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Seasonal Patterns, and Ambient $PM_{0.1}$ Emission Sources in the Hokuriku Region in Japan

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Abstract

Size fractionated airborne particulates including $PM_{0.1}$ were simultaneously monitored at three different sites in the Hokuriku region of Japan. These were Kanazawa, Suzu and Toyama. Research was conducted over a three-year period between 2014 and 2016 in order to collect information concerning the PM status and related seasonal patterns. Possible local emission sources of $PM_{0.1}$ and the influence of long-range transportation are discussed in relation to mass concentration and diagnostic parameters defined by particle-bound carbonaceous components such as organic and elemental carbon, and their ratios. The influence of trans-boundary air mass transport from outside Japan is also discussed based on $PM_{0.1}$ characteristics and air mass trajectory analyses. The seasonal behavior for PM concentrations were similar between sites reflecting similar meteorological characteristics. Due to larger numbers of emission sources, the PM at the Toyama site was the largest between the three sites while at the Kanazawa site, precipitation in the spring and the summer was higher than in the autumn and winter seasons and this may have resulted in a decrease in PM levels. The concentration and influence of secondary organic carbon on the $PM_{0.1}$ carbon content were largest at the Toyama site. The Py-OC/O4 ratio was consistent with increases in the number of hotspots in the spring and autumn. Carbonaceous components in the $PM_{0.1}$ fraction could be largely explained by local emission sources. However, explaining the influence of the trans-boundary transportation of air pollutants only by the behavior of carbonaceous components in $PM_{0.1}$ may not be sufficient, and a more detailed discussion of various chemicals in different sizes of particles is needed.

Key Words: air mass trajectory analysis, biomass burning, carbonaceous components, size-fractionated particles, ultrafine particles

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I. INTRODUCTION

In the East Asia region including North East and South East Asia, during the last decades, the transboundary influence of air pollution between countries has now become a serious and important environmental problem. The long-range transport of dust and related anthropogenic air pollutants from Asian sources over the Sea of Japan, and haze episodes in Southeast Asia caused by the open burning of forests and agricultural crop residues, for example, are of great concern (Fujii *et al.*, 2015, 2014; Oanh *et al.*, 2011; Le *et al.*, 2014; Phairuang *et al.*, 2019, 2017). In addition, East Asia is now a huge source of air pollutants, particularly of airborne particulates, and these pollutants are affecting countries not only within the region but also regions outside as well (Koo *et al.*, 2014; Dotse *et al.*, 2016; Wang *et al.*, 2017). Such air pollution could cause serious health risks that are closely related to the inhalation of air contaminated by airborne fine particulates (Delfino *et al.*, 2005; Knibbs *et al.*, 2011; Oberdörster *et al.*, 2005; Tobaldini *et al.*, 2018) with diameters of less than 2–3 μm, or $PM_{2.5}$. The reason for this is that the fine particles frequently contain high levels of hazardous chemicals and especially particles less than 0.1 μm, or $PM_{0.1}$, which are small enough to enter the deepest part of human respiratory system, or, the alveoli region. In order to assess health risks and to manage emission sources, it will be necessary to evaluate the chemical characteristics of ultrafine particles ($PM_{0.1}$) and understanding their behavior is particularly important. However, detailed information on the status and behavior of $PM_{0.1}$ in East and Southeast Asia (Oanh *et al.*, 2011; Thuy *et al.*, 2018; Phairuang *et al.*, 2019; Seto *et al.*, 2012) is lacking.

To address this situation, the East Asia Nanoparticle Monitoring Network (EA-NanoNet) was established in 2013 to share information on the status, local emission sources, transboundary influence and possible health risks of ambient $PM_{0.1}$ between researchers participating from more than 10 countries in Northeast and Southeast Asia (Yoshikawa *et al.*, 2015) and some important results have been reported concerning haze episodes (Fujii *et al.*, 2011; Thuy *et al.*, 2018; Phairuang *et al.*, 2019; Amin *et al.*, 2019). As a branch of the EA-Nanonet, the Hokuriku NanoNet has been an important participant in activities of the Japan NanoNet, a sub-net of the EA-NanoNet that consists of 7 monitoring sites in Japan (Hongtieab, 2017). The reason for this that the Hokuriku area is located on the Sea of Japan side where the influence of the long range transport of particulate matter over the Sea of Japan is more significant than that in other areas on the Pacific Ocean side. However, information concerning the long term observation of seasonal behaviors of ambient aerosol nanoparticles ($PM_{0.1}$) in this area has not yet been reported.

In the present study, size fractionated airborne particulates including $PM_{0.1}$ were simultaneously monitored at three different sites in the Hokuriku region, or, Kanazawa, Suzu and Toyama over a period of three years between 2014 and 2016 in an attempt to collect information regarding their status and seasonal behavior. Possible local emission sources of $PM_{0.1}$ and the influence of long range transport were evaluated in relation to the mass concentration and diagnostic parameters defined for particle-bound carbonaceous components such as organic and elemental carbon, and their ratios. The influence of transboundary air mass transport from outside Japan was also evaluated based on the characteristics of $PM_{0.1}$ and air mass trajectory analyses.

II. METHODOLOGY

1) Sampling Sites

For a better understanding of the contribution of local emissions in the form of traffic and open burning of crop residues as well as the influence of long range transport, the PM monitoring was conducted at three locations spread over the Hokuriku region (Fig.1). As the most northern site where the influence of long range transportations would be more pronounced than other locations, the Suzu site was selected while as a typical local city with rather large populations in this area, Kanazawa and Toyama were selected.

The Kanazawa site was located at the Kakuma campus of Kanazawa University (KU) in an outskirt of Kanazawa city (37°27'03.5"N, 137°21'32.2"E), the capital of Ishikawa prefecture with a population of about

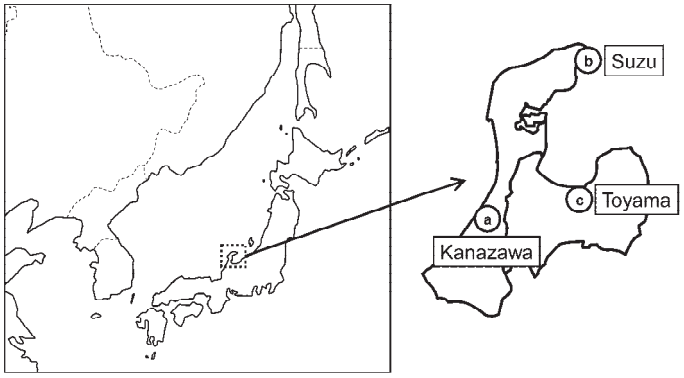

Fig. 1 Locations of sampling sites: Kanazawa, Suzu and Toyama in Hokuriku region, Japan.

0.46 million. The KU is located in a wooded area behind residential areas and is isolated from main roads while there are temporal open biomass burning sources in the neighboring local orchards. The sampling site was on a balcony on the sixth floor of a 7-story building and is a distance of 12 km from the seashore from the North West of the site.

The Toyama site was located on the rooftop of a 3-story building (Building-M of Mechanical Engineering), National Institute of Technology, Toyama College in Toyama city (36°39'03.0"N, 137°14'37.9"E) that is also the capital of Toyama prefecture with a population of about 0.42 million. The Toyama site was located in the southern periphery of the city area surrounded by areas of mixed land uses that include paddy fields, residential areas with local community roads. It was also a distance of about 400 m from the Hokuriku expressway which is located south of the site and could be an important local emission source.

The Suzu site was located on the rooftop of a 3-story lecture hall building of the Noto School in Suzu city (37°27'03.5"N, 137°21'32.2"E), a city that is located on the northeastern tip of the Noto Peninsula with a population of about 14 thousand. The site was in a small local community adjacent to a beach in its eastern side (~120 m) and is surrounded by managed forest areas with small agricultural fields. Although the influence of traffic would likely be negligible, temporal open biomass burning is conducted in the neighboring local fields.

2) Sampling Methods

A cascade air sampler, termed here as an Ambient Nano Sampler (ANS), that was developed by Furuuchi *et al.* (2010) and can be used to collect $PM_{0.1}$, PM_1, $PM_{2.5}$, PM_{10}, TSP at an air flow rate of 40 l/min was used as the sampler. Quartz fibrous filters (QFF) (2500 QAT-UP, Pall Corp., USA) of ∅55 mm were used to collect particles (>10, 2.5-10, 1.0-2.5, 0.5-1.0, and <0.1 μm). The filters had been pre-baked at 350 °C in an oven for 1 hour then conditioned at 21.5 ± 1.5 ℃, and 35 ± 5 % RH in a $PM_{2.5}$ weighing chamber (PWS-PM2.5, Tokyo Dylec Corp., Japan) for 48 hours before and after sampling. An inertial filter (IF) consisting of webbed stainless steel fibers (average fiber diameter d_f =9.8 μm, Nippon Seisen Co. Ltd., felt type, SUS-316) plugged in a cartridge nozzle of ∅ 5.25 mm (Furuuchi *et al.*, 2010; Otani *et al.*, 2007) was used for the separation of $PM_{0.1}$ particles. Before assembling the inertial filter cartridge, the stainless steel web was cleaned with ethanol to reduce the blank value for carbon. Each prepared filter was wrapped in aluminum foil and then stored in a plastic bag during transport to the sampling sites along with blank filters to account for possible contaminants during the filter transportation. Samples were stored at temperatures of under –25 °C in a refrigerator until analyzed.

3) Sampling Procedure

Depending on the situation at each site, the sampler was installed in a suitable type of shelter. The sampling at the Kanazawa site has been used continuously since 2010 while it was started in 2014 at the Toyama and Suzu sites. At all sampling sites, the duration for each sampling was set as continuous 7 days, twice a month. Information regarding the sampling is summarized in

Table 1 where Spring, Summer, Autumn and Winter are defined as March to May, June to August, September to November and December to February. 2110 available samples in 356 sets from the 3 sampling sites in the Hokuriku region were collected as a total. Meteorological information during the study period was obtained from the Japan Meteorological Agency (JMA, 2019).

4) Analysis of Carbonaceous Components

The thermal/optical analyses of carbonaceous components in particles collected on the QFF were conducted on a square, punched filter sample (10 x 15 mm) using a carbon analyzer (Sunset Laboratory, Carbon Aerosol Analyzer), following the IMPROVE protocol (Chow *et al.*, 2004; Han *et al.*, 2007; Kim *et al.*, 2011a, 2011b). Briefly, the OC fractions were determined at four temperature steps in 100% helium: OC1 at 120 °C, OC2 at 250 °C, OC3 at 450 °C, and OC4 at 550 °C. The EC fractions were determined for three temperature steps in a mixture of 2 % oxygen and 98 % helium: EC1 at 550 °C, EC2 at 700 °C, and EC3 at 800 °C. Prior to each set of carbon analyses, the TC value was calibrated with reference to a reference chemical, sucrose ($C_{12}H_{22}O_{11}$) (196-00015, Sucrose, Wako Pure Chemical Industries, Ltd., Japan). OC was defined as OC1+OC2+OC3+OC4+ Py-OC while EC defined as EC1+EC2+EC3–Py-OC, where Py-OC denotes the pyrolyzed fraction of organic carbon. Char-EC, defined as EC1–Py-OC and soot-EC, defined as EC2 + EC3 were also evaluated (Han *et al.*, 2009). The repeatability of the analyses of the punched filter samples with deposition spots of ambient particles was preliminarily confirmed to be reasonably good, with a coefficient of variation (CV) defined by (standard deviation)/(average value) less than 3.2 % for OC and 7.9 % for EC except 17.8 % for EC in particles > 10 μm. A blank filter was also analyzed to correct the results obtained for samples.

5) Backward Trajectory and Hotspots

72 hour backward trajectories of air parcels arriving at each monitoring site at a distance of 100 meters from the average ground level (AGL) were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory Model version 4 (HYSPLIT4) (ALR, 2019), where the meteorological data from the Global Data Assimilation System (GDAS) resolution 0.5 degree from the NOAA were used (NOAA, 2019). Geographic locations of hotspots or active fires in Japan and other neighboring countries with a resolution of 1 km × 1 km that are available from Moderate Resolution Imaging Spectroradiometer (MODIS) satellite remote sensing imagery were used to specify possible areas corresponding to biomass burning (MODIS, 2019).

III. RESULTS AND DISCUSSION

1) The Status of Seasonal Characteristics Particle Mass Concentration

Figures 2 (a) - (c) show the monthly average mass concentration of $PM_{0.1}$, $PM_{2.5}$ and PM_{10} respectively at the Kanazawa, Suzu and Toyama sites. The average mass concentration of each size fraction of particulate matter (PM) for the four seasons is summarized in Table 2. $PM_{2.5}$ at all sites was below the National Ambient Air Quality Standards (NAAQS) (35μgm^{-3}, 1-day average) and PM_{10} was below the NAAQS for SPM (100μgm^{-3}, 1-day average). There were similar seasonal fluctuations at all sites such that the largest PM concentration was observed in April or May (Spring) and the smallest was observed to be in winter (Dec.–Feb.) although there was a slight difference probably because of a difference in snow fall. The $PM_{0.1}$ fraction was similar at all locations and increased in the winter season although the concentration decreased and the became smallest in December at the Kanazawa and Suzu sites while this occurred in February at the Toyama site. Such behavior in the PM concentration during the winter season may be consistent with the precipitation via rain and snow fall during this period shown in Table 1. The peak concentration of a coarse fraction as >1 μm in the spring period should be related to the influence of dust storms. Although fine fraction of particles emitted in China and secondary particles could be transported (*e.g.*, Hidemori *et al.*, 2014; Yamaguchi *et al.*, 2019), the contribution from local sources may also be important as discussed later.

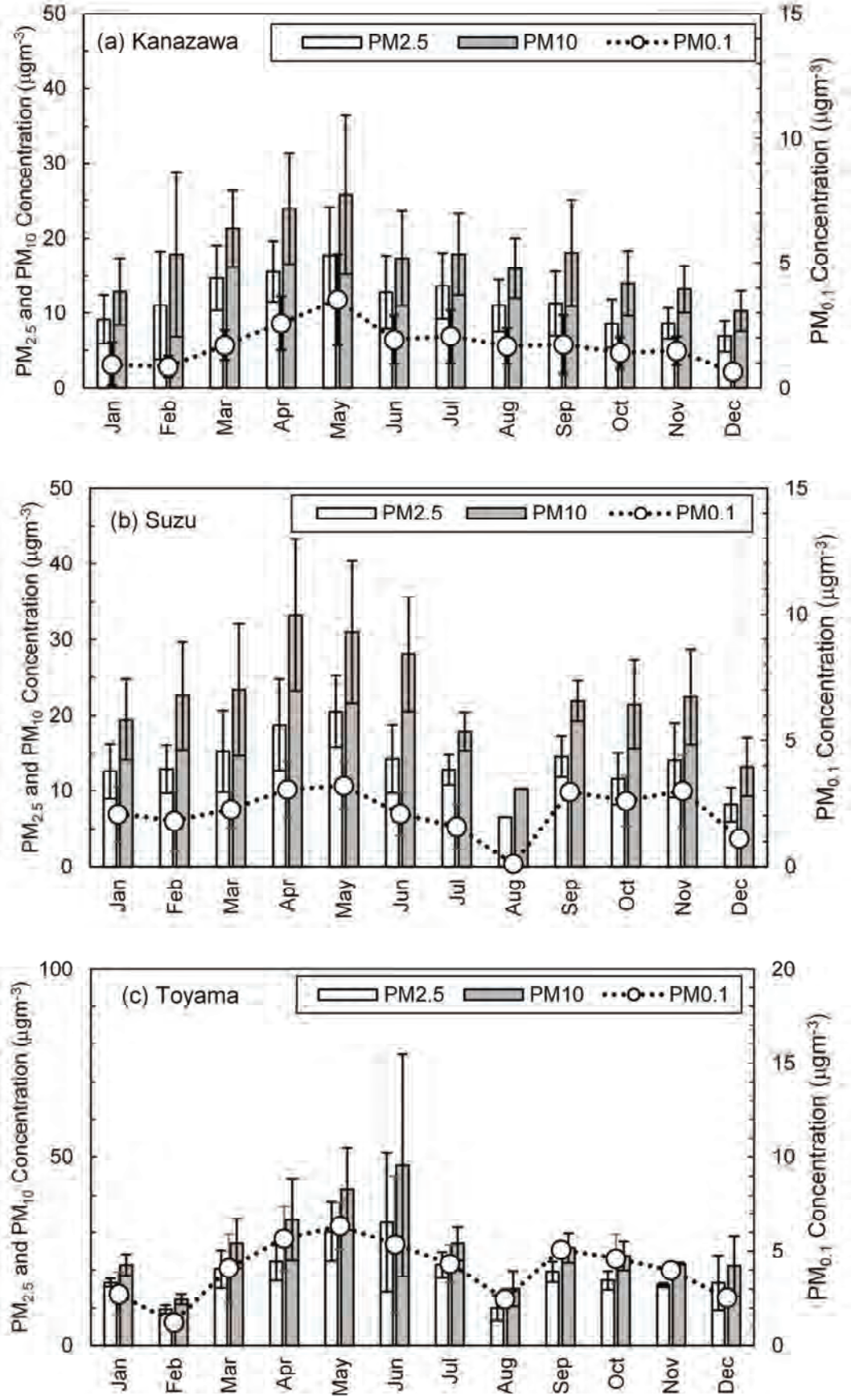

Fig. 2 Monthly averaged PM mass concentration at the (a) Kanazawa, (b) Suzu and (c) Toyama sites in 2014–2016.

Table 1 Average precipitation and snow accumulation (mm/day) of the sampling locations in 2014-2016 (Japan Meteorological Agency).

Location	Parameter	Season				Average
		Spring	Summer	Autumn	Winter	
Kanazawa	Precipitation	4.74±1.38	6.23±2.33	6.63±1.56	8.61±3.79	6.55±2.54
	Snow accumulation	1.8 ± 3.1	0	0	22.6± 5.7	6.1 ± 10.4
Suzu	Precipitation	3.72±1.31	5.48±1.83	5.63±0.37	7.89±3.76	5.68±2.43
	Snow accumulation	1.8 ± 3.0	0	0	34.8±17.5	9.1 ± 17.2
Toyama	Precipitation	4.30±1.65	6.45±2.06	6.38±1.52	8.42±2.98	6.39±2.37
	Snow accumulation	2.3 ± 4.0	0	0	18.8± 5.7	5.3 ± 8.7

Table 2 Season averaged particle mass concentration in different size ranges at the study sites in 2014-2016 (μgm^{-3}).

Location	Particle size	Season				Average
		Spring	Summer	Autumn	Winter	
Kanazawa	PM0.1	2.61±1.17	0.83±0.52	1.88±0.92	1.54±0.78	1.71±0.85
	PM0.1-0.5	2.84±2.59	1.48±0.64	1.58±0.56	1.23±0.42	1.87±1.99
	PM0.5-1.0	4.31±1.88	3.88±1.62	5.18±2.03	4.12±2.23	5.01±2.48
	PM1.0-2.5	4.31±1.88	2.81±1.61	3.81±1.76	2.59±1.06	3.5±1.88
	PM2.5-10	7.68±4.41	4.63±2.59	4.57±1.81	5.57±2.72	5.8±3.83
	>PM10	3.42±1.67	1.91±1.04	2.07±1.18	2.31±0.95	2.51±1.51
	PM0.1 /PM2.5	0.16±0.24	0.25±0.36	0.15±0.12	0.16±0.24	0.15±0.2
	PM0.1 /PM10	0.12±0.15	0.18±0.29	0.04±0.09	0.12±0.16	0.09±0.13
	PM0.1 /TSP	0.1±0.08	0.16±0.18	0.03±0.07	0.11±0.1	0.09±0.09
Suzu	PM0.1	2.84±0.92	1.67±0.86	1.26±0	2.85±0.88	2.36±1.12
	PM0.1-0.5	3.4±1.91	2.01±0.58	2.43±0	1.66±1.05	2.48±1.68
	PM0.5-1.0	5.22±1.66	4.03±1.05	5.08±1.34	5.08±1.34	5.29±2.13
	PM1.0-2.5	5.22±1.66	3.51±1.18	3.79±0.88	3.79±0.88	4.08±1.6
	PM2.5-10	11.04±5.57	7.16±3.01	8.5±2.11	8.5±2.11	9.12±4.85
	>PM10	5.28±2.54	3.81±1.5	5.7±1.8	5.7±1.8	4.93±2.8
	PM0.1 /PM2.5	0.16±0.17	0.21±0.41	0.15±0.28	0.21±0.24	0.16±0.23
	PM0.1 /PM10	0.09±0.1	0.14±0.27	0.07±0.16	0.15±0.18	0.09±0.14
	PM0.1 /TSP	0.08±0.06	0.12±0.15	0.06±0.1	0.12±0.11	0.08±0.09
Toyama	PM0.1	5.37±1.6	2.18±0.66	4.06±1.72	4.55±0.57	4.57±1.94
	PM0.1-0.5	3.82±1.85	3.99±2.82	1.91±0.66	1.53±0.34	2.93±2.22
	PM0.5-1.0	8.06±2.22	4.62±0.35	8±3.05	6.42±1.01	7.17±2.93
	PM1.0-2.5	6.96±1.9	3.5±0.68	7.37±3.08	5.06±0.56	6.22±2.78
	PM2.5-10	9.77±4.27	3.94±0.92	8.6±4.5	6.15±0.97	8.22±5.27
	>PM10	4.04±1.73	2.06±0.82	2.86±1.58	3.48±0.38	3.53±1.99
	PM0.1 /PM2.5	0.22±0.27	0.19±0.21	0.15±0.21	0.26±0.31	0.21±0.24
	PM0.1 /PM10	0.13±0.17	0.18±0.13	0.11±0.16	0.21±0.21	0.14±0.19
	PM0.1 /TSP	0.12±0.12	0.16±0.12	0.1±0.1	0.18±0.15	0.12±0.14

2) Possible Influences from Local Emission Sources

The level of PM concentration and its behavior were different between the various sites. This may also be attributed to a difference in local emission sources and a degree of influence by the transboundary movement of air pollutants other than from meteorological conditions. The PM concentration at the Toyama site was consistently larger than other two sites, except for February when it decreased to a level smaller than that at the Suzu site. Such a difference is significant for $PM_{0.1}$ as shown in Fig. 3 and that appears to be related to anthropogenic sources. Since the Toyama site was located in the middle of a sub-urban area largely surrounded by local residential communities and close to the express way in the south, the influence of traffic may be a larger throughout the year and an increased energy consumption in winter as well as industries located along northern coast of the city. The PM concentration at the Kanazawa site was not as large as the size of city adjacent to the site because of the rather isolated location and more extensive precipitation than other sites in the late autumn and winter seasons. The PM concentration at the Suzu site appeared to be slightly larger, since it is surrounded by very few anthropogenic emission sources. This may be related to a contribution from seas salt particles as well as smoke particles from biomass burning in surroundings, as described later.

Figures 4 (a) - (c) show the seasonal difference of the mass fraction of each carbonaceous component to the total carbon (TC) in $PM_{0.1}$ at the study sites. Correspondingly, the monthly averaged OC, EC and OC/EC ratios are shown in Figs. 5 (a) - (c), where the OC/EC ratio is used as an index for the contribution of emission sources (Duan *et al.*, 2005; Hou *et al.*, 2011; Kim *et al.*, 2011b; Liu *et al.*, 2016; Vodi *et al.*, 2015; Zhan *et al.*, 2019). The OC concentration and its fraction were found to increase in spring and summer where secondary formation may be of importance in the summer. This was clear at the Toyama site for the maximum OC/EC = 6.92 in August, indicating a larger amount of emission of VOC from various activities including natural sources (Tassi *et al.*, 2013; Montero-Montoya *et al.*, 2018; Li *et al.*, 2019). As also discussed below, it is possible that the OC/EC ratio may have a tendency to be shared between the OC generation by biomass burning in spring and autumn, secondary formation in the summer, the rain and snow fall that can suppress OC from biomass burning, and the emission of soot caused by energy consumption for heating in winter. The OC/EC ratio was the smallest in winter and was in the range of 2.72–3.64, essentially in the range of vehicle emissions (Duan *et al.*, 2005).

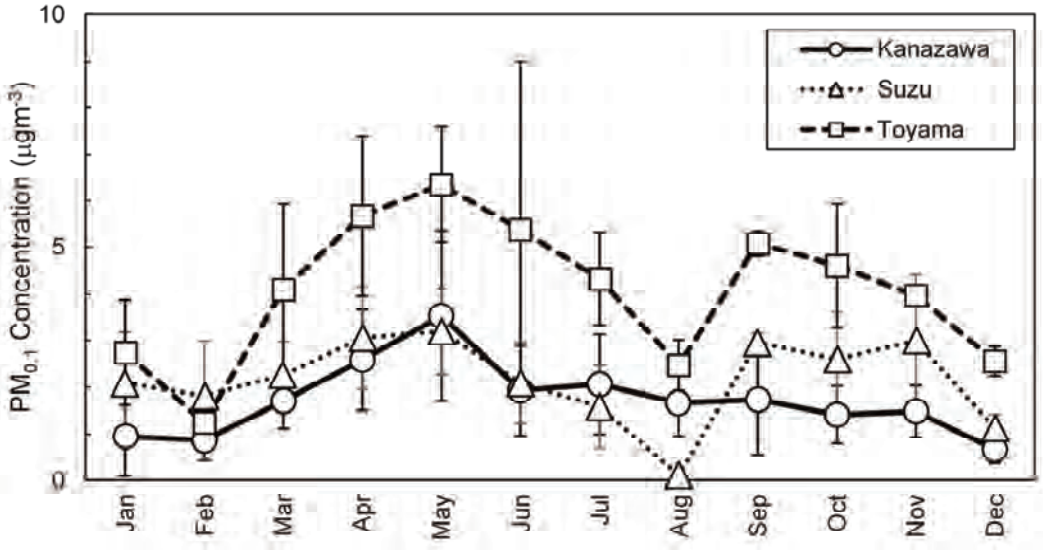

Fig. 3 Monthly averaged $PM_{0.1}$ mass concentration at the study sites in 2014–2016.

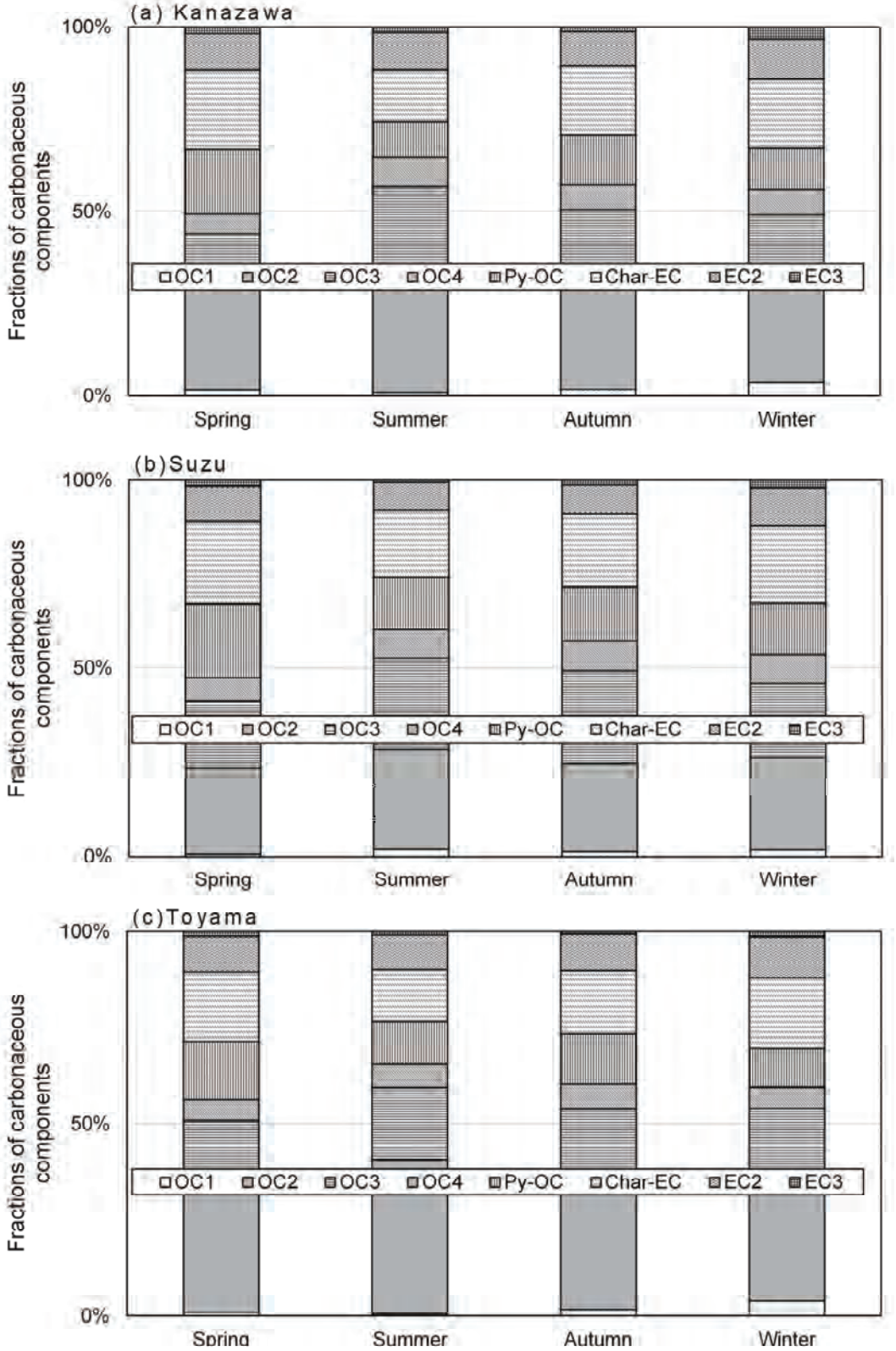

Fig. 4 Season averaged mass fractions of carbonaceous components in $PM_{0.1}$ at the (a) Kanazawa, (b) Suzu and (c) Toyama sites in 2014–2016.

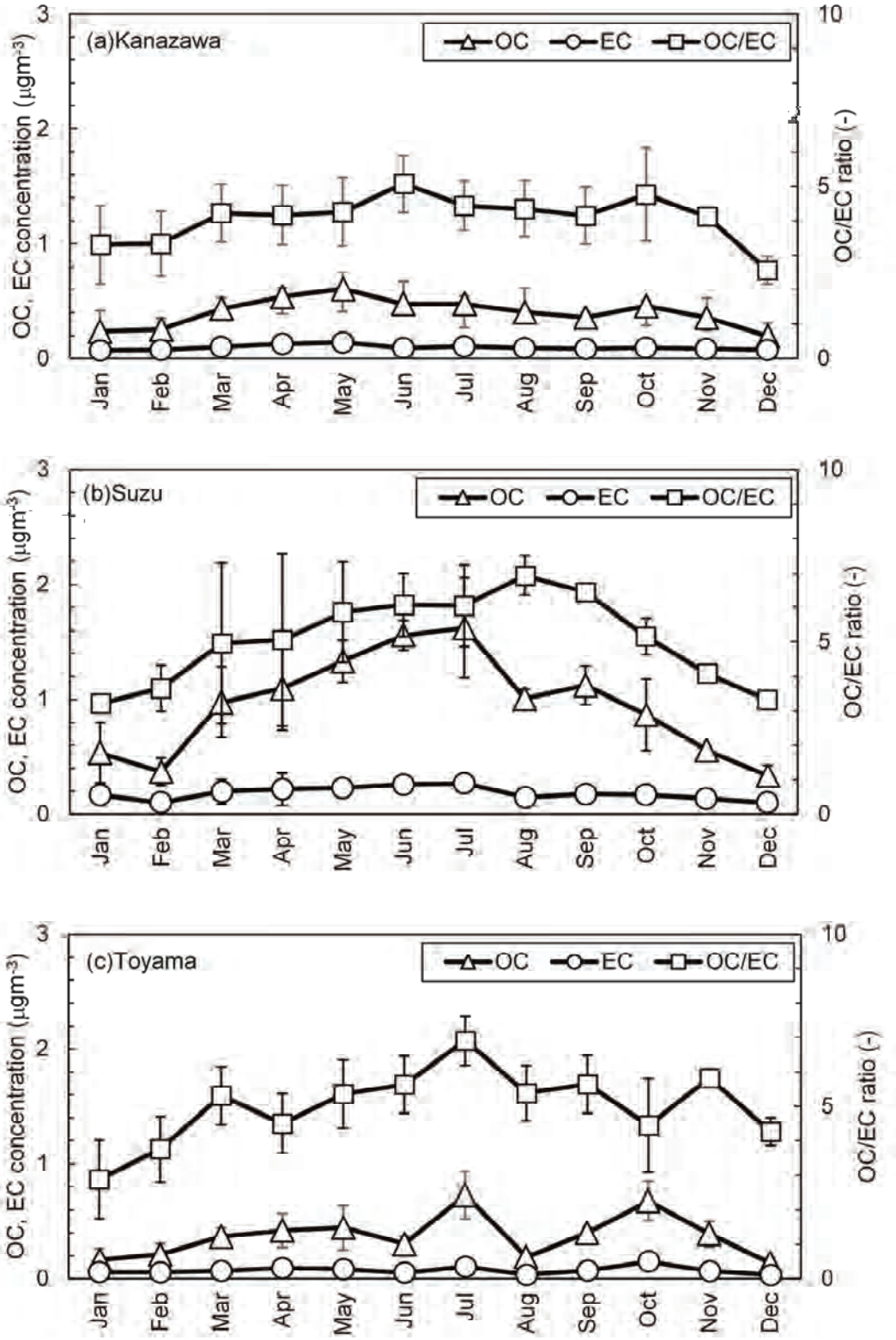

Fig. 5 Monthly averaged concentration and ratio of OC and EC at the (a) Kanazawa, (b) Suzu and (c) Toyama sites in 2014–2016.

To discuss the contribution of biomass burning and traffic, or typical local emission sources, a ratio of char-EC to soot-EC and a ratio of soot-EC to TC are plotted respectively in Figs. 6 (a) and (b), where char-EC/soot-EC and soot-EC/TC could be parameters respectively of the relative influence of biomass burning and that of any emission of soot, particularly from traffic (Chen *et al.*, 2016; Han *et al.*, 2010; Furuuchi *et al.*, 2014). The char-EC/soot-EC ratio for $PM_{0.1}$ is originally of diesel soot so that the value is normally below unity (Phairuang *et al.*, 2019; Furuuchi *et al.*, 2014). Values obtained for the present study are, hence, reasonable and there is a slight tendency for the values to be lower at the Toyama site, probably corresponding to the influence of more soot emission in Toyama as was also seen from the soot-EC/TC that is ~1 for diesel soot (Furuuchi *et al.*, 2014). However, the difference is not so significant compared to the fluctuation in the data. Hence, the relative influence of soot emission as traffic to $PM_{0.1}$ may be rather constant regardless of the season and

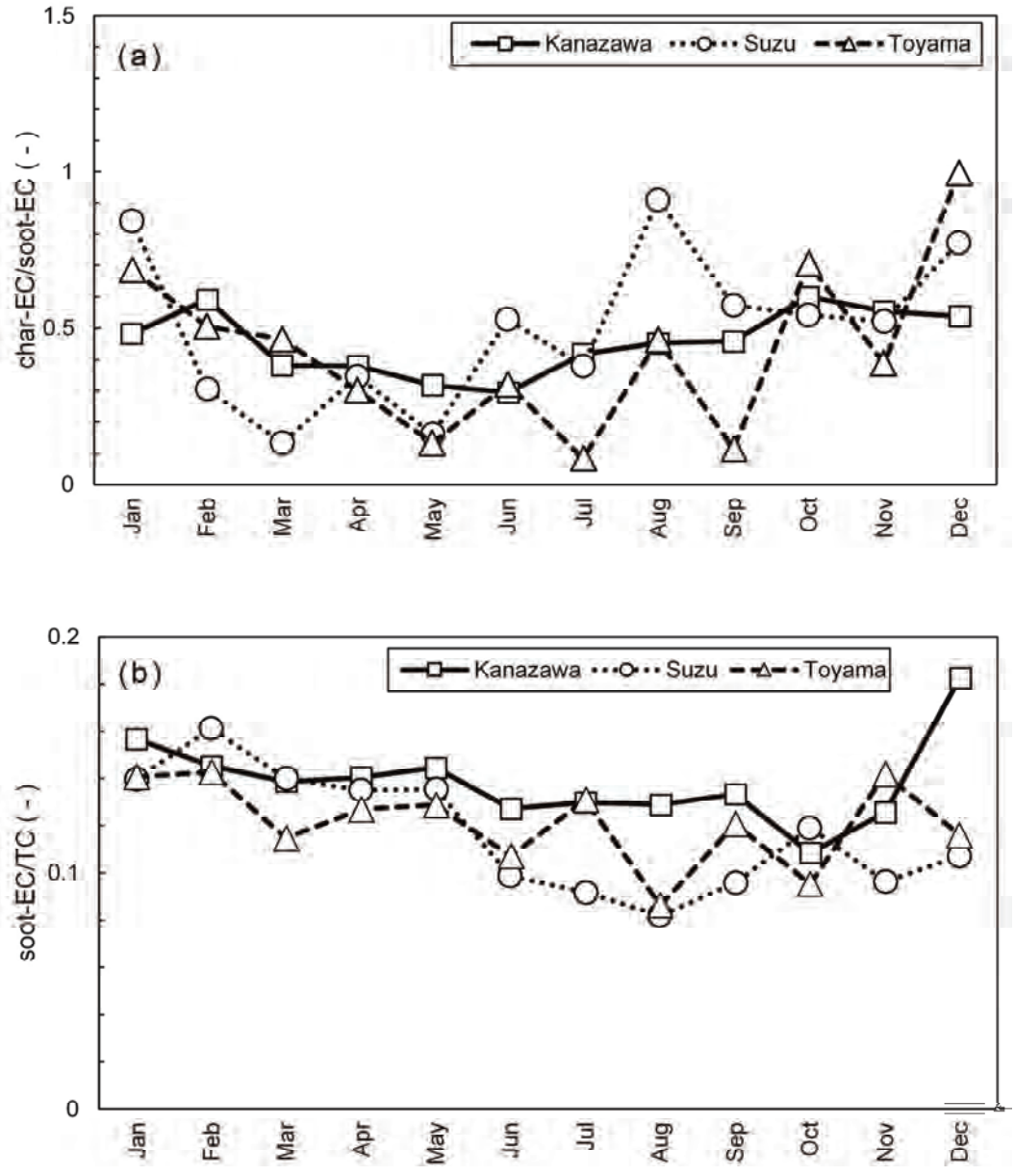

Fig. 6 Monthly averaged diagnostic ratios between selected carbonaceous components at the study sites in 2014–2016: (a) char-EC/soot-EC and (b) soot-EC/TC.

mainly be from local sources.

As shown in Fig. 4, the Py-OC in $PM_{0.1}$ particles increased in the spring and autumn. As suggested by Fujii *et al.* (2015), the Py-OC/OC4 ratio, a key parameter in peatland fires, may also explain the above situation so that it is plotted in Fig. 7. The value of Py-OC/OC4 increased in the spring and autumn while it decreased in the winter and mid-summer except in December at the Suzu site. According to Amin *et al.* (2019), the Py-OC/OC4 ratio for fine and ultrafine fractions of particles is sensitive to biomass burning including both peatland fires and the burning of crop residues. Hence, it can be concluded that the influence of biomass burning is very prominent in these seasons. A rather large level (~2) at the Suzu site in Nov.–Dec. may be attributed to the temporal usage of a wood stove in a building next to the site. Such a tendency for the influence of open biomass burning should be consistent with the number of "hotspots" corresponding to an area of elevated temperature. Since small scale open biomass burning that may dominate open burning in local areas in Japan cannot be easily detected as hotspots, the total number of hotspots in Japan is shown in Fig. 8 and provides an overview of open burnings for agricultural purposes. There was a large increase in the spring and a slight increase in October while peaks in the summer may not

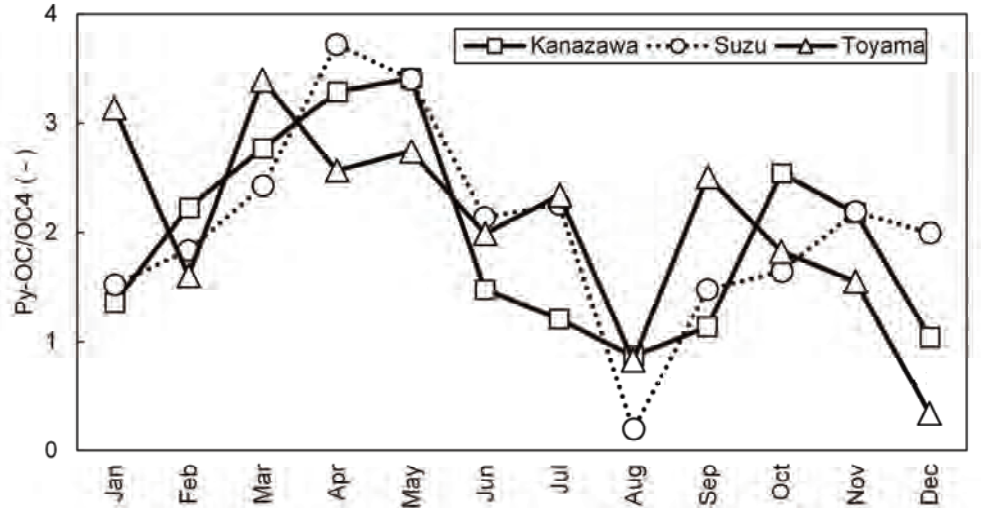

Fig. 7 Py-OC/OC4 ratio for $PM_{0.1}$ at the study sites in 2014–2016.

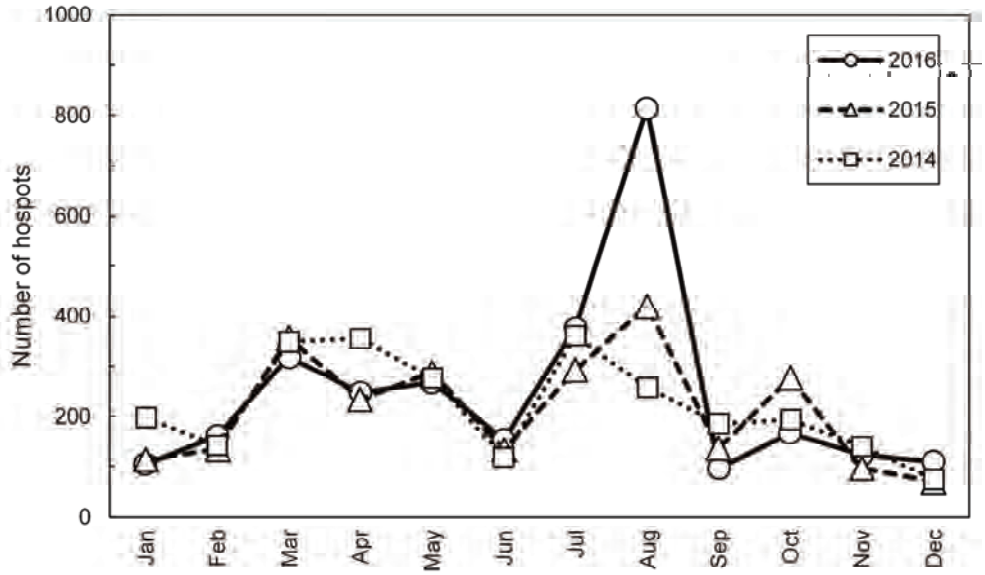

Fig. 8 Number of hotspots observed in Japan in the period 2014–2016.

be related to open biomass burning but rather to increases in the ground surface temperature caused by solar radiation and energy consumption. Such a tendency may be similar to that in the Hokuriku region and is somewhat consistent with the present results.

3) Influence of air mass transport

Figures 9 (a) - (d) show air mass trajectories for selected months in different seasons. As discussed previously on the PM concentration, the difference in the behavior of different size of particles with seasons was not large. During the spring period (*e.g.* in May), the air

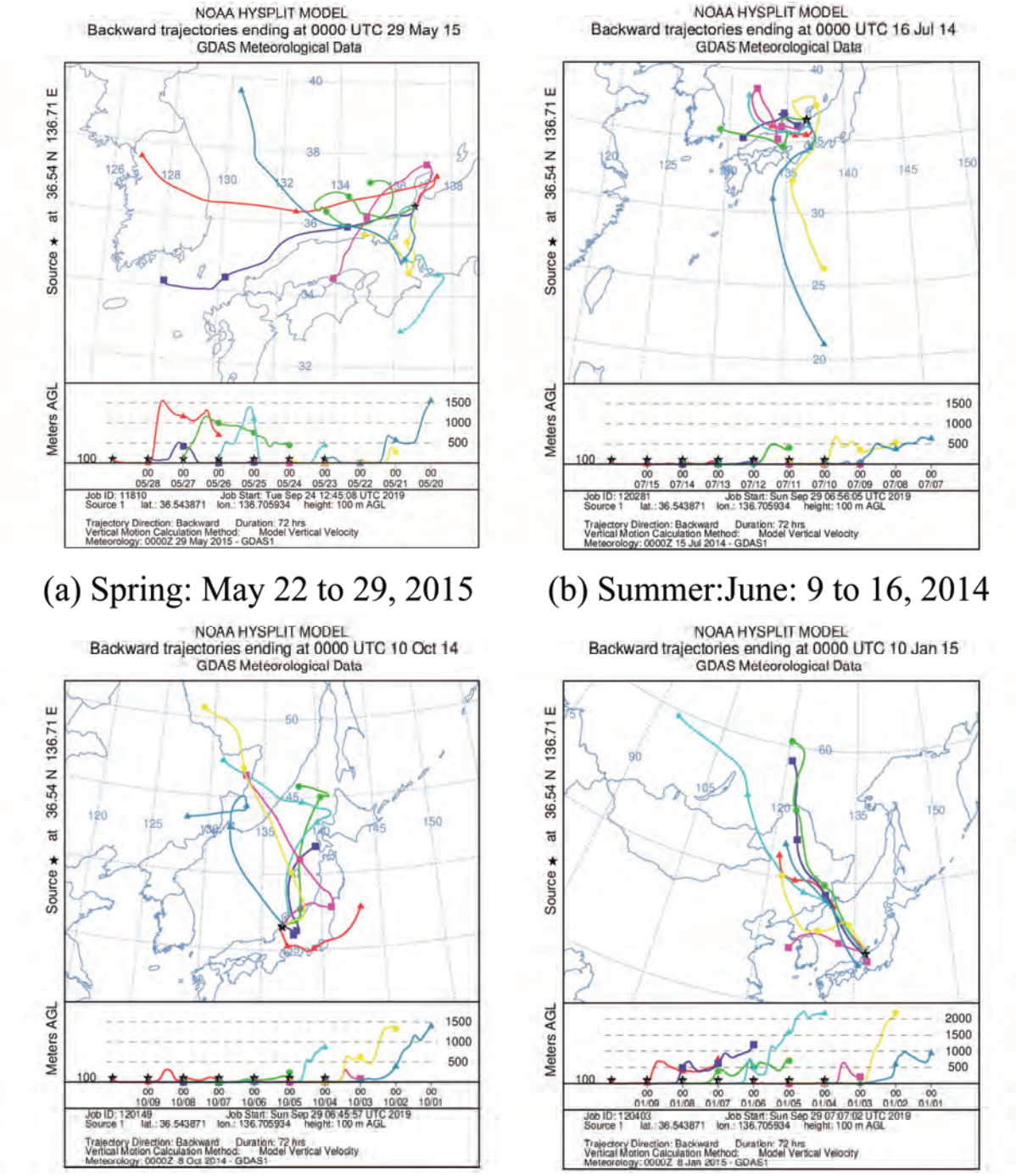

Fig. 9 72-hour back trajectories for Kanazawa for a typical 7-day period in each season.

mass to the study sites is likely to come from west and north west of Japan, indicating that the transport of PM generated in these areas should have an influence on the overall process. Peaks corresponding to the concentration of coarse fractions as > 1 μm in the Spring (April-May) were consistent with a dust storm that occurred during this period where dust was generated in west and north west of Japan. However, it may be difficult to conclude that fine fractions as $PM_{0.1}$ at the study sites were also influenced by air mass movement from areas located on western to north western sides of Japan since the behavior of $PM_{0.1}$ was also consistent with those of local emission sources, as described above.

As described by Amin *et al.* (2019), the influence of peatland fires, or biomass burning, by air mass transportation was clearly found in a core size range of ambient PMs in the size range of 0.5–1 μm and the influence of the coagulation of ultrafine particles, the secondary formation of ultrafine particles as well as the washout of particles (*e.g,* Seto *et al.*, 2012) should also be taken into account. For a further understanding the influence of air mass transportation, therefore, the behavior of chemicals not only on carbonaceous components but also other chemicals such as heavy metals, water soluble organic carbon (WSOC) and ions on other size of fractions should be discussed.

IV. CONCLUSION

In the present study, size fractionated airborne particulates in sizes down to $PM_{0.1}$ were simultaneously monitored at three different sites in the Hokuriku region, or, Kanazawa, Suzu and Toyama over a three year period between 2014 and 2016 on an attempt to evaluate their status, seasonal behavior, possible local emission sources as well as the influence of transboundary air mass transport from outside Japan. The seasonal behavior of the PM concentration at all sites were basically similar reflecting similar meteorological characteristics although there were slight differences that were rather consistent

Table 3 Season averaged carbonaceous components (μgm^{-3}) and ratios between selected components in $PM_{0.1}$ at the three sites in 2014-2016.

Location	Parameter	Season				Average
		Spring	Summer	Autumn	Winter	
Kanazawa	OC	0.53±0.08	0.45±0.04	0.39±0.06	0.23±0.03	0.4±0.12
	EC	0.12±0.02	0.1±0.01	0.09±0.01	0.08±0	0.1±0.02
	OC/EC	0.03±0	0.03±0.01	0.03±0	0.03±0	0.03±0
	Py-OC/OC4	0.09±0.02	0.07±0.01	0.06±0	0.05±0	0.07±0.02
	char-EC	0.36±0.04	0.39±0.08	0.54±0.07	0.54±0.05	0.45±0.1
	soot-EC	4.21±0.05	4.62±0.4	4.35±0.36	3.07±0.44	4.06±0.69
	char-EC/soot-EC	3.16±0.34	1.18±0.31	1.95±0.73	1.54±0.61	1.96±0.9
	soot-EC/TC	0.14±0	0.13±0	0.12±0.01	0.16±0.02	0.14±0.02
Suzu	OC	0.41±0.04	0.41±0.28	0.49±0.16	0.17±0.04	0.37±0.19
	EC	0.08±0.01	0.06±0.04	0.1±0.05	0.05±0.01	0.07±0.03
	Py-OC/OC4	0.01±0.01	0.02±0.01	0.54±0.02	0.02±0.01	0.02±0.01
	OC/EC	0.07±0.01	0.04±0.03	0.06±0.03	0.03±0.01	0.05±0.02
	char-EC	0.21±0.12	0.61±0.27	0.54±0.03	0.64±0.29	0.5±0.25
	soot-EC	5.06±0.48	5.98±0.82	5.3±0.75	3.64±0.7	4.99±1.07
	char-EC/soot-EC	3.18±0.67	1.53±1.16	1.77±0.37	1.78±0.24	2.07±0.91
	soot-EC/TC	0.14±0	0.09±0.01	0.1±0.01	0.14±0.03	0.12±0.02
Toyama	OC	1.13±0.18	1.4±0.34	0.85±0.28	0.41±0.11	0.95±0.43
	EC	0.21±0.02	0.22±0.07	0.16±0.02	0.12±0.04	0.18±0.06
	Py-OC/OC4	0.05±0.02	0.04±0.02	0.04±0.03	0.05±0.02	0.05±0.02
	OC/EC	0.17±0.03	0.18±0.08	0.12±0.03	0.07±0.02	0.13±0.06
	char-EC	0.3±0.17	0.29±0.19	0.4±0.3	0.73±0.25	0.43±0.27
	soot-EC	5.29±0.5	6.35±0.5	5.23±1.18	3.4±0.23	5.07±1.26
	char-EC/soot-EC	2.77±0.64	1.72±0.79	1.96±0.49	1.74±1.4	2.03±0.89
	soot-EC/TC	0.12±0.01	0.11±0.02	0.12±0.02	0.13±0.01	0.12±0.02

with differences in the amount of rainfall and snow fall. Probably because of a larger amount of pollutants from local sources such as traffic and residential energy use, the PM at the Toyama site was the largest between the three sites during nearly all of the study period while that at the Kanazawa site was not as large as the size of a city adjacent to the site because of the rather isolated location and the larger precipitation than at the other sites in the autumn and winter seasons. The concentration and influence of secondary organic carbon for the $PM_{0.1}$ carbon content were the largest at the Toyama site. The Py-OC/O4 ratio that can be used to describe the influence of biomass burning showed clear peaks in the spring and autumn at all sites, being largely consistent with increases in the number of hotspots. The influence of carbonaceous components in the $PM_{0.1}$ could be largely attributed to contributions of local emission sources. However, this may not be sufficient to explain the influence of the transboundary transportation of air pollutants by air mass although, *e.g*., the origin of the air mass during spring, or peak season of PM was from the western or north western areas of Japan. For a further understanding, therefore, more detailed information concerning the various chemicals in different sizes of particles should also be examined. Plans to accomplish this are scheduled for the near future.

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北陸地域の大気中$PM_{0.1}$の季節変動特性と発生源の考察

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要 旨

本研究は，北陸地方の金沢，珠洲および富山の3地点で，粒子径が0.1μm以下の$PM_{0.1}$を含む大気中浮遊粒子（PM）を，2014～2016年の3年間に粒子径別に継続的に捕集して，粒子状物質による大気汚染の状況とその季節変動特性を把握するとともに，$PM_{0.1}$の測定点近傍の発生源を粒子質量濃度だけでなく，粒子中の有機・無機炭素成分濃度および各種の炭素成分に関係付けられた発生源指標に基づいて議論したものである。さらに，これらの粒子濃度・各種成分特性と国内外から観測点に到達する空気塊の後方軌跡の解析結果を比較することで，域外からの$PM_{0.1}$汚染への影響を考察した。これらの結果，気象条件と近傍発生源が類似していることからPM濃度の変動特性は3カ所で同様であるが，富山測定点での年間を通じた道路交通等の人為影響，金沢測定点での降雨・降雪量の影響，珠洲観測点での海塩，野焼きの影響が相対的に大きいこと，$PM_{0.1}$に対するバイオマス燃焼指標は春季・秋季に増加し，観測点周囲での主に農業系野焼き起源の影響が明らかになるなど，$PM_{0.1}$への近傍発生源影響が比較的明確であることが示された。また，国外からの汚染物質輸送については，比較的大きな1μm超の粒子については黄砂現象と対応させて説明できるが，$PM_{0.1}$のような近傍発生源への影響が明確な超微粒子域への越境汚染の影響は炭素成分のみでは明確に説明することが困難であり，粒子径別の情報を様々な成分で議論することの必要性が示された。

キーワード：粒子径別サンプル，超微粒子，炭素成分，バイオマス燃焼，後方軌跡解析

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