

Chemical composition of nanoparticles in roadside atmosphere in Japan

Akihiro Fushimi^{1,*}, Shuichi Hasegawa¹, Katsumi Saitoh², Yuji Fujitani¹
Katsuyuki Takahashi¹, Kiyoshi Tanabe¹ and Shinji Kobayashi¹

¹ National Institute for Environmental Studies

² Akita Prefectural Research Center for Public Health and Environment.



1. Introduction

Atmospheric nanoparticles (<0.05 μm) have caused great concern recently because their effects on human health may be stronger than those of larger particles. High number concentrations of nanoparticles are present in roadside atmosphere, and it has been suggested that diesel vehicles are the primary sources of roadside nanoparticles¹. However, little is known for chemical composition, sources and atmospheric behavior of roadside nanoparticles.

To understand sources and behavior of roadside nanoparticles, we measured evaporation characteristics and chemical composition of nanoparticles at roadside with heavy traffic in Kawasaki City, Japan. The overview and some typical results are described below.

2. Methods

Size-resolved particles including nanoparticles fraction were collected by cascade low-pressure impactors (LPI, DEKATI) at roadside in Kawasaki City (Fig.1). Diesel exhaust particles from 3L diesel truck was collected using chassis dynamometer.

Elemental carbon (EC) and organic carbon (OC) were analyzed by the Carbon Analyzer (DRI, Model 2001) based on the thermal method under the IMPROVE protocol. 26 elements were quantified by particle induced X-ray emission (PIXE) method.

Organic analysis was conducted by thermal desorption-gas chromatography/ mass spectrometry (TD-GC/MS). TD-GC/MS enabled organic analysis in small amount of particles ($\approx 30 \mu\text{g}$). Thermal desorption was carried out by the pyrolyzer (Py-2010iD, Frontier Laboratories) from 50 $^{\circ}\text{C}$ to 450 $^{\circ}\text{C}$ in a flow of helium.

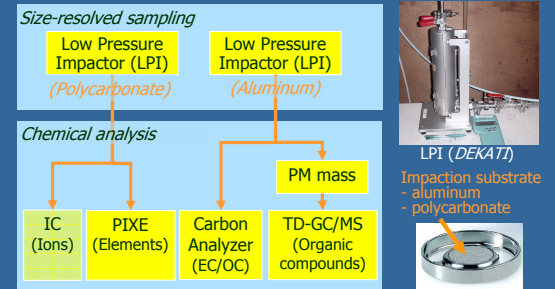


Fig.1. Sampling and analytical methods.

24 h samplings by two or three LPIs were conducted in winter and summer from 2003 to 2005.

3. Results & Discussion

3.1 Evaporation Characteristics

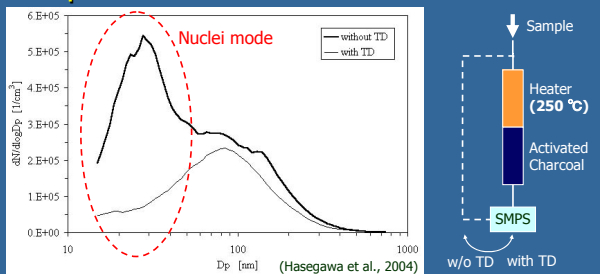
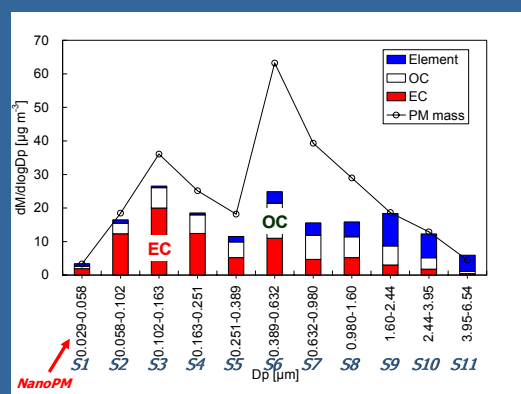


Fig.2. Number size distribution and evaporation characteristics of roadside atmospheric particles. The measurements were conducted by scanning mobility particle sizer (SMPS, TSI) with and without thermal denuder (TD) alternately every 15 min, and the data were averaged, respectively.

It was suggested that compounds that vaporize below 250 $^{\circ}\text{C}$ were dominant for roadside nuclei-mode particles (<0.030 μm).

3.2 Elemental/organic carbons & Elements



(Kawasaki, Nov 20–21, 2003)

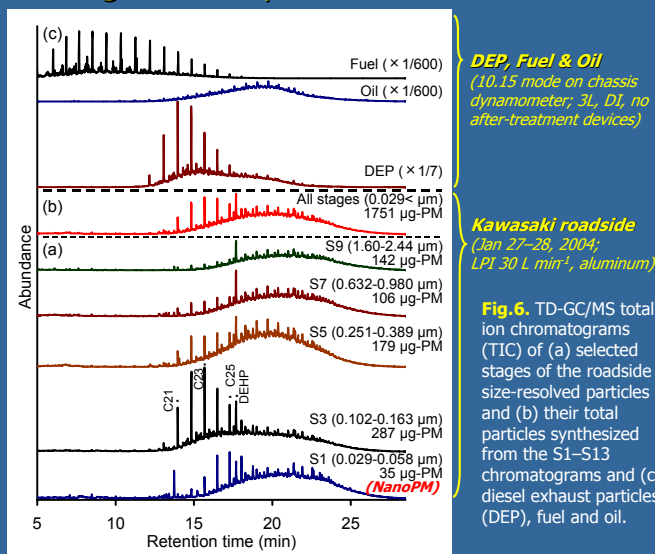
LPI (30 L min⁻¹, aluminum): PM mass & EC/OC
LPI (10 L min⁻¹, polycarbonate): Elements

Fig.3. Size distributions of particle (PM) mass, elemental/organic carbons (EC/OC) and total elements concentrations at roadside.

The PM mass and EC concentrations showed bimodal distribution with larger peak at around 0.1 μm and smaller peak at submicron to 2 μm in winter. Highest EC concentrations were observed at around 0.1 μm .

Total elements concentrations were higher for coarse particles. Total elements concentration for nanoparticles (0.029–0.058 μm) was slightly larger than that for S3 (0.102–0.163 μm) particles.

3.3 Organic compounds



DEP, Fuel & Oil
(10.15 mode on chassis dynamometer; 3L, DI, no after-treatment devices)

Kawasaki roadside
(Jan 27–28, 2004;
LPI 30 L min⁻¹, aluminum)

Fig.6. TD-GC/MS total ion chromatograms (TIC) of (a) selected stages of the roadside size-resolved particles and (b) their total particles synthesized from the S1–S13 chromatograms and (c) diesel exhaust particles (DEP), fuel and oil.

The TIC trend of S3 particles was similar to that of DEP. For the TIC of nanoparticles, C23 alkane or less volatile compounds were dominant. After scaling the abundances, the TIC pattern and abundance, and the mass spectra of the nanoparticles with retention time (RT) >23min were equivalent to those of lubricating oil. However, with RT <23min, the TIC abundance of nanoparticles got smaller than that of lubricating oil with earlier RT.

It is suggested that lubricating oil strongly affected to the roadside nanoparticles, and more-volatile organic compounds in the nanoparticles evaporated in the atmosphere. Fuel seemed to slightly (up to $\approx 20\%$) contribute to the nanoparticles composition.

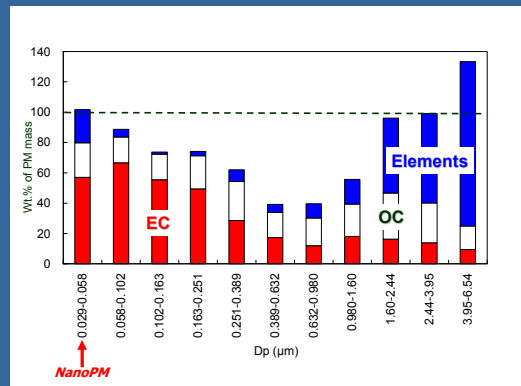


Fig.4. Weight percentage of EC/OC and total elements to PM mass by particle size at roadside.

EC and OC constituted a large proportion of PM mass, especially at around 0.06–0.16 μm , where EC peak concentrations were observed for diesel exhaust particles (DEP). Therefore, it was suggested that DEP remarkably contributed to the particles at around 0.06–0.16 μm .

Total carbon (TC) constituted 80% of the PM mass for nanoparticles (0.029–0.058 μm). EC constituted around 80% of TC for S3 (0.102–0.163 μm) particles, and EC/TC ratio was slightly smaller for nanoparticles than S3 particles.

For nanoparticles, the percentages of OC and total elements to the PM mass were greater and the percentage of EC was smaller than those for S2 (0.058–0.102 μm) and S3 particles. For nuclei-mode particles (<0.030 μm), the percentages of OC and total elements may be greater than those for nanoparticles (0.029–0.058 μm).

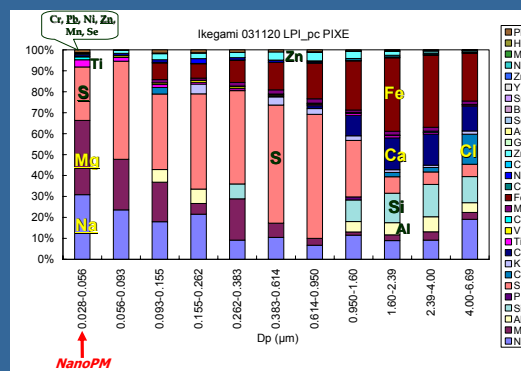


Fig.5. Proportions of elements by particle size at roadside.

For >1.6 μm particles, Fe, Ca, Si and Al, likely to be originated from soil, dominated the mass of the total elements. For submicron particles (0.155–0.950 μm), high concentration of sulfur, likely to exist as sulfate, was observed.

Na, Mg and S, may be originated from lubricating oil of automobiles, were detected in the nanoparticles.

4. Conclusions

- It was suggested that compounds that vaporize below 250 $^{\circ}\text{C}$ were dominant for roadside nuclei-mode particles (<0.030 μm).
- For roadside nanoparticles (0.029–0.058 μm), the weight percentages of organic carbon (OC) and total elements to the PM mass were greater and the percentage of elemental carbon (EC) was smaller than those in the 0.058–0.102 μm and the 0.102–0.163 μm particles. For nuclei-mode particles, the percentages of OC and total elements may be greater than the 0.029–0.058 μm particles.
- Na, Mg and S, may be originated from lubricating oil of automobiles, were detected in the nanoparticles.
- Thermal desorption-gas chromatography/ mass spectrometry (TD-GC/MS) enabled organic analysis in small amount of particles ($\approx 30 \mu\text{g}$). From the analysis of chromatogram pattern and the mass spectra, it is suggested that lubricating oil strongly affected to the roadside nanoparticles, and more-volatile organic compounds in the nanoparticles evaporated in the atmosphere.

Acknowledgement

This work was supported by a contract research fund from the Japan Ministry of the Environment.

Reference

- Hasegawa et al. (2004). J. Environmental Science and Health, Part A, A39, 10, 2671–2690.

*Contact Address

Akihiro FUSHIMI, Ph.D.

Environmental Chemistry Division, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-8506 Japan
Tel: +81-29-850-2752, Fax: +81-29-850-2531
E-mail: fushimi.akihiro@nies.go.jp