Investigation into Characteristics and Emission Sources of Ambient Nano-particles (PM0.1)

Dissertation Abstract

Investigation into Characteristics and Emission Sources of Ambient Nano-particles ($PM_{0.1}$)

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Abstract

Characteristics of $PM_{0.1}$, that is a fraction of ambient particles smaller than 0.1 μm and has the largest potential health risk due to its permeability to the deepest part of the human respiratory system, were discussed to specify the present status at locations where no information is available as well as its importance as a tool to describe influences of local emission sources and transboundary transportation of emitted particles. For this purpose, three different categories of area each of which had a different environmental background, were selected to discuss clearly the contribution of different emission sources and meteorological conditions. Selected areas were Hokuriku area in Japan, an inland city in Nigeria and cities in Southeast Asia. The air sampling has been conducted at each sampling site under the collaboration of the East Asia Nano-particle Monitoring Network (EA-NanoNet) for selected periods. Various chemical components as carbons, ions, water soluble and insoluble organic carbons contained size segregated ambient particles including $PM_{0.1}$ were analyzed to discuss local emission sources along with the analysis of air mass movement and hot spots that were used to discuss influences of the transboundary transportation of air pollutants emitted by open biomass burning. As results, $PM_{0.1}$ was confirmed to well describe primary particles from local sources as well as components by the secondary formation from gaseous pollutants. For the transboundary transportation of primary and secondary particles, behavior of $PM_{0.1}$ was found to be not so sensitive. Hence, when $PM_{0.1}$ is clearly influenced by the transportation, the influence should be regarded as being significant. Behavior of some chemical components as WISOC in Nigeria can be understood only by examining characteristics of $PM_{0.1}$. $PM_{0.1}$ can be a useful and unique platform to understand behaviors of ambient particles particularly emitted from local sources.

1 Introduction

Ambient aerosol nanoparticles have been getting an increasing attention from their health risk point of view because of high deposition possibility in the alveoli region. Less information on the status and characteristics of ambient aerosol nanoparticles as well as their emission sources than fine particles yet. Because of high cost of the devices capable of monitoring and sampling nanoparticle, status and characteristics of the ambient aerosol nanoparticles have not been compared between different locations in different countries so far. In this study, characteristics of $PM_{0.1}$, particles smaller than 0.1 μm, were discussed on its ability as a tool to describe influences of emission sources and transboundary transportation of emitted particles. For this purpose, three different categories of area each of which has a different environmental background, were selected to discuss the contribution of different type of emission sources and meteorological conditions, or, Hokuriku area in Japan, an inland city in Nigeria and cities in Southeast Asia. The air sampling has been conducted at each sampling site for selected periods then chemical components of size segregated ambient particles including $PM_{0.1}$ were analyzed to discuss emission sources along with the analysis of air mass movement and hot spots that were used

to discuss influences of the transboundary transportation of air pollutants emitted by open biomass burning.

2 Methodology

2.1 East Asia Nano-particle Monitoring Network (EA-NanoNet)

As the platform of the present study, East Asia Nano-particle Monitoring Network (EA-NanoNet) played an important role. It had been established in March, 2013 by members consisting of 11 countries located in Northeast and Southeast Asia (East Asia), 24 universities, 5 institutes, 1 governmental agency and 1 company (Nov., 2020). **Fig.1** shows the location of sites participating the EA-NanoNet. The network activity is based on researcher's interest and volunteer under the management by 2 leaders (Japan (Furuuchi, KZU) and Thailand (Tekasakul, PSU)) and 3-cordinators (general (Thailand), material and samples (Japan)). In addition to these members, two institutes in Nigeria and University of Vienna in Austria have been collaborating with the network. A common tool is an "air sampler" for $PM_{0.1}$ developed and provided by Kanazawa University described in the followings. The simultaneous monitoring campaign has been conducted for 4 times since 2016, focusing on events haze in northern Thailand and the peatland fire in Indonesia. The workshop has been held every year from 2014

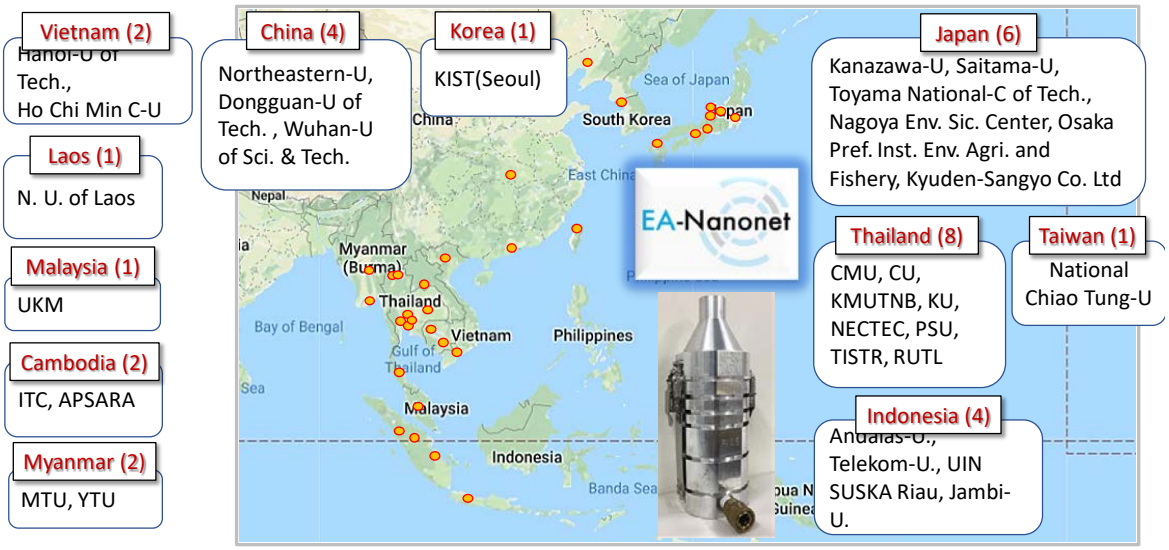

Fig.1 Schematic map of East-Asia Nanoparticle Monitoring Network (EA-NanoNet) at 2020.

alternately in Kanazawa and Thailand to share results and knowledge.

2.2 Air sampling

A cascade air sampler, termed here as an Ambient Nano Sampler, that can collect $PM_{0.1}$, $PM_{0.5}$, PM_1, $PM_{2.5}$, PM_{10}, TSP at an air flow rate of 40 *l/min* was used as a common sampler. Quartz fibrous filters of ∅55 mm that had been pre-baked at 350 °C in an oven for 1 hour then conditioned at 21.5 ± 1.5 ˚C, and 35 ± 5 % RH in a PM2.5 weighing chamber for 48 hours before and after sampling were used to collect particles. An inertial filter consisting of webbed stainless steel fibers (average fiber diameter d_f

=9.8μm, Nippon Seisen Co. Ltd., felt type, SUS-316) plugged in a cartridge nozzle of ∅ 5.25 mm was used for the separation of $PM_{0.1}$.

2.3 Analysis of chemical components

The thermal/optical analyses of carbonaceous components in particles collected on quarts fibrous filter (QFF) were conducted using a carbon analyzer, following the IMPROVE protocol. Water soluble ions and organic carbon were analyzed by using an ion chromatography and a TOC analyzer, respectively after extracting sample filters in ultra-pure water.

2.4 Backward trajectory and hotspots

72 hour backward trajectories of air parcels arriving at each monitoring site at a distance of 500 meters from the average ground level were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory Model version 4. 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 MODIS satellite remote sensing imagery were used to specify possible areas corresponding to biomass burning.

3 Results and discussion on each target area

3.1 Hokuriku region in Japan

***Procedure*:**

For a better understanding of the contribution of local emissions as traffic and open burning of crop residues as well as influence of the long range transportation, the PM monitoring was conducted at three locations spreading over Hokuriku region (See **Fig.2**).

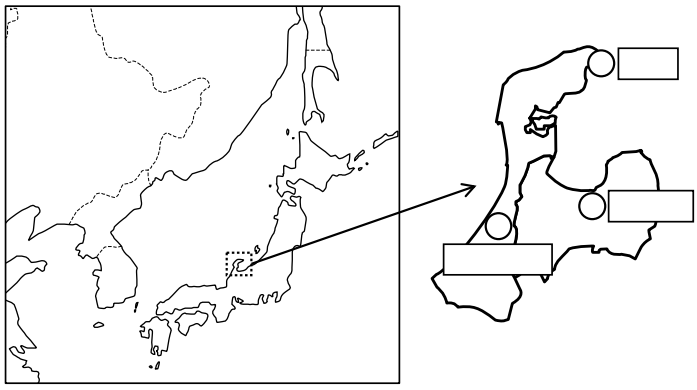

Fig.2 Locations of sampling sites: Kanazawa, Suzu and Toyama in the Hokoriku region, Japan.

The Kanazawa site was located in the Kakuma campus of Kanazawa University in an outskirt of Kanazawa city that is the prefectural capital of Ishikawa prefecture. The sampling site was on a balcony on the sixth floor of a 7-story building. The Toyama site was located on the rooftop of a 3-story building, National Institute of Technology, Toyama College in Toyama city. The Toyama site was located in a southern periphery of the city area surrounded by areas of mixed land uses by paddy fields, residential areas with local community roads. The Suzu site was located on the rooftop of a 3-story lecture hall building of the Noto School in Suzu city that is the city located most north in Noto Peninsula. The site was in a small local community adjacent to a beach in its eastern side (~120 m) and surrounded by managed forest area with small agricultural fields. The sampling at the Kanazawa site has been continued since 2010 while it was started in 2014 at the Toyama and the Suzu sites. At all sampling sites, the duration for each sampling was set as continuous 7 days, twice a month. 2110 available

samples in 356 sets from the 3 sampling sites in Hokuriku region were collected as a total. The information on the sampling, concentrations and ratio of PM fractions is summarized in **Table 1** where Spring, Summer, Autumn and Winter were here defined as March to May, June to August, September to November and December to February.

Table 1 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

***Summary on Hokuriku region*:**

1) The seasonal behavior of the PM concentration at all sites were basically similar reflecting similar meteorological characteristics.
2) 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 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.

3) The concentration and influence of secondary organic carbon for the $PM_{0.1}$ carbon content were the largest at the Toyama site.
4) Evidences may not be sufficient to explain the influence of the transboundary transportation of air pollutants by air mass.
5) For a further understanding, more detailed information concerning the various chemicals in different sizes of particles should also be examined.

3.2 Inland local city in Nigeria

Procedure: The sampling site was located in Akure city, which is the largest and capital city of Ondo state in the south west geopolitical zone of Nigeria. The sampling site was located on the roof of a building at the Federal College of Agriculture (FCA). The FCA is located in a suburban residential area surrounded by agricultural fields, 350 m south from a highway and approximately 1.3km west from another high running road between the Akure city area and the sampling site (See **Fig.3**). The site was surrounded by trees in the tropical rainforest zone, residential buildings, tarred and untarred roads for low levels of vehicular traffic, farms, and a waste dump site. The air sampling for 24 hours was conducted for a period between Oct. 14, 2017 and Oct.20, 2017. In **Table 2**, concentrations of PM and selected carbonaceous components as well as their ratios are summarized.

Fig.3 Map showing the sampling site in Akure city, Nigeria.

Table 2. Average concentrations of particle-bound carbon components and its ratio.

Parameter	Particle size range (μm)				
	<0.1	0.5-1.0	1.0-2.5	2.5-10	>10
Particle mass conc. (μg/m^3)	43.14±18.90	40.48±11.87	18.22±6.11	58.93±22.95	24.51±6.28
OC (μg/m^3)	16.84±13.26	3.16±1.70	1.32±1.34	1.91±0.85	0.50±0.14
EC (μg/m^3)	0.86±0.40	0.54±0.15	0.38±0.31	0.27±0.18	0.10±0.04
OC/EC (-)	19.72±17.04	5.80±2.44	3.49±1.40	12.01±10.05	5.84±2.32
Char-EC (μg/m^3)	0.43±0.40	0.61±0.20	0.40±0.38	0.26±0.17	0.33±0.08
Soot-EC (μg/m^3)	0.44±0.18	0.35±0.15	0.17±0.17	0.32±0.15	0.09±0.04
Char-EC/Soot-EC (-)	1.12±0.98	1.98±0.90	2.70±1.17	1.60±2.76	4.36±1.70
Py-OC (μg/m^3)	0.65±0.41	0.63±0.37	0.15±0.36	0.64±0.34	0.14±0.08
Py-OC/OC4 (-)	0.36±0.03	0.59±0.22	0.41±0.24	0.64±0.23	0.39±0.16

***Summary on Nigeria*:**

1) Average $PM_{0.1}$ mass concentration (43.1μg/m^3) was quite large comparing to other countries including developing countries in Southeast Asia.
2) The $PM_{0.1}$ fraction was nearly 2 times larger than those in other locations in the world.
3) Organic carbon (OC) in $PM_{0.1}$ was found to dominate the mass of particulate matter (PM) and the most of OC was water insoluble (WISOC) that had a weak correlation to soot-EC, or, fissile fuel burning.
4) Water soluble organic carbon (WSOC) in $PM_{0.1}$ was clearly correlated to SO_4^{2-} and oxalate, indicating WSOC in $PM_{0.1}$ was very much related to particles from the secondary formation of emitted matters from the oil burning.
5) Since the air mass passed through the ocean located south of Nigeria, the transboundary influence of open biomass burning on local air pollution by PM could be negligible, while local emission from the burning of fossil fuel and biomass appeared to dominate and influences of emission in oil field located south of the study area could be possible.
6) Behaviors of $PM_{0.1}$ in Akure, Nigeria were quite different from those in different countries.
7) $PM_{0.1}$ can be said as a parameter sensitive to local emission sources including the secondary formed particles

3.3 Cities in South East Asia

***Procedure*:**

In the Southeast Asia (SEA), 4-different campaigns had been conducted from 2016 - 2018 focusing on difference purposes as the forest fire in northern Thailand and the peat land fire in Indonesia as well as the dust storm in China. **Table 1** shows sites participating each campaign. The first campaign was conducted in March to April 2016 corresponding to the forest fire period in Chiang Mai or northern of Thailand and the dust storm season in the northeast Asia. The second campaign was during the Indonesia forest fire in 2017, or, from July to October. This was mainly for the smoke spreading over the southern part of Southeast Asia. The third campaign (2018A) was aimed on the Chiang Mai forest fire during January to April. In the latest campaign in 2018 during early September (2018B), the Asian Game organized in Indonesia was a focused point. Through all campaigns, influences of local emission sources and the transboundary

Table 1 Monitoring sites for each campaign

Country	No.	Location	2016	2017	2018A	2018B
Japan	1	Kanazawa	○	○	○	○
	2	Toyama	○	○	○	○
	3	Suzu	○			
	4	Nagoya	○	○	○	○
	5	Osaka	○	○	○	○
	6	Saitama	○	○	○	
	7	Fukuoka		○	○	
Korea	8	Seoul		○	○	○
Vietnam	9	Hanoi	○	○	○	
	10	Ho Chi Minh City	○	○	○	
Cambodia	11	Phnom Penh	○		○	○
Thailand	12	Chiang Mai	○	○	○	
	13	Khlong Luang		○	○	○
	14	Central Bangkok		○	○	○
	15	Northeast Bangkok	○	○		○
	16	Northwest Bangkok	○	○	○	
	17	Hat Yai	○	○	○	○
Indonesia	18	Riau	○			○
	19	Jambi				○
	20	Bandung			○	○
	21	Padang				○
Malaysia	22	Bangi	○	○	○	○

transportation of air pollutants were discussed as key points to clarify the importance to discuss characteristics of $PM_{0.1}$.

Fig.4 shows the outline of the procedure of campaigns. There were two cores in Japan and Thailand, or, Kanazawa University (KU) and Prince of Songkla University (PSU). Each core manages mainly Northeast Asia and Southeast Asia, respectively. Filters were weighed in Japan and distributed to members except Thailand. PSU managed filters for members in Thailand for campaigns in 2018. After the sampling, filter samples were sent back to KU to be weighed and for chemical analysis. Carbonaceous components were analyzed by KU while ions and WSOC were analyzed by Research Institute of Environment, Agriculture, Fisheries, Osaka Prefecture (RIEAFOP) or the Nagoya City Institute for Environmental Sciences (NCIES). Results were shared members through workshops and publications. The sampling duration at each site was decided between 1 day to 1 week depending of the expected PM concentration to collect an enough amount of particles for the chemical analysis. **Fig.5** shows the average mass concentration of size fractionated particles for each monitoring campaign.

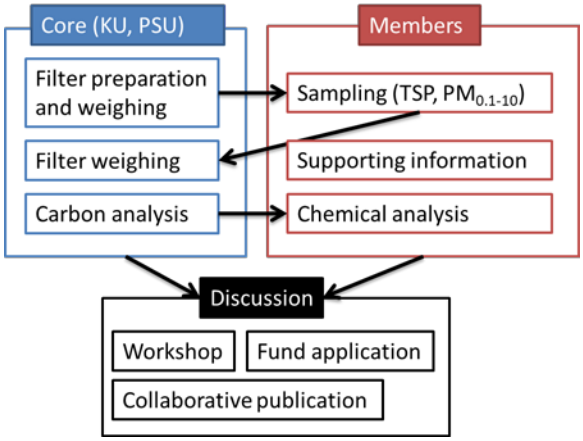

Fig.4 Procedure of campaign.

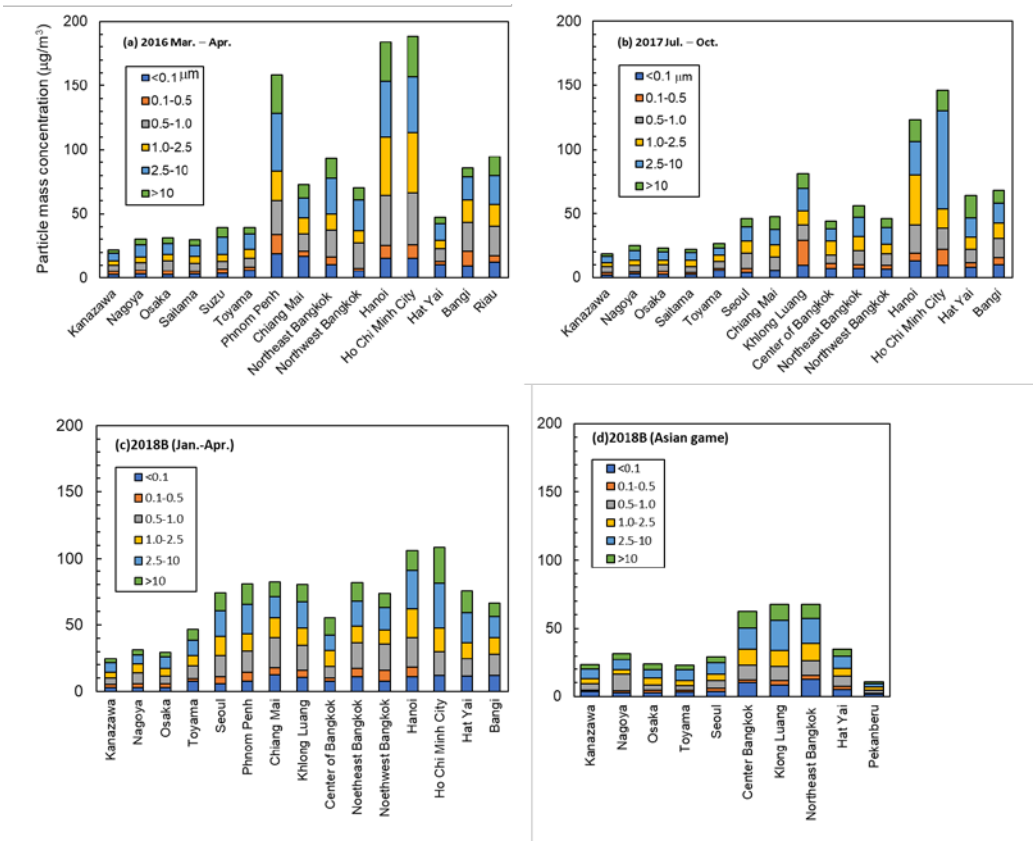

Fig.5 Average mass concentration of size fractionated particles: (a) 2016, (b) 2017, (c) 2018A and (d) 2018B.

***Summary on cities in Southeast Asia*:**

1) Much larger mass concentration of $PM_{0.1}$ compared to cities in Japan and Korea was founded in cities in Southeast Asia.
2) The mass concentration of $PM_{0.1}$ was not so sensitive to seasonal conditions as the rain precipitation while this was not in the case for coarse fractions as road dust (>10 μm). This was clear in large cities in SEA as Phnom Penh, Hanoi and Ho Ci Minh City.
3) During the peatland fire season in Indonesia, an influence was clear in Hat Yai in spite of the rainy season. This may be due to the transboundary influences.
4) Influences of events as forest fire in Chiang Mai was clear only in Chiang Mai, indicating the transboundary influence to characteristics of $PM_{0.1}$ was not so clear in this area during the dry season and local emission as the traffic dominated characteristics of $PM_{0.1}$.
5) The Behavior of OC/EC vs. EC in $PM_{0.1}$ was similar between cities in East Asian countries when the event as forest fires are not happened.

4 Conclusion

1) $PM_{0.1}$ was confirmed to well describe primary particles from local sources as well as components by the secondary formation from gaseous pollutants.
2) For the transboundary transportation of primary and secondary particles, behavior of $PM_{0.1}$ was found to be not so sensitive. Hence, when $PM_{0.1}$ is clearly influenced by the transportation, the influence should be regarded as being significant.
3) Behavior of some chemical components as WISOC in Nigeria can be understood only by examining characteristics of $PM_{0.1}$.
4) $PM_{0.1}$ can be a useful and unique platform to understand behaviors of ambient particles particularly emitted from local sources.

令和３年　２　月　２　日

学位論文審査報告書（甲）

１．学位論文題目（外国語の場合は和訳を付けること。）

Investigation into Characteristics and Emission Sources of Ambient Nano-particles (PM0.1)

（大気中ナノ粒子（PM0.1）の特性と発生源に関する考察）

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３．審査結果の要旨（600～650字）

提出された論文に対し，書面および口述審査を実施し，以下のように判断した。

本論文は，肺深部への高い沈着率と有害成分比率およびその圧倒的な個数濃度から健康リスクが懸念される大気中に浮遊するナノ粒子（PM0.1）に着目し，様々な地点での観測からその現状と特性を詳細に把握し，発生源および越境汚染の影響を考察して，環境指標としてのナノ粒子の持つ特徴と意義を明らかにしたものである。経済状況・発生源・越境汚染の影響が大きく異なる日本・ナイジェリア・東南アジア各地の３地域を観測対象として，主たる影響因子を差別化した。北陸地方では，黄砂時期のPM0.1濃度上昇，秋季の野焼き影響，降雪のPM0.1粒子のウォッシュアウト効果の高さ，ナイジェリア内陸都市では，PM0.1濃度と粒子中の非水溶性炭素成分比率の卓越的な高さおよびナノ粒子発生源としての無秩序な廃棄物燃焼の重要性を明らかにした。さらに，東南アジア研究者と連携した多点同時観測から，ナノ粒子が道路交通等のローカル発生源の指標としてだけでなく，森林火災のような強度のバイオマス燃焼汚染の指標としても有用であること等を示した。

以上のとおり，本論文で示された環境指標としてのナノ粒子の特性とその意義は，ナノ粒子リスクの把握とその対策のための指針を示す上で重要なブレイクスルーを達成するとともに，大気中ナノ粒子の特性と発生源に関する様々な新しい知見も与えている。一連の成果は１編の英語論文にまとめられ，国内外の学会・ワークショップで英語での発表も多くあることから，英語の語学力も十分と認められる。以上より，博士（学術）の学位を授与するに値すると判断する。

４．審査結果　(1) 判　　定（いずれかに○印）　（合　格）・　不合格

(2) 授与学位　　博　士（　学術　）