffic environment variables such as traffic volume, heavy duty vehicle mixing ratio, and vehicle speed.

Vehicle emissions are a source of ultrafine particles, however, photochemical nucleation disburses ultrafine particle everywhere. The particle growth rate at an urban background monitoring site was observed and the rate of photochemical nucleation showed more than two times the rate of vehicle emission. The particle growth in fine particles of more than 500 nm was also found in a planetary boundary layer in the Tokyo atmosphere. Organic carbon is a main component of the secondary particles. However, since carbonaceous aerosol involves many carbonaceous compositions and changes with photochemical oxidation, its source contribution and ambient behavior is not well known. Carbon isotope (^{14}C) analysis is an effective way to distinguish the carbon source between fossil fuels and biomass. From large-scale observations of summer and winter in the southern Kanto area, source contribution of carbonaceous components in $PM_{2.5}$ was estimated.

KEYWORDS Nanoparticle, Ultrafine Particle, Number Concentration, Volatile Component, Particle Growth, Traffic, Diesel, Biomass, Elemental Carbon, Organic Carbon, Carbon Isotope

1. Introduction

The Japanese Ministry of Environment (MOE) promulgated the air quality standard of $PM_{2.5}$ on September 2009. In the MOE report of 2010 fiscal year (http://www.env.go.jp/press/press.php?serial=14869), an achievement ratio of $PM_{2.5}$ air quality standard determined at an ambient monitoring station was 32.4% and vehicle emission monitoring stations was 8.3%. Because the annual average concentration of $PM_{2.5}$ in remote areas with very little anthropogenic emission has values close to the air quality standard, it is difficult to achieve the standard in urban areas. In order to decrease $PM_{2.5}$ concentrations and to understand the source contribution, chemical composition analysis was started to be performed at each local government site.

The vehicle emissions were major contributors to particulate matter (PM).[1] However, with recent advances in emission reduction technology, the elemental carbon (EC) concentration that was a representative of the primary particle in $PM_{2.5}$ decreased in Tokyo noticeably. **Figure 1** shows EC and organic carbon (OC) concentration trend in fine PM ($PM_{2.1}$) by year of 2004.[2] In recent years, in spite of diesel vehicle emission reduction, the EC concentration has not shown a concentration reduction commensurate with reduced emissions in Tokyo.[3] Therefore, it is

necessary to review the ambient PM behavior involving nanoparticle formation and growth, the emission source contribution in PM especially in carbonaceous aerosol.

The diesel vehicle exhaust purification technology changes a roadside nanoparticle condition dramatically in this decade. Today, because there is no systematic research on roadside ultrafine particles, which is less than 100 nm, this review shows the results before installation of a diesel particulate filter (DPF). Carbonaceous aerosol involves many carbonaceous compositions and changes with photochemical oxidation. Its source contribution and ambient behavior is not well known.[4] Secondary organic aerosols (SOA) concentration prediction using an air quality simulation model has results which are less than observed results in many cases.[5] Research of undetected emission sources, such as VOC of from biomass origin (BVOC) or VOC of difficult to volatilize (SVOC), has started.[6] This review shows the source estimation results using the carbon profiler and carbon isotope analysis.

2. Tail Pipe Ultrafine Particle and the Behavior in Ambient Roadside Condition

Minoura et al.[7] investigated the tail pipe particles of 2.98-litter diesel vehicle (Toyota Quick-Delivery, 2002MY) with the oxidative catalyst and the relation with driving conditions during JCAP-II (Japan Clean Air Program Phase-II, http://www.pecj.or.jp/ japanese/ jcap/jcap2/index_jcap2.html), as shown in **Fig. 2**. The particle measurement less than 560 nm (as scanning mobility diameter) was carried out using the engine exhaust particle seizer (EEPS 3090, TSI), which is the first type of scanning mobility particle seizer (SMPS).

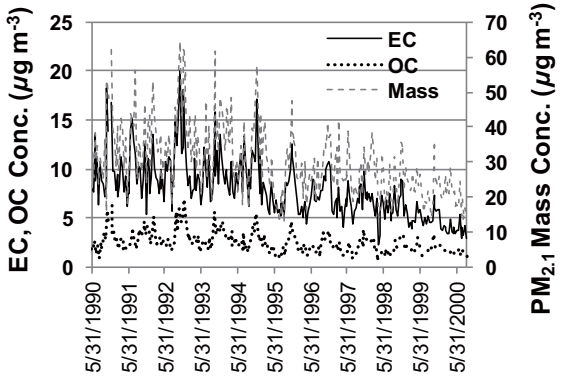

Fig. 1 Concentration trend in $PM_{2.1}$ observed at Tokyo, Japan.

Figure 2 was obtained based on 31 times exhaust measurements, and increased particle volume was observed at high vehicle speed and acceleration. This vehicle exhaust impacts gave the roadside atmosphere lasts a few second after passing through the measurement site as shown in **Fig. 3**. From the time described as (i) which the target vehicle passed, the exhaust gas was observed at roadside at the time described as (ii) which was overdue for about 2 seconds, and high concentration measured for about 4 seconds. Figure 3 shows temporal variation of size distribution of exhaust and ambient particles using four sets of EEPS at the same time. The particles passing through the thermo denuder (TD) heated at 350°C are the solid particle such as soot. The difference between the number size distributions with and without TD means the number size distribution of volatile particles. The temporal variation of the Fig. 3(c) was larger than that of Fig. 3(d), and it became clear that volatile

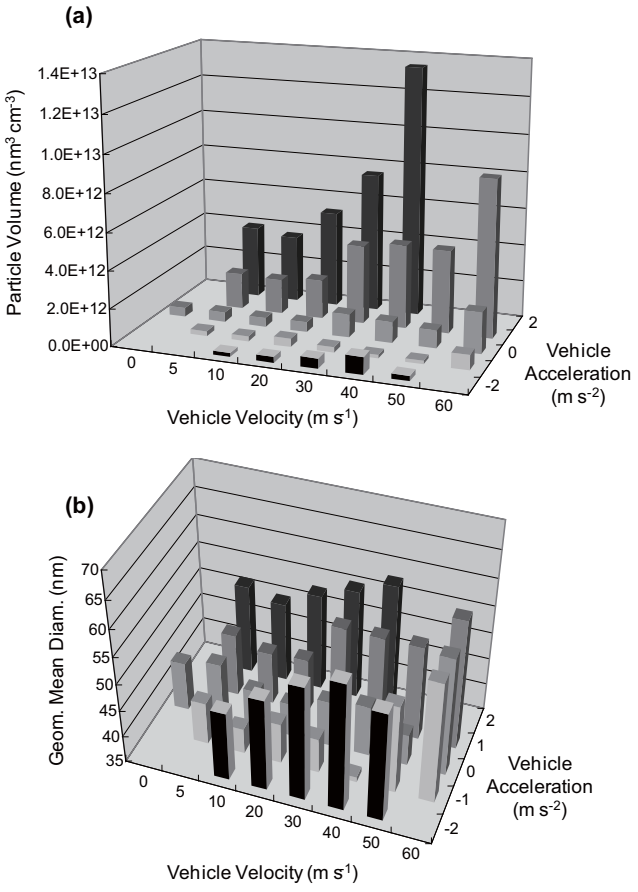

Fig. 2 Exhaust PM characterization of on-board vehicles as a function of driving states.
(a) Volume of volatile components.
(b) Geometric mean diameter of non-volatile particles.

particles from the vehicle exhaust had an impact on ambient number concentrations of ultrafine particles (UFPs) of less than 100 nm for a few seconds. The impact of individual vehicle exhaust overlap, a concentration of a roadside UFP shows a very complicated variation. Traffic volume is one of the large factors of the fluctuations, and the temporal variation of UFP character was summarized as a function of an elapsed time of a traffic signal as shown in **Fig. 4**. Figure 4 was obtained from 10 Hz measurement for ten hours (8:00 – 18:00) on July 30, 2005 at a curbside of near the Noge park intersection of the Ring 8 industrial road in Tokyo. With the increase of traffic volume, the number concentration was increased. The number concentrations of non-volatile particles (NCwtTD) measured at a height of 1 m showed consistent change with those measured at 3 m. This means particle dispersion was negligible. The difference of number concentration including volatile particles (NCwoTD) means the number of volatized particles during the advection from 1 m to 3 m. The temporal variation of the volume of the volatile component (VVC) is shown in Fig. 4(d). The change in VVC was greater at 3 m than 1 m, in a condition where diffusion dispersion was negligible, creation and evaporation of semi-volatile particles had been suggested. As shown in **Fig. 5**, while VVC was proportional to the traffic volume, the number concentration showed hysteresis change. This is thought to be the result of two different time-dependent processes of particle nucleation and evaporation accompanying particle separation occurred at the same time. Supply of primary particles that is proportional to the traffic volume was involved in this phenomenon, but as shown in Fig. 4(b), the impact of volatile particle to the number concentration was large.

The relationship between UFP number concentration and traffic volume depends on the traffic environment. **Figure 6** shows the results of measurement of UFP in eleven typical traffic environments in Tokyo which was classified as traffic volume, average vehicle speed, and mixing rate of heavy duty vehicle.[8] Site 1 in Fig. 6 shows measurement results of residential roads with less traffic, the site 9a and 9b were the result of an industrial road with many heavy duty vehicles (HDVs). The site 2 had been recorded as narrow streets with low traffic volume but high HDV mixing ratio in the 1999 traffic census. Number concentration was affected by not only the traffic volume but also HDV mixing ratio as shown in Figs. 6(a) and (b). On the other hand, in

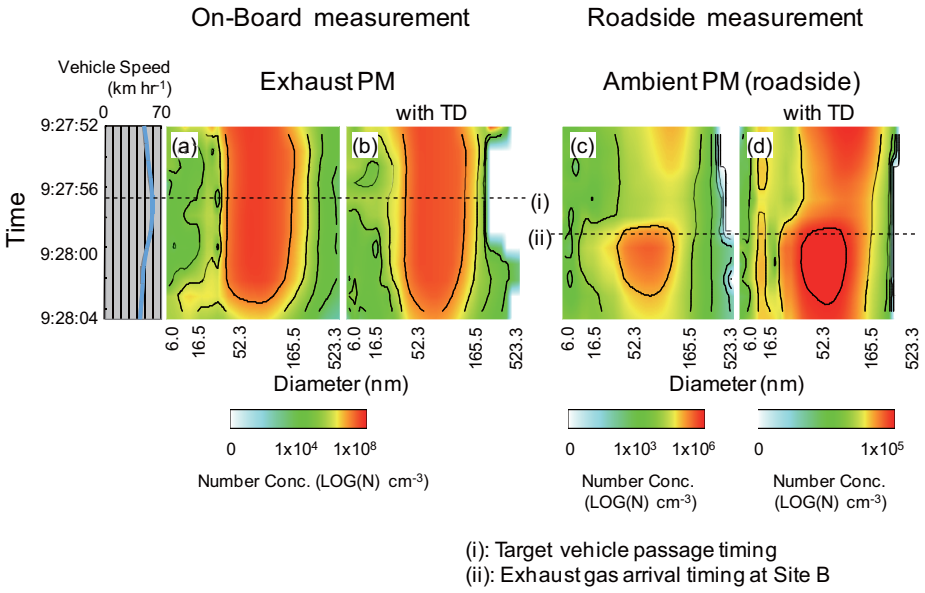

Fig. 3 Impact of the vehicle exhaust emission on the roadside number size distribution (a comparison of the temporal variation of the number size distribution).
(a) Temporal variation of number size distribution of the vehicle emission.
(b) Temporal variation of number size distribution of the vehicle emission after having passed the Thermo-denuder.
(c) Temporal variation of number size distribution of the ambient air at roadside.
(d) Temporal variation of number size distribution of the ambient air at roadside after having passed the Thermo-denuder.

regarding to vehicle speed, a positive correlation with number concentration was found in a group of many HDVs (site 2, site 9a, and site 9b), but other groups (many gasoline passenger car group) showed a negative correlation. The UFP number concentrations decreased as vehicle speed increased. This suggests the diffusion of UFP in the air occurs due to drag wind of vehicles. The negative correlation was considered due to the drag wind dispersion. On the other hand, vehicle emission increased in proportion to the vehicle speed. The positive correlation suggested tail pipe emissions exceeded the dispersion effect. From the results shown in Figs. 6(a) and (e), the HDVs exhaust provides a large number of small particles (ultrafine soot particles). At the site 7 where many gasoline passenger cars were running, the geometric mean diameter showed highest except site 1a and 1b of the background sites. This result is considered due to the particle growth through the condensation process of semi-volatile particles from above discussion. After introduction of diesel particle filters for HDVs, the number concentration of the ultrafine soot particles (non-volatile UFP) decreased year by year.[9] Therefore, it is necessary to review the relationship between the roadside UFPs and traffic environment today.

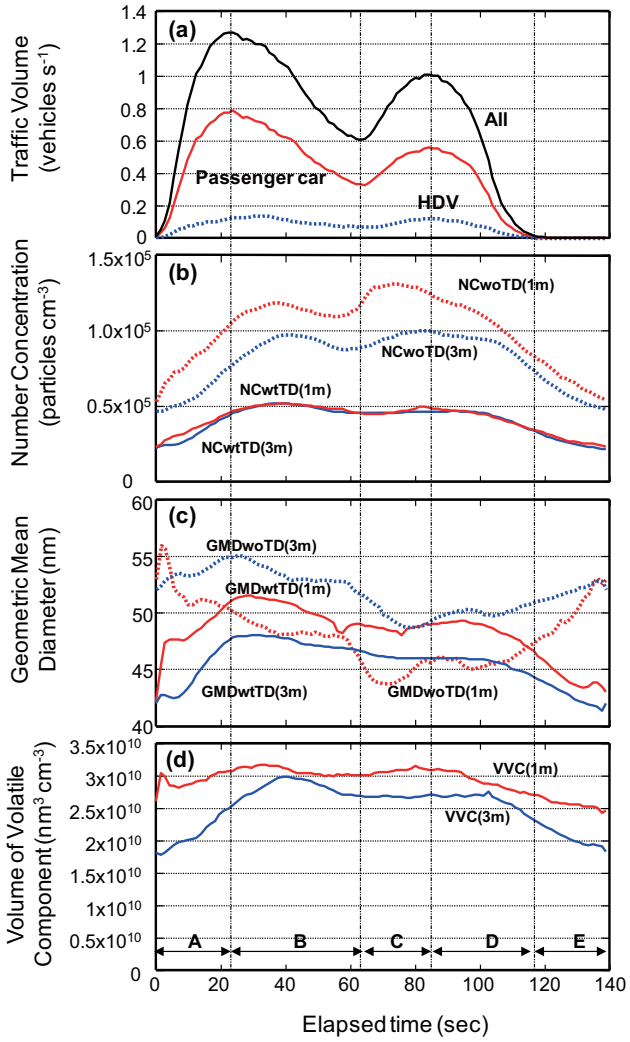

Fig. 4 Average values as a function of signal elapsed time at the Noge Park intersection, Tokyo, Japan observed from 10:00 to 18:00 on July 28, 2005.
(a) Traffic volume (TV).
(b) Number concentrations (NC) of ambient particles with/without Thermo-denuder (TD) measured at 1 m height and 3 m height.
(c) Geometric mean diameter (GMD).
(d) Volume of volatile component (VVC).

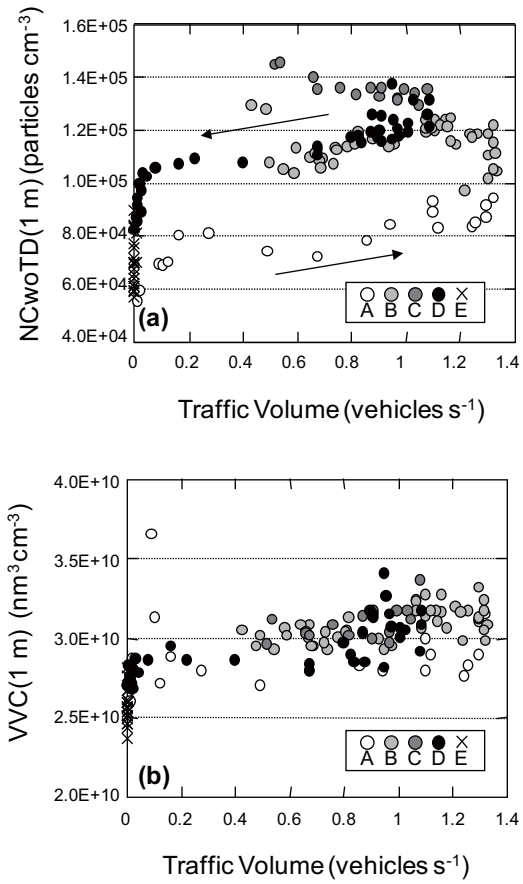

Fig. 5 Traffic volume and correlation with NC (upper) and correlation with VVC (lower); the relation was derived from the data shown in Fig. 4. "A" was provided from the data between the time from the signal elapsed time equals zero to the first peak of TV (t = 22 sec). "B" was provided from the data between the first peak of TV to the first bottom of TV (t = 65 sec). "C" was provided from the data between the first bottom of TV (to the second peak of TV (t = 83 sec). "D" was provided from the data between the second peak of TV to the time of the signal stopping (t = 115 sec). "E" was provided from the data during the signal stopping.

3. Urban Background UFP

Traffic emission is one of the creation sources of UFPs. However, photochemical nucleation occurs everywhere. **Figure 7** shows the average UFP observation results for one month in August and December 2001 using SMPS at Toyota Central R&D Labs., Inc. in Nagakute, Japan.[10] The nearest pollution source was a trunk road (a traffic volume of 36,116 vehicles day-1 based on a 2002 traffic census), which is on the north side 440 m from the observation site, and traffic rush was found in the morning and in the evening. This site located in the eastern part of Nagoya (population about 2.2 million) about 20 km from the city center, and 40 km north from Mikawa plane where many industrial facilities exists, and southern wind transports air pollution to the observation site in summer. In winter, a peak number concentration was observed at about 40 nm during the morning rush, and a peak number concentration around 70 nm was continuously seen with little size variation (Fig. 7(a)). The growth rate of the particle from 6:00 to 10:00 was 7.6 nm hr^{-1}. On the other hand, a peak number concentration of about 40 nm was recorded at 11:00 and 16:00 in the summer (Fig. 7(b)). The growth rate of the particle size from 11:00 to 14:00 was 7.9 nm hr^{-1}, and the second one of 14.7 nm hr^{-1} was obtained from 16:00 to 19:00. The winter peak was considered due to the vehicle emission of the north road. The second peak in summer at 14:00 was considered due to

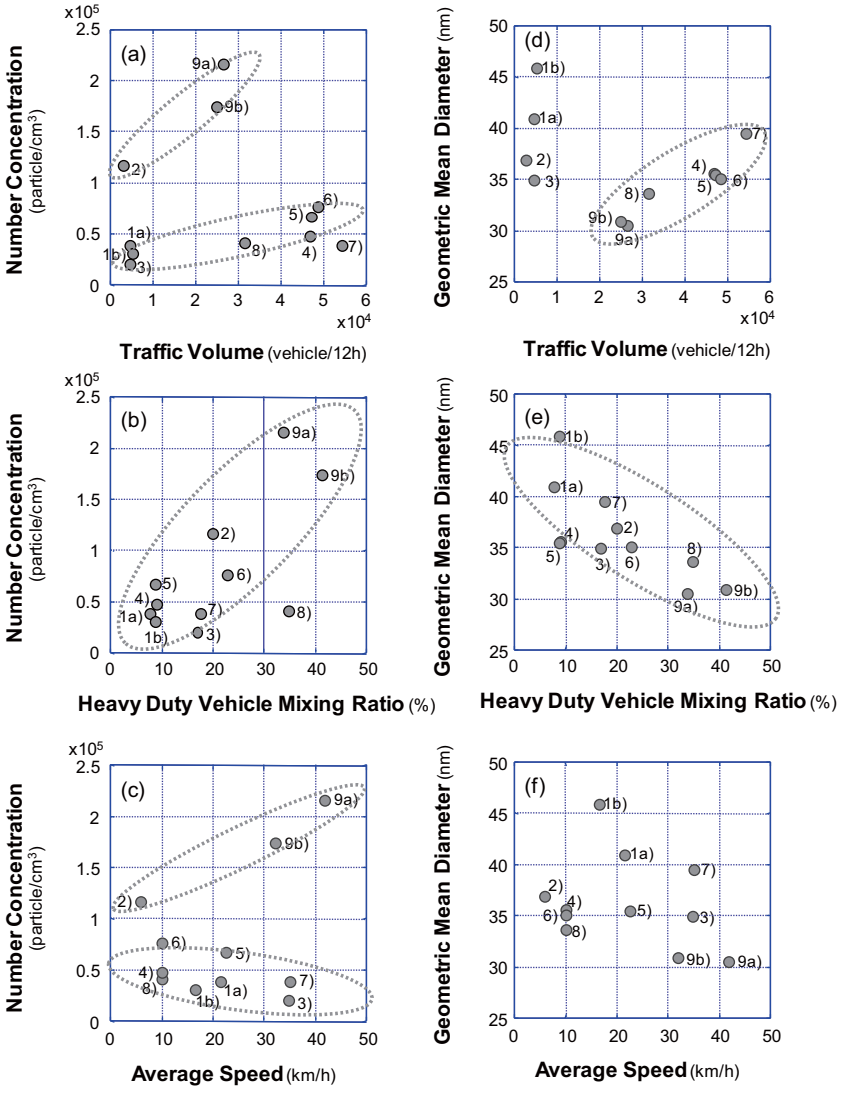

Fig. 6 Correlation between traffic parameters and average particle number concentrations (a, b, c), and geometric mean diameters (e, f, g), observed in different traffic environment in Tokyo from October 7 to October 17, 2002. The traffic information was derived from the Traffic Census 2002.

photochemical nucleation from the transported pollutants from south. **Table 1** shows the summary of the air quality situation when a peak particle diameter of less than 60 nm was observed. In winter, when the small particle was observed, air quality showed high NO concentration and vehicle emission was suggested to be involved. In summer, it was found in the condition of high ozone and low NOx concentration in addition with high solar radiation intensity, which suggests UFP formation through photochemical nucleation. The number concentration of UPF in winter was six times higher than in summer due to the pollutants stagnation in the thin planetary boundary layer in winter. But the particle growth rate was double in summer in comparison with in winter. The semi-volatile component is considered highly impact on the particle growth, and the photochemical reaction supports it in summer. But in winter, by the distribution of growth substance, a lot of primary particles might lower the particle growth rate.

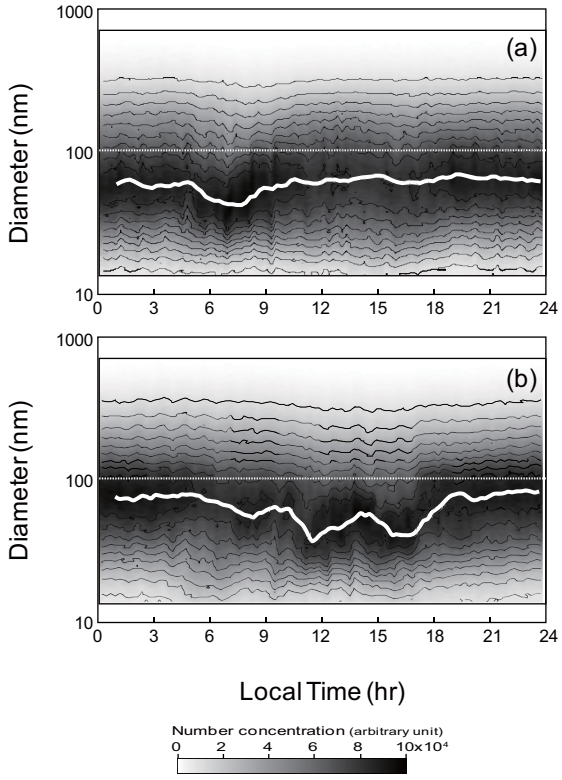

Fig. 7 The averaged temporal variation in particle size distribution observed at urban background in Nagakute, Japan. Particle size distribution was normalized by the total number concentration and averaged at every local time for the entire observation time period, except for Saturday and Sunday. The white solid line shows a moving average value for one hour of the peak diameter of size distribution.
(a) The distribution in winter observed from December 21, 2001 to January 17, 2002.
(b) The distribution in summer observed from July 23 to August 27, 2001.

Particle growth by photochemical reaction can be found also in fine particle. **Figure 8** shows the particle number concentration and mean diameter variations as a function of distance from the seashore of Urayasu observed using air craft in August 2010 during the JATOP (Japan Auto-Oil Program) intentional observation campaign.[11] The particle number concentration and average particle size of more than 500 nm was measured by APS model 3321 (TSI, USA). During the round trip flight from Tokyo Bay to Kisai traveling north-northwest at 600 m altitude, increased number concentration and decreased particle size was observed. From the ground observation network, highly polluted air was observed in northern area, and the results shown in Fig. 8 confirmed the typical patterns of spatial distributions of the pollutions in south Kanto region. The number concentration and its relationship with mean particle diameter showed a well-organized distribution, as shown in **Fig. 9**. The white dots are the observation results of inland flight, and the black dots are obtained during the flight at costal line at flight altitude of 200 m. In coastal areas, the distribution was skewed toward larger particles

Table 1 The average conditions of weather and air quality observed with a smaller size distribution of peak diameters less than 60 nm. The number in parenthesis shows the data number used for the average. The line written as "all" is the reference value with an average of all data.

		Weather				Air Quality			
		Wind Speed	Temperature	Relative Humidity	Solar Radiation	NO	NO_2	O_3	SPM
		(m/sec)	(°C)	(%)	(ly/min)	(ppb)	(ppb)	(ppb)	(μg/m³)
summer	D<60nm (141)	0.51	30.1	74.6	0.53	3.7	12.4	50.3	24.9
	all (3651)	0.55	27.7	83.4	0.27	3.3	13.3	31.6	19.5
winter	D<60nm (141)	0.40	2.2	92.6	0.11	40.1	22.1	1.6	19.7
	all (2702)	0.91	4.4	85.7	0.09	21.2	20.6	10.7	15.4

compared with the distribution of particles inland. An axis of particle volume was drawn, assuming spherical particles, as shown in Fig. 9. Volumetric changes of more than 3-fold were seen in the distribution of particles sampled in inland areas, whereas no clear volumetric changes were seen in the distribution of particles sampled along the coast. This suggests that particles along the coast underwent physical coagulation and separation without a volumetric change. On the other hand, volumetric increase accompanying secondary particle condensation was seen in the inland area. Figure 9 is the result obtained during the nine round-trip flights which carried out for three days, and similar particle change was confirmed each flight. The particle growth rate was estimated from the local time observations, as 3.79 nm hr^{-1}. Particle growth rates are often discussed as nano-size particles. Laaksonen et al.[12] reported nano-particles

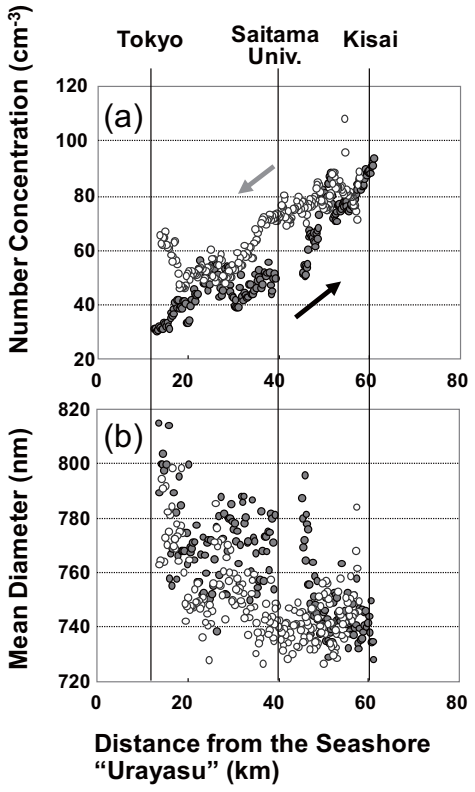

Fig. 8 An example of spatial variation of (a) particle number concentration and (b) mean diameter between the central Tokyo and Kisai rural area, as a function of the distance from the seashore "Urayasu". These data were measured using on-board APS spectrometer during the round level flight from Tokyo to Kisai. The observation of flight was from 15:35 to 16:52 on July 31, 2008 and the average altitude was 619 m (590-667 m). Outbound journey values are indicated by black dots, while the return journey values are white dots.

growth rate of around 1 nm hr^{-1} from measurements in the Finnish forest sky. Liu et al.[13] showed growth rates of 2.2-19.81 nm hr^{-1} based on measurements of Chinese city skies. According to above discussion of Minoura and Takekawa,[10] photochemical particle growth rate in a Japanese suburb was 14.7 nm hr^{-1}. As mentioned above, the growth rate of particles larger than 500 nm was 3.79 nm h^{-1}, which fell in the 1-20 nm h^{-1} range that Kulmala et al.[14] cited as a typical growth rate in cities. Kalafut-Pettibone et al.[15] observed the variation of particle volume using an APS and SMPS in Mexico City and showed a daytime increase in particle volume for particles 700 nm in size. This particle growth rate calculated here is the first value measured in the upper planetary boundary layer of the Tokyo sky. We should keep in mind, however, that this value was obtained including part of the growth of the tail of the nucleation mode particles smaller than 500 nm.

4. Carbonaceous Compositions from Vehicle Exhaust and Contribution to the Regional $PM_{2.5}$

It was shown that the vehicle exhaust has affected the mass concentration of particles and number concentration as primary particles and secondary particles. In order to reduce the $PM_{2.5}$ concentration, primary particles can be reduced by the filter technology such as diesel particulate filter (DPF), many

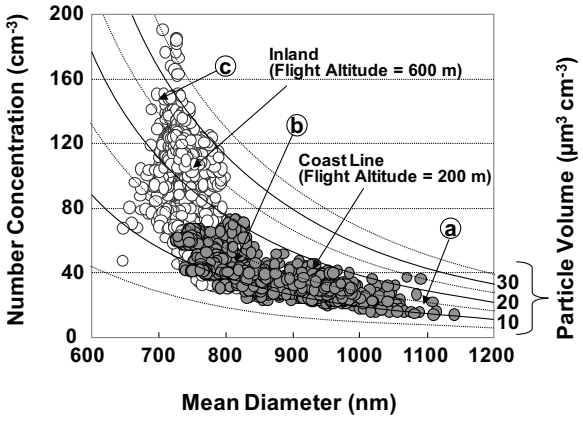

Fig. 9 Number concentration and the relationship with mean particle diameter observed from July 30 to August 1, 2008 at Tokyo Bay coastline and inland flight from Tokyo to Kisai. Particles sampled at an altitude of 200 m in coast line areas are shown by black dots and particles sampled at 600 m in inland areas are shown by white dots. An axis of particle volume was drawn, assuming spherical particles.

researchers focus on measures of secondary particles. Carbonaceous aerosol involves many carbonaceous compositions and changes with photochemical oxidation. Its source contribution and ambient behavior is not well known.[4,16] Secondary organic particles concentration prediction using an air quality simulation model has results which are less than observed results in many cases.[5,17] Research of undetected emission sources, such as VOC of from biomass origin (BVOC), has started.[6] To evaluate the effective improvement in $PM_{2.5}$ concentration, two intentional observations camping were conducted in summer of 2008 and in winter of 2009 by the JATOP (Japanese Auto-Oil program; www.pecj.or.jp/english/jcap/index_e.asp) program.

Carbon isotope (^{14}C) analysis is an effective way to distinguish the carbon source between fossil fuels and biomass. Measurements on carbon isotope were conducted during JATOP intentional observation campaigns in summer of 2009 and in winter of 2009.[18] The percent modern carbon (pMC) which is an index of biomass origin, is estimated on the basis of the ^{14}C concentration in 1950 as reference value (pMC = 100%, $\Delta\ ^{14}C$ = 0‰), and corrected the isotope fractionation effect by normalizing the sample $\delta^{13}C$ value to –25.0‰. **Figure 10** shows the correlation between pMC and levoglucosan, which is known as the trace substance of biomass burning. BTC, which is total carbon of biomass origin, showed good correlation with levoglucosan, except the data offset at BTC of 0.3 μg m^{-3} (possible reasons will be discussed later). **Figure 11** shows spatial distribution of pMC in $PM_{2.5}$ obtained from seven sites in south Kanto for two weeks sampling during the summer campaign of 2008. The pMC of TC at Kudan, which was the sampling site in central Tokyo, was the lowest (29%), and had the highest result at NIES (47%), which was the rural site in Tsukuba. As expected, results showed a high biomass contribution in the suburbs. Additionally, it became apparent that biomass emission contributed to nearly 29% of TC in the central Tokyo. Possible biomass combustion sources in central Tokyo are cooking smoke, tobacco smoke, and garbage incineration (private communication with researchers of Tokyo government). At the Yoyogi site, which was close to the Kudan site, it should be noted that the pMC value was 12% higher than Kudan. Since Yoyogi Park is one of the largest metropolitan parks in central Tokyo, it is improbable large-scale biomass combustion occurred there. The organic carbon from biogenic VOC (BVOC) origin without combustion is considered to be one of the sources.

In the 2009 winter campaign, pMC was measured from not only TC but also from EC of the same sample.

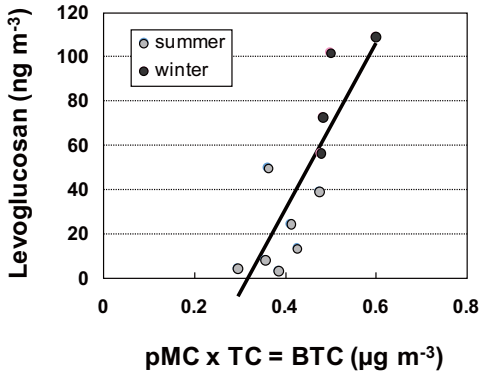

Fig. 10 Relationship with biogenic total carbon (BTC) and levoglucosan concentration.

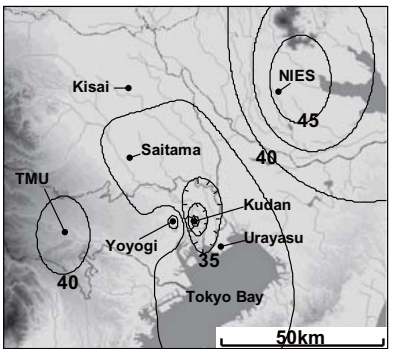

Fig. 11 Spatial distribution of percent modern carbon (pMC) in $PM_{2.5}$ sampled from July 28 to August 11, 2008.

Table 2 Summary of pMC involved in carbon components.

	pMC	Urayasu	Kudan	Saitama	Kisai	NIES	TMU	Yoyogi	average
Summer 2008	TC	37.32 ± 0.14	29.14 ± 0.12	35.48 ± 0.13	38.79 ± 0.15	46.97 ± 0.15	41.01 ± 0.16	41.07 ± 0.14	38.5
Winter 2009	TC	46.73 ± 0.16	48.15 ± 0.17	49.37 ± 0.18	59.32 ± 0.16				50.9
	EC	35.02 ± 0.16	35.23 ± 0.12	38.23 ± 0.13	45.54 ± 0.16				38.5
	OC	53.60	54.99	55.21	66.72				57.6

Table 2 shows the summary of pMC observed both seasons. The pMC of OC (pMC_{OC}) was the estimated value by using the following Equation (1):

$$pMC_{OC} = [EC]/[OC] \times (pMC_{TC} - pMC_{EC}) + pMC_{TC} \quad \cdots\cdots\cdots\cdots\cdots (1)$$

where pMC_{TC} and pMC_{EC} means pMC based on TC and EC, respectively. Furthermore, as restriction conditions, Equations (2) and (3) have been established:

$$[TC] = [EC] + [OC] \quad \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

$$[BTC] = [BEC] + [BOC] \quad \cdots\cdots\cdots\cdots\cdots (3)$$

where [BTC], [BEC], and [BOC] means concentration of TC, EC, and OC of Biomass origin, respectively.

The higher pMC was observed in the suburbs compared to central Tokyo, and in winter compared to summer. Since the north wind was prevailing in the winter, it supported the hypothesis of biomass contributions being transported from the northern rural (agriculture) area. The tendency where pMC in Kudan during the winter increased to 48% from 29% in the summer agreed with a previous study observed in 2004,[19] as shown in **Fig. 12**. Fossil fuel emission contribution at the four main sites on average was 61% and 49% in the summer and winter, respectively. These values for the Japan rural area are about 20% higher than the Europe rural background.[20]

From results shown in Table 2, approximately 58% of carbonaceous aerosols originated as BOC, and contribution of BOC was higher than BEC even in the winter season. Since it is expected that large quantities of VOCs with bio-origin evaporate in summer compared to the winter, increased BOC contribution is also expected in summer. It is hypothesized that the high pMC value at the Yoyogi site had a high BOC contribution. Using the pMC values obtained in Table 2, concentration was estimated according to the origin of carbonaceous aerosol, and is shown in **Fig. 13**. As shown in Fig. 13(a), carbonaceous aerosol of fossil fuel origin (FTC) exceeded the biomass origin (BTC) and emissions of industrial areas near Tokyo Bay increased FTC concentration of the neighborhood site. The FTC concentration of Urayasu was low (1.1 μg m^{-3}), since emissions are dispersed to Tokyo Bay. However, the ratio of FTC contained in TC (FTC/TC) became the highest (63%) of all sites. It is necessary to investigate fossil fuel emission sources in detail, such as vessels or and oil refining facing Tokyo Bay. Winter results are shown in Fig. 13(b). This has similar FTC concentration results of about 3 μg m^{-3} for all observation sites. EC from fossil fuel origin (FEC) involves Soot-EC, which is EC produced with high temperature combustion.[21] However, Soot-EC showed a different tendency than the inland high concentrations. This implies that some portion of Char-EC, which is EC produced with low temperature combustion, was involved in FEC. In the future, it will be necessary to inspect FEC content included in Char-EC. Furthermore, it was hypothesized that the majority of FTC was in the state of EC, but it became clear that OC contribution to FTC was large (average 56%).

BTC showed good correlation with levoglucosan. However, as shown in Fig. 10, the approximate line

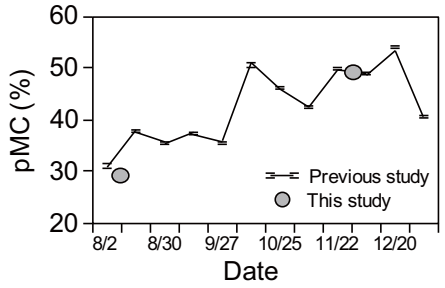

Fig. 12 Seasonal change in pMC observed at Kudan, Japan. Previous study means the pMC results based on two weeks $PM_{2.1}$ sampling in 2004. This study means the pMC values of $PM_{2.5}$ sampled in summer of 2008 and in winter of 2009.

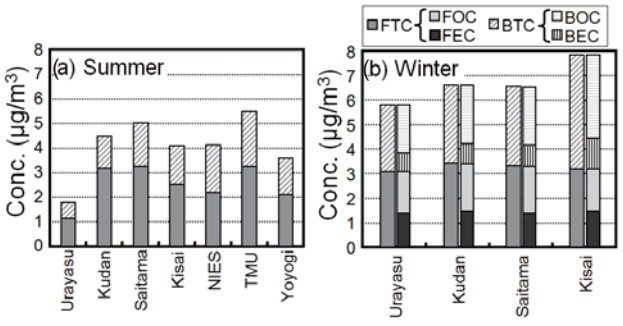

Fig. 13 Summary of carbonaceous aerosol concentrations and their estimated origin.
(a) Results from the summer campaign of 2008.
(b) Results from the winter campaign of 2009.
BTC: biogenic total carbon, FTC: fossil fuel total carbon, BOC: biogenic organic carbon,
BEC: biogenic elemental carbon, FOC: fossil fuel organic carbon, FEC: fossil fuel elemental carbon.

offset at BTC was 0.3 μg m^{-3}. This could be due to two processes. The first is a process in which BTC stays in the air for a long period as a background component, until the time when levoglucosan decomposes and disappears. The second is a process in which BTC (BOC) is generated from a non-combustion origin. The majority of BTC was expected to be in the form of OC (average 73%), and the concentration of BOC showed increased tendency along inland. Accumulation of BVOC in inland areas and a photochemical change to OC were suggested. Weber et al.[22] stated that 70-80% of carbon in water-soluble OC was from biogenic origin in Atlanta in summer as determined by radiocarbon measurements. Szidat et al.[23] showed 59-80% biogenic contribution to OC particle formation was found for daytime samples. Therefore, further investigation regarding the bio-origin of OC as a component of $PM_{2.5}$ formation is required.

BEC showed similar concentrations in all sites except in Kisai. In Japan prior to 2009, since the use of biofuels was small, BEC were considered mainly due to other combustion sources such as daily tobacco and cooking smoke. Moreover, biomass combustion on an industrial scale such as garbage incineration may have occurred in Kisai.

Study of carbonaceous aerosol behavior using carbon isotope is in its infancy. In order to clarify the origin of carbonaceous aerosol, seasonal or daily observation with improved measurement accuracy is needed, and the time and spatial variation of the carbonaceous aerosols of fossil fuel origin and biomass origin should be understood.

4. Conclusions

Impact of vehicle exhaust on the ambient particles was investigated from the points of the nucleation, condensation, and evaporation processes of ultrafine particles at a roadside, the context of the traffic environment, impact to a urban background and relation with photochemical reaction, particle growth in a planetary boundary layer in urban sky, and source contribution to particles in south Kanto area, the following conclusions are obtained.

1. The unstable behavior of ultrafine particles in a roadside atmosphere is due to many volatile components that vary with condensation and evaporation. During one signal cycle, a variation in volatile components with a variation in traffic volume became clear.
2. The number concentration shows a correlation involving hysteresis between traffic volumes in one signal cycle, because it varies with some processes, i.e. not only nucleation, coagulation, and deposition but also condensation and evaporation. However, the temporal variation in the number concentration of volatile particles can be explained by the variation in traffic volume with the consideration of coagulation and deposition processes.
3. A motor vehicle creates a different environment of the number concentration due to its driving state. At the spot where velocity or acceleration is large, the number concentration rises and the volume of volatile components increases. In addition, good correlation was seen with traffic volume and the volume of volatile components.
4. Particle number concentrations increase in proportion to traffic volume and a significant increase in particle number concentrations was found in the vicinity of high heavy duty vehicle (HDV) mixing ratio in urban roads. Particle number concentrations were decreased with the increment in vehicle speed due to diffusion of vehicle emissions in the air; however, particle number concentrations increased at the same time because of emissions from vehicles (especially HDVs) under heavy load driving conditions.
5. With an increment in the HDV mixing ratio, the number concentrations of smaller ultrafine particles was increased. An increase in particle size was observed under high average vehicle speed conditions, which is suggested due to particle growth through condensation of semi-volatile particles.
6. In urban background, traffic origin ultrafine particles were observed during rush hour accompanying with high NOx concentration. The growth rate of those particles from 6:00 to 10:00 was 7.6 nm hr^{-1}. On the other hand, ultrafine particles which originated from photochemical nucleation were observed in summer afternoons. The growth rate of particle size from 16:00 to 19:00 was 14.7 nm hr^{-1}. The semi-volatile component is considered to have a high impact on particle growth, and the photochemical reaction in summer supports this thinking. Since the number concentration of primary particles are high in winter, the quantity of secondary growth substance which condenses on each particle surface may decrease, and particle growth rate may become low.
7. The particle growth of fine particles more than

500 nm aerodynamic diameter was also confirmed from aircraft observation. As flying from Tokyo Bay to Kisai of north-northwest inland area at altitude of 600 m, the particle volume increase of 3-hold was observed and the growth rate of 3.79 nm hr^{-1} was obtained.

8. Carbonaceous components play an important role in nucleation, particle growth, and so on, but its source contribution and ambient behavior is not well known. It became clear from the carbon isotope analysis using ^{14}C that the carbon from biomass origin comprised 29% of total carbon in the summer, and 48% in the winter even at Kudan in the central Tokyo. The tendency for biomass contribution increased about 10% in the suburbs and the northern remote area.
9. Particle concentration of fossil fuel emission origin (FTC) was about 3 μg m^{-3} (40-50% of total carbon) during the observation campaign in winter of 2009. A regional difference was not found in south Kanto region due to a wide spared emission source such as diesel emission. Percentage of organic carbon in total carbon is large. Approximately 56% of FTC was organic carbon of fossil fuel origin. 73% of the particles of biomass origin (BTC) observed in the winter were organic carbon of biomass origin.

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