

Roadside observation for chemical composition and size distribution of fine particles using Aerosol Mass Spectrometer in Tokyo

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INTRODUCTION

Measurement of fine particulate chemical composition and size-resolved mass distributions of several types of compounds has been carried out at the roadside of arterial roads in Tokyo, during a field observation under Japan Clean Air Program (JCAP) II in February-March 2004. Main purpose of this observation was to obtain data on spatial properties of number concentrations of nanoparticles around typical heavily-trafficked roads in the city using ten units of Scanning Mobility Particle Sizer (SMPS) simultaneously, and to compare the observation data with the data on CO₂ and NO_x concentrations in terms of wind velocity, temperature and traffic conditions.

I am concerned here with the observation results of chemical properties of fine particles obtained using Aerosol Mass Spectrometer (AMS), which was also used in the field observation.

AEROSOL MASS SPECTROMETER

Measurement has been carried out using a unit of AMS developed by Aerodyne Research, Inc. The instrument is composed of three main sections: aerosol sampling chamber, particle sizing chamber and particle detection chamber. Each chamber is separated by critical apertures and is differentially pumped. Particles in the sampled air flow are converged in a particle beam, and particles are accelerated according to their size with an aerodynamic lens. Size of the particles is determined based on a time-of-flight (TOF) measurement between chopper wheel and detector. In the detection section, volatile or semi-volatile compounds in particles are vaporized on a resistively heated source. Then they are ionized by an electron impact ionizers and molecular fragments are measured using a quadrupole mass spectrometer.

In this observation, AMS was operated under the following conditions: 2.4cc/s in sampling rate, 610°C in the temperature of heater and 0 to 300 amu in the range of MS scanning. The number of MS for size distribution measurement was selected based on the MS spectrum as a dominant fragment.

OBSERVATION CONDITIONS

Meteorological data during observations had been obtained every minute and averaged out for every ten minutes. Wind directions of the relevant day were roughly divided into two groups: (1) parallel to the road in the morning and after 16:00 and (2) from the back of observation site to the road in the afternoon before 16:00. Assuming the wind blowing parallel to the road behaves no effect on particle transportation from the road to backward, diffusion behavior of roadside particles was examined based on the data observed during the hours classified as (1).

For comparison of the characteristics of fine particles, sampling point alone was changed repeatedly from roadside (0 m) to the backward from the roadside (20 m at the maximum) while measurement was carried out continuously under steady conditions. A long TYGON tube connected to AMS inlet was used for aerosol sampling, of which the length (13 m) was sufficient to reach every sampling point easily. Data of total mass concentrations and size-resolved mass distribution of nitrate, sulfate, chloride and organic compounds were obtained at the sampling points of 0, 5 and 20 m from the roadside respectively, and the data were compared to each other. For further characterization of particles at each point, several types of analysis of organic compounds were tried.

RESULTS AND DISCUSSION

(1) Chemical compositions

Chemical composition of particles was calculated at each sampling point by accumulating the data obtained during the period. Ratio of organic compounds at 0m-point is higher than that at other points. It was showed that chemical composition of organics components alone was changed according to the distance from the road, whereas the other components (sulfate, nitrate and chloride) showed almost same values through this area. Decrease in concentrations of organic compounds occurred mainly within 5m from the roadside, and little change was observed between the data at 5 and 20m.

(2) Size distributions

Whereas no significant difference was observed in the case of sulfate, nitrate and chloride in all range of the particle size and organic compounds in larger particle size, a considerable change in mass loading of organic compounds was observed as the distance from roadside increased in the case of particles with around 100 - 200 nm in modal aerodynamic diameter. Changes in mass loading mainly occurred in the range of 0 to 5 m from the roadside, i.e. higher concentrations were observed at 0 m, and little difference was observed between the observation results at 5 and 20 m. This tendency was intensified when wind blew from the direction of the road. Difference in size distribution of organic compounds between 0 and 5m can be considered because of the effect of the road, and in the case of 0 m, the peak was observed around 100nm in particle diameter, which meant the specific distribution pattern..

(3) Organic compounds m/z analysis

Size distribution for some m/z was compared each other to examine the types of organic compounds in more detail. Comparing the data at 5m to those at 0m, little difference was observed on the size distribution for m/z 44 (CO_2^+ ; dicarboxylic acids) throughout all range of particle sizes. On the other hand, concentrations of m/z 57, 71 and 85 (C_4H_9^+ , $\text{C}_5\text{H}_{11}^+$ and $\text{C}_6\text{H}_{13}^+$ respectively) showed a significant decrease in all range of particle sizes. Size distributions for m/z 43 (C_3H_7^+ , $\text{C}_2\text{H}_3\text{O}^+$) showed a different behavior. Concentration decrease was shown in the smaller mode only, while high concentrations were remained unchanged in the larger mode.

It suggests that the effect of road on smaller mode diameter is mainly caused by non-oxygenated hydrocarbons, and main components of organics in larger mode diameter are oxidized ones.

SUMMARY

Based on the results, it is assumed that properties of roadside particles are strongly affected by traffic conditions, and the application of AMS to field observation has potential for making the particle property alteration processes clear.

Another field observation has been planned to carry out under JCAP II for getting better understanding of roadside particle properties, their dependence on traffic conditions and meteorological parameters.

ACKNOWLEDGMENTS

This study has been and is performed as a part of JCAP II research activities. JCAP is a collaboration program between automobile and petroleum industries, subsidized by the Ministry of Economy, Trade and Industry, and conducted by Japan Petroleum Energy Center (JPEC).

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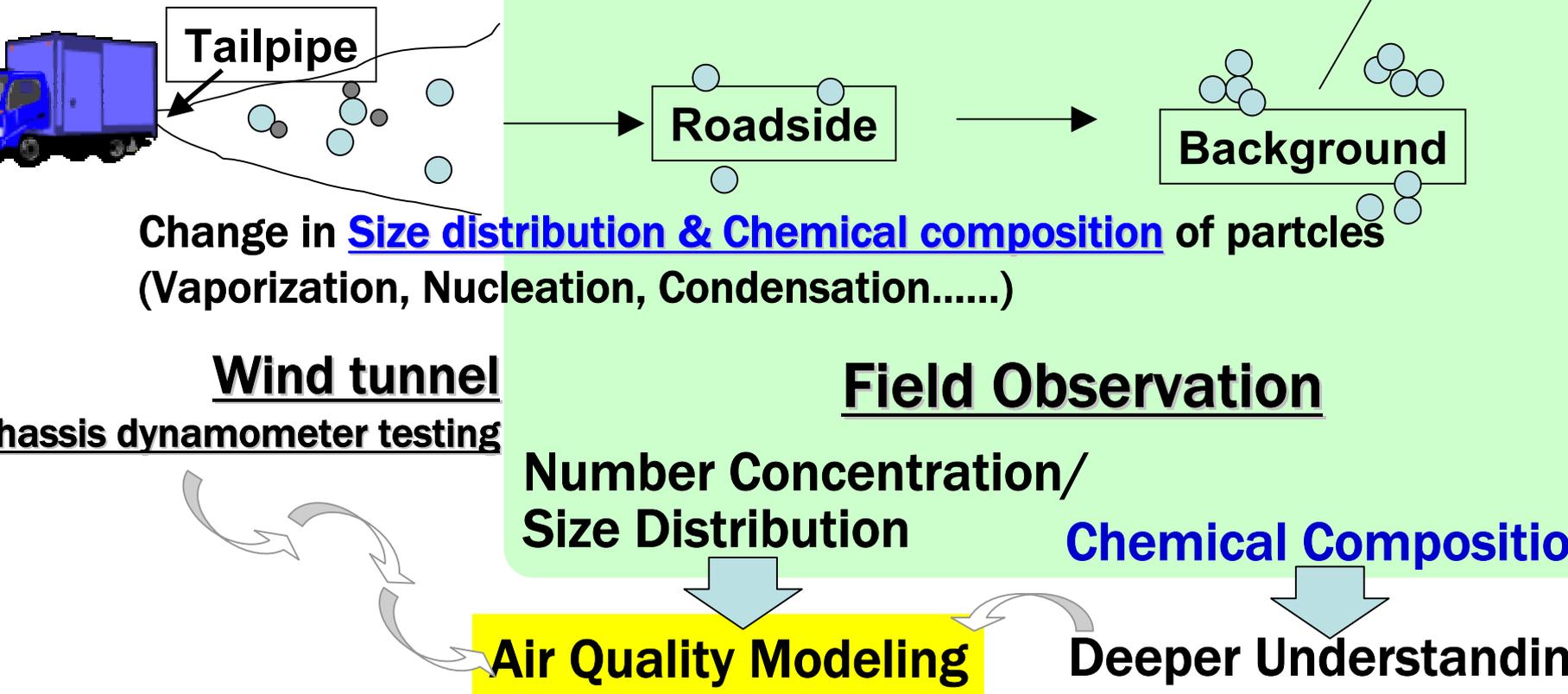
Dynamics on Particles from Tailpipe to Urban area

CAP II Air Quality Study Group

Develop Air Quality Simulation Models

Predict the effect of emission reduction measures on Air Quality

Provide suggestions for future air quality improvement.



JCAPII Field Observations

Site & Date

Periphery of NOGE Park, Setagaya-ward, Tokyo
February 2004 (1 month)

Objective

Figure out spatial properties
of nanoparticle number
concentrations at roadside

Instrumentation

AMS*2

(SMPS/CPC/NO_x/CO & CO₂ meter)*6

(SMPS/Thermo-denuder)*4

(Anemometer/Thermometer/Hygrometer)*6

(Speed gun/Video recorder)*6

DMS*2, EEPS*1(optional)



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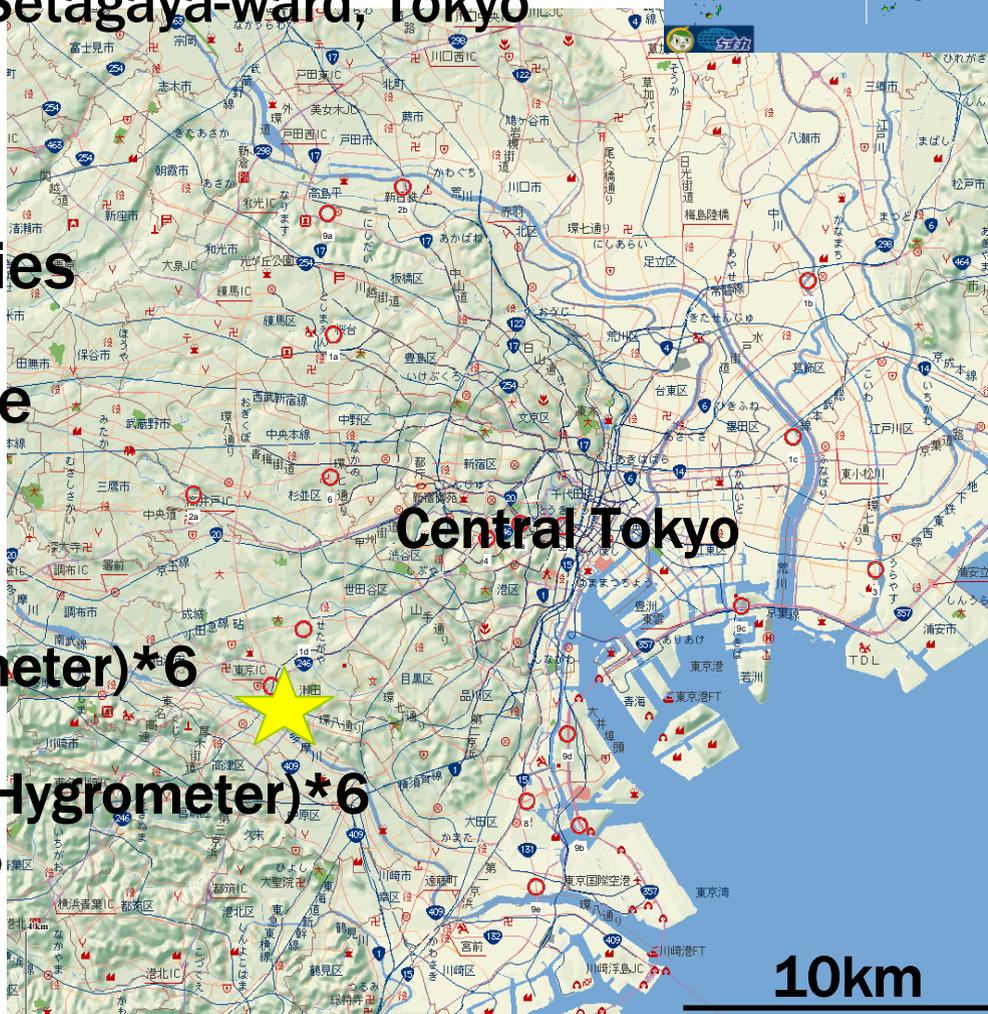
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(SMPS/Thermo-denuder)*4

(Anemometer/Thermometer/Hygrometer)*6

(Speed gun/Video recorder)*6

DMS*2, EEPS*1(optional)



Observation Site



NOGE Park

Background

Ideal wind direction

Roadside
5m
20m
50m
100m

NOGE Park

Loop 8
One of the
heaviest-trafficked
arterial roads
in Tokyo

Loop 8

Observation Site



NOGE Park

Aerosol Mass Spectrometer

**Aerosol Beam
Generation**

Particle
Acceleration

**Aerodynamic
Sizing**

Velocity
measurement

Detection

Mass Spectrum
(No Size information)

Size distribution
(Fixed MS Detection)

Aerodynamic Lens

Aerosol Beam

Chopper

**Quadrupole
Mass Spectrometer**

Inlet →

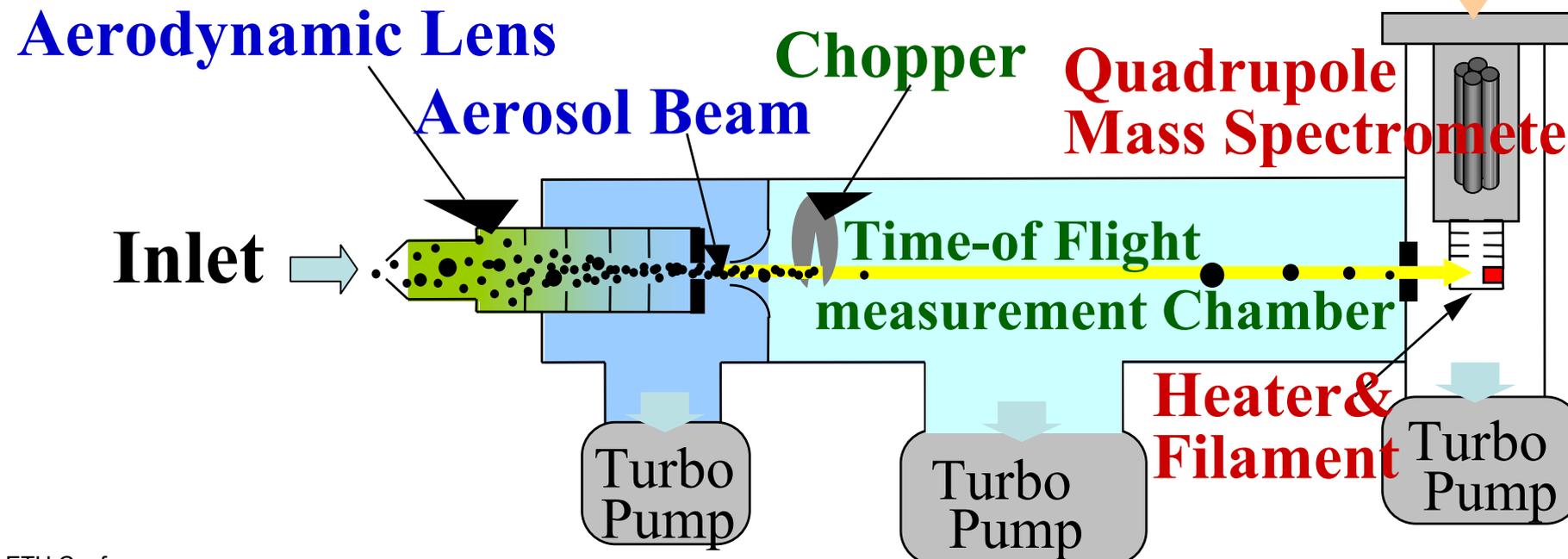
**Time-of-Flight
measurement Chamber**

**Heater &
Filament**

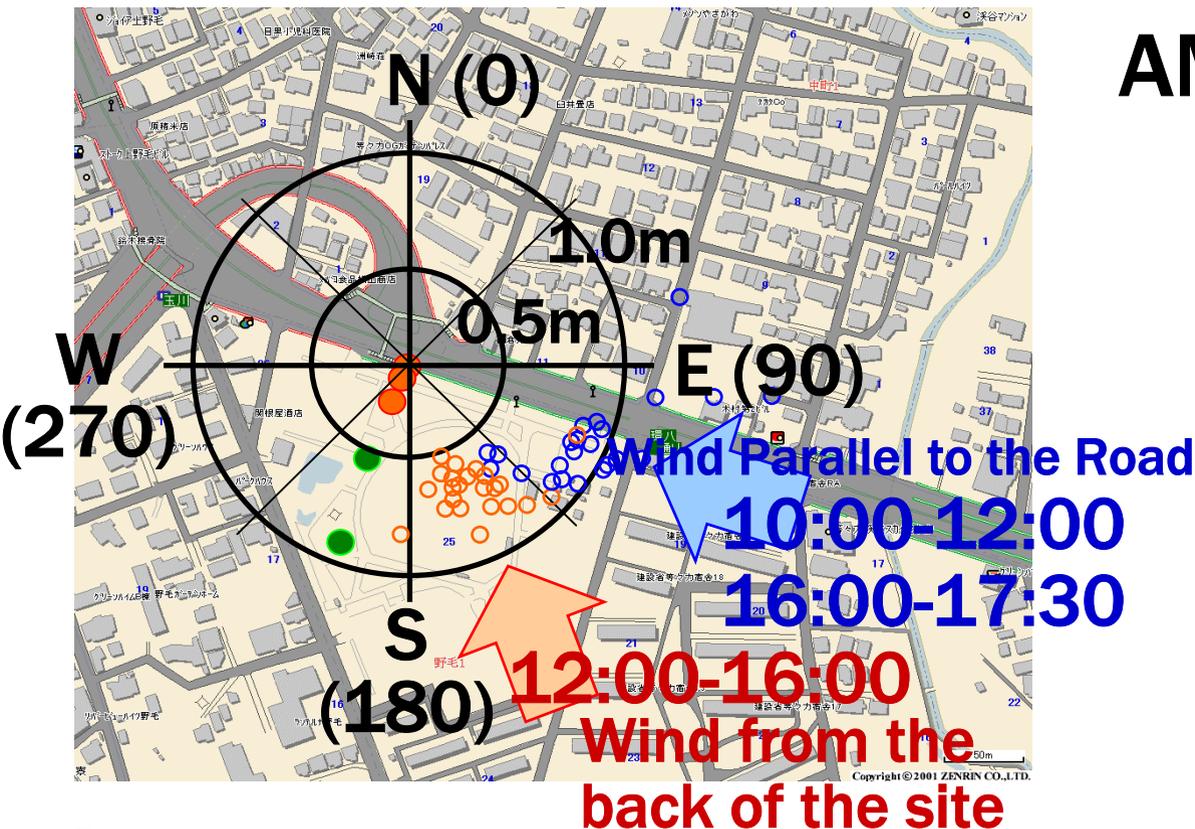
Turbo
Pump

Turbo
Pump

Turbo
Pump



Observation Conditions



AMS Conditions

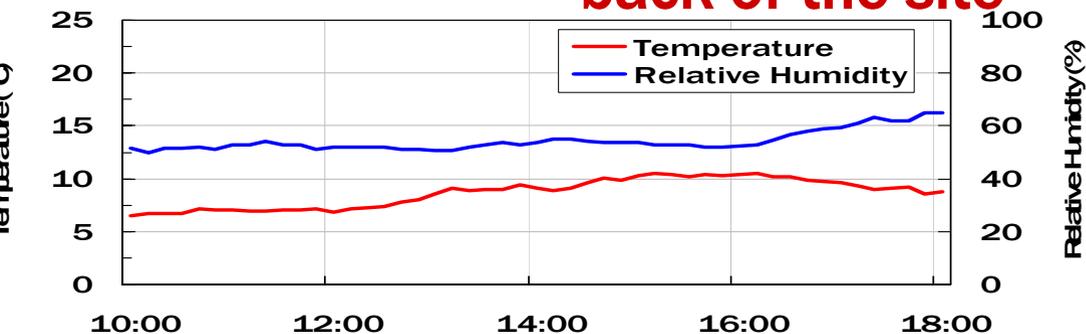
Sampling rate:
2.4 cc/second

Heater Temperature
610 °C

MS Scanning :
0 to 300 amu

Selected MS for TOF
measurement:

- 16, 18, 28, 29, 30,
- 36, 41, 43, 44, 46,
- 48, 55, 57, 64, 69,
- 71, 73, 77, 83, 85,
- 91, 128



Sampling

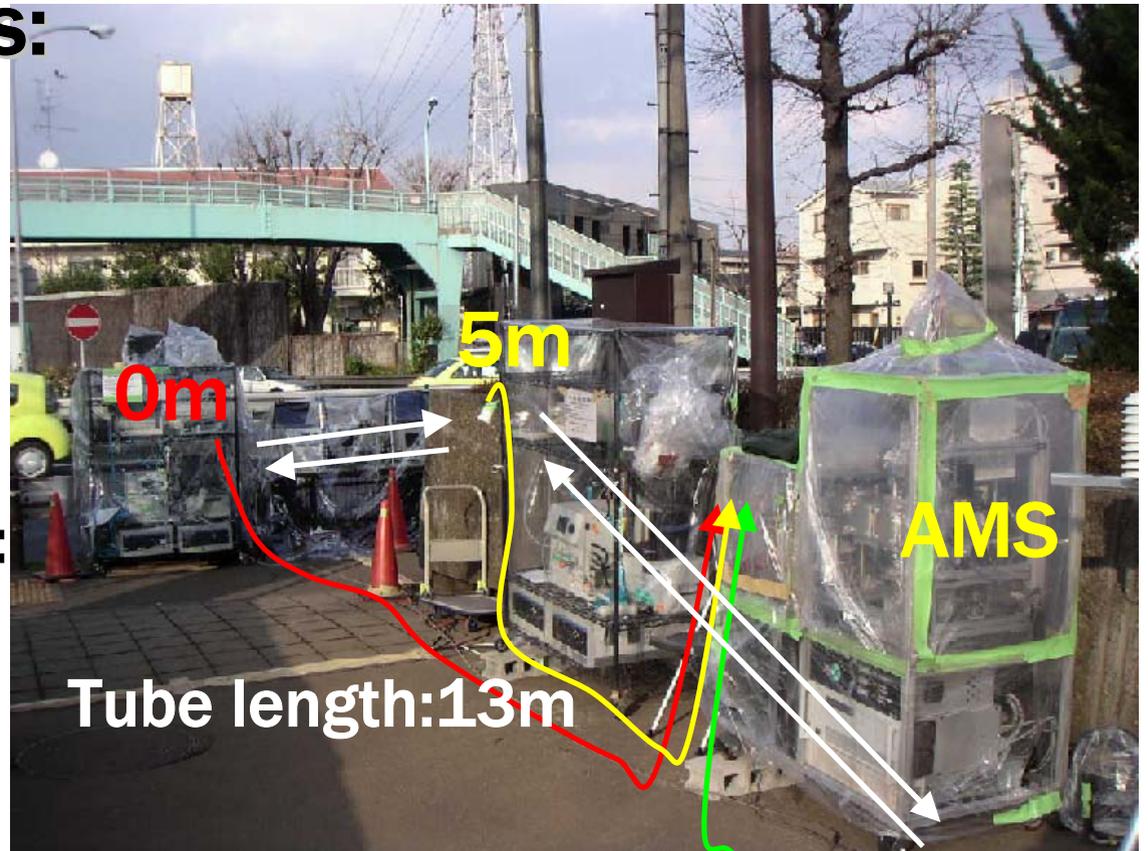
AMS: Continuous measurement under a stable condition

Sampling Points:

Point switchover:
 every 10min

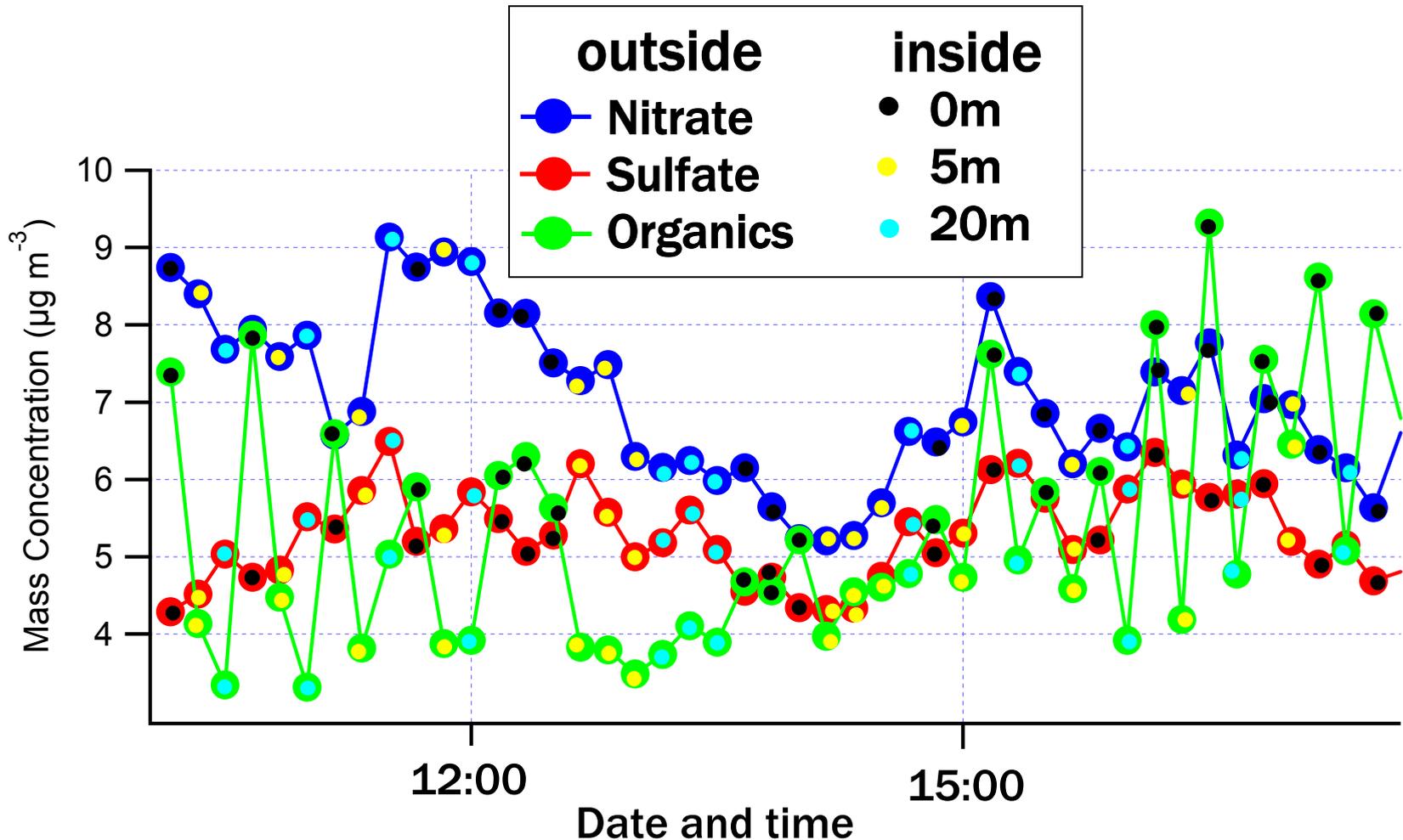
Gas replacement:
 3min

Data accumulation:
 7min



to 20m

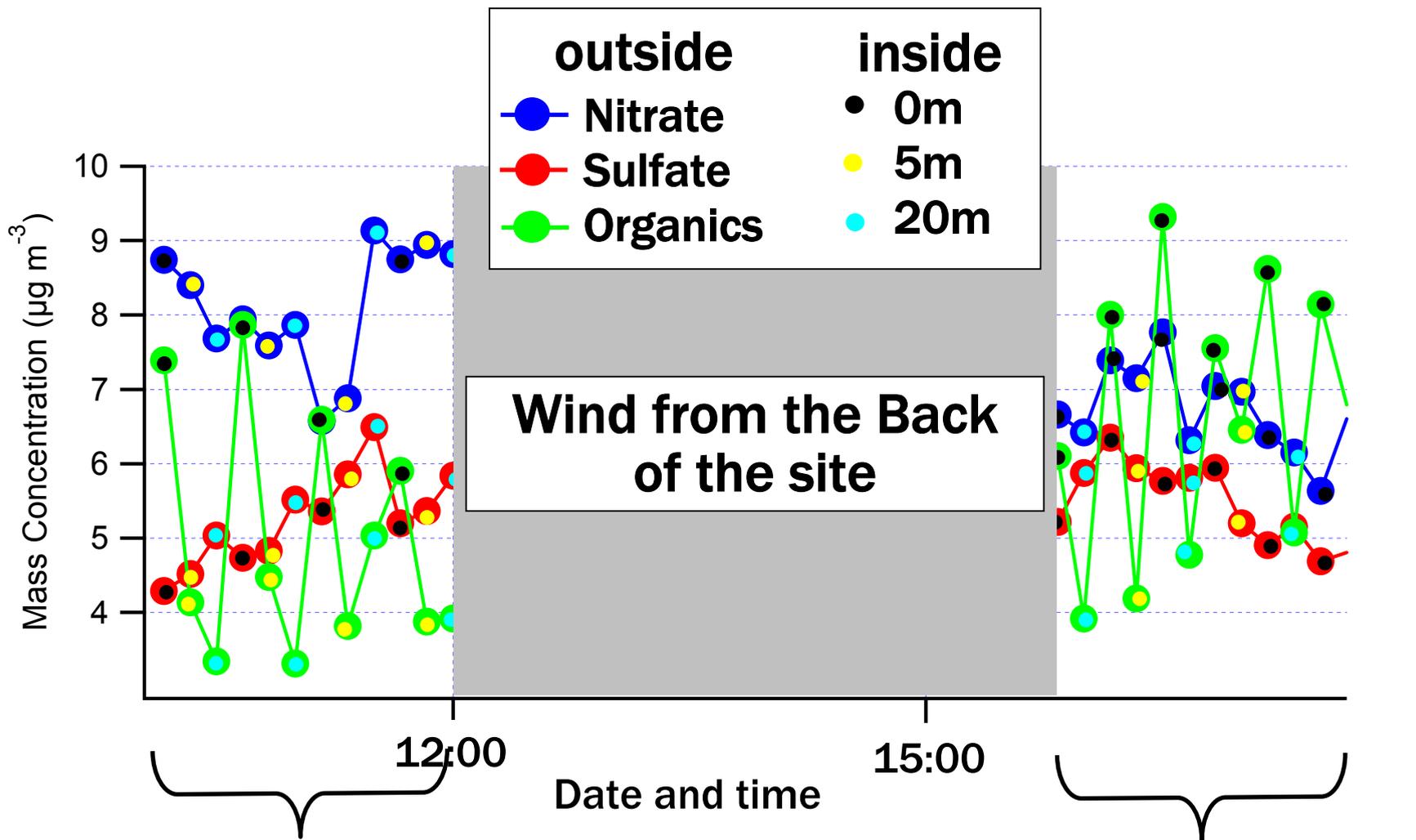
Mass Loadings



Organic compound: Data vary by sampling point.

Other species: Data vary independently of sampling point.

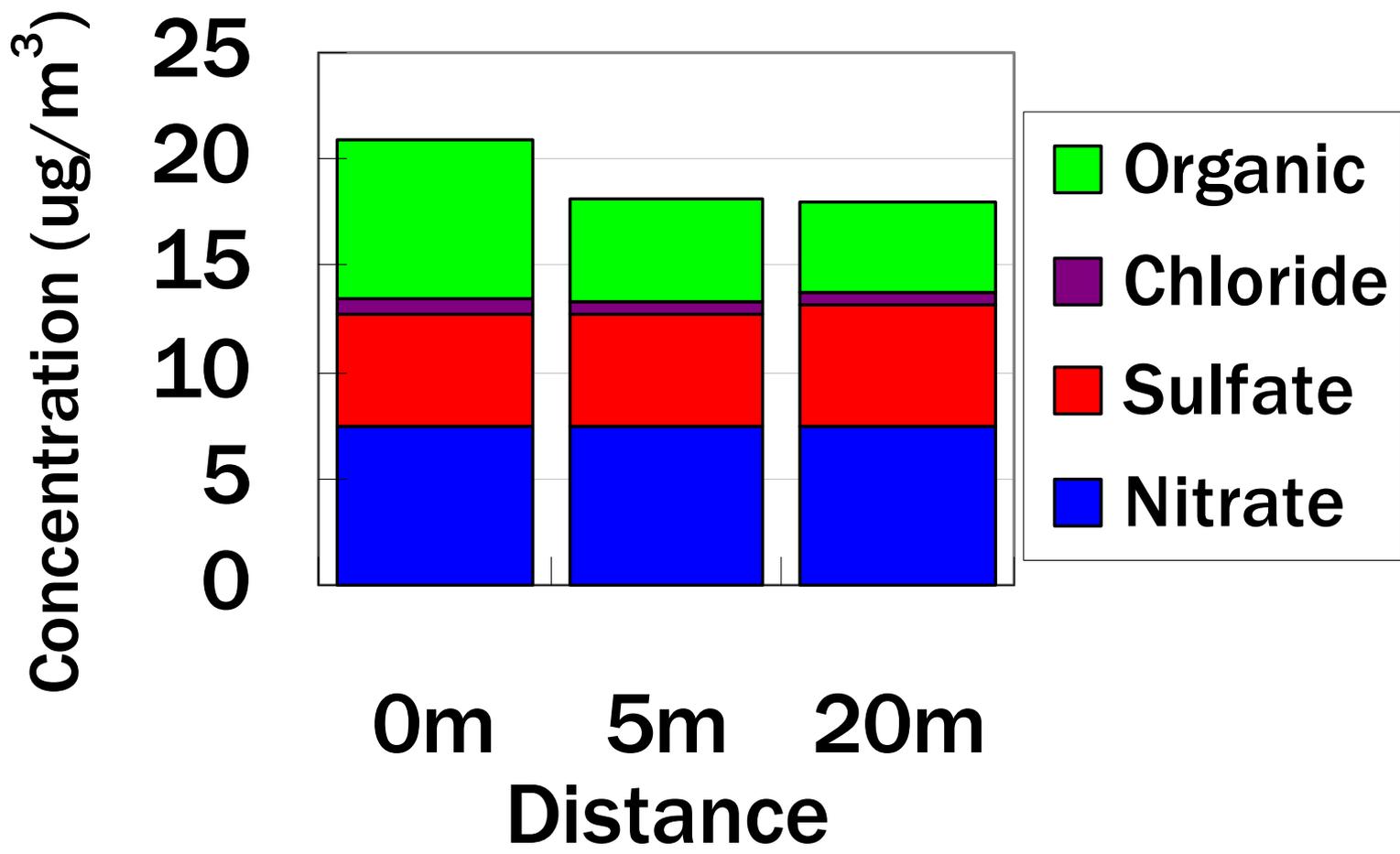
Mass Loadings



Average at each sampling point

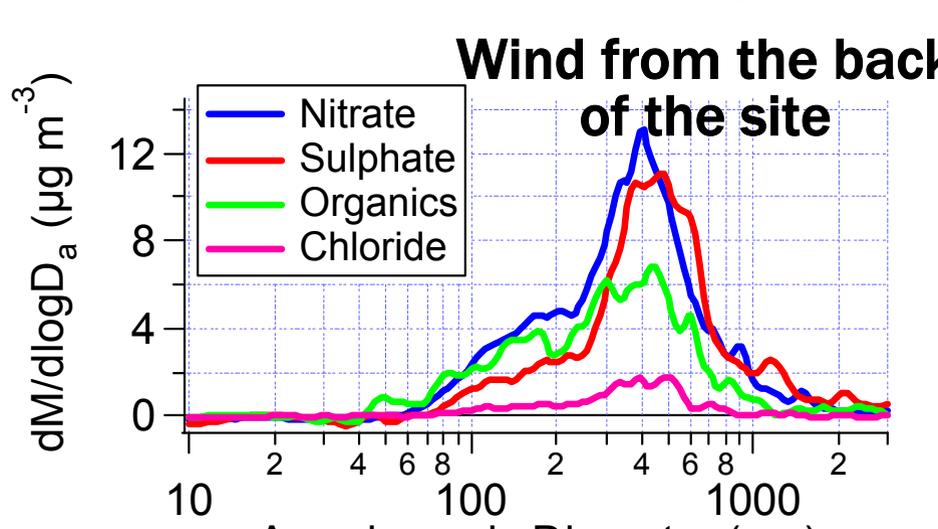
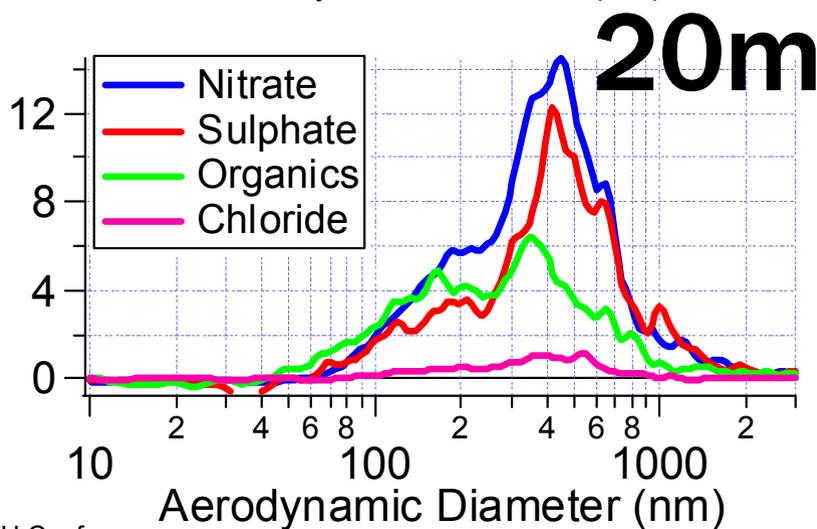
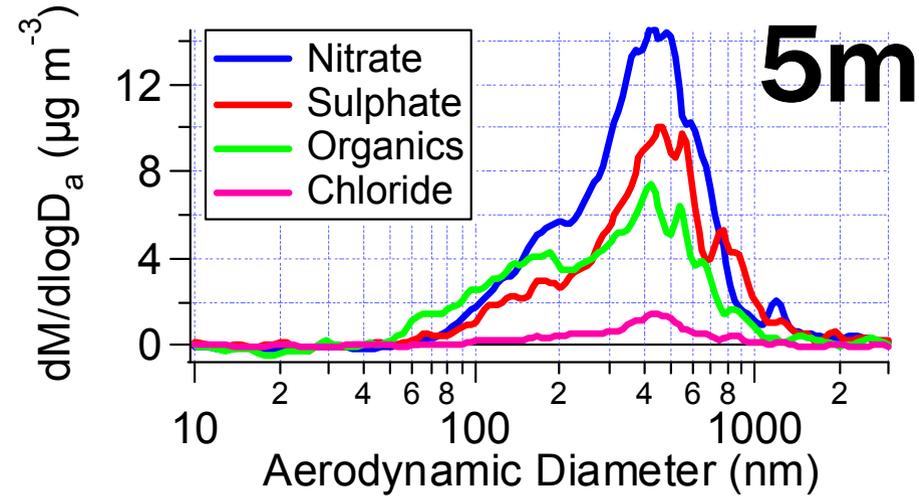
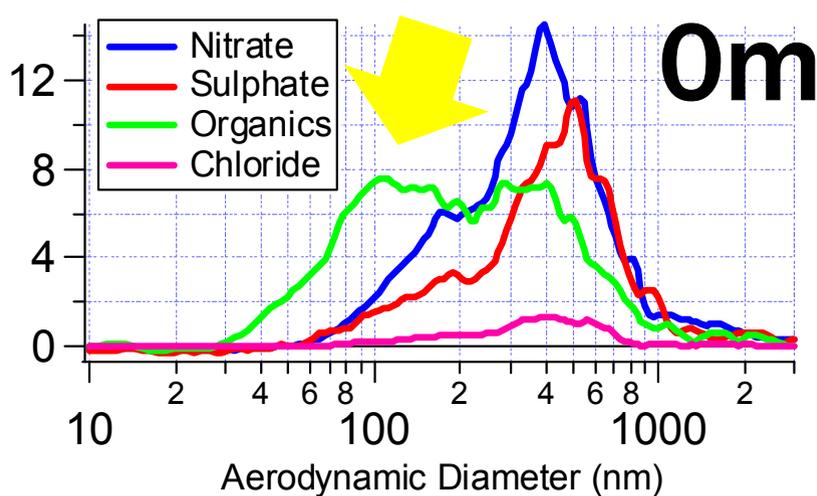
Particle Chemical Component at each Sampling Point

At 0m-point, ratio of Organic Compound is larger than that of the other species.



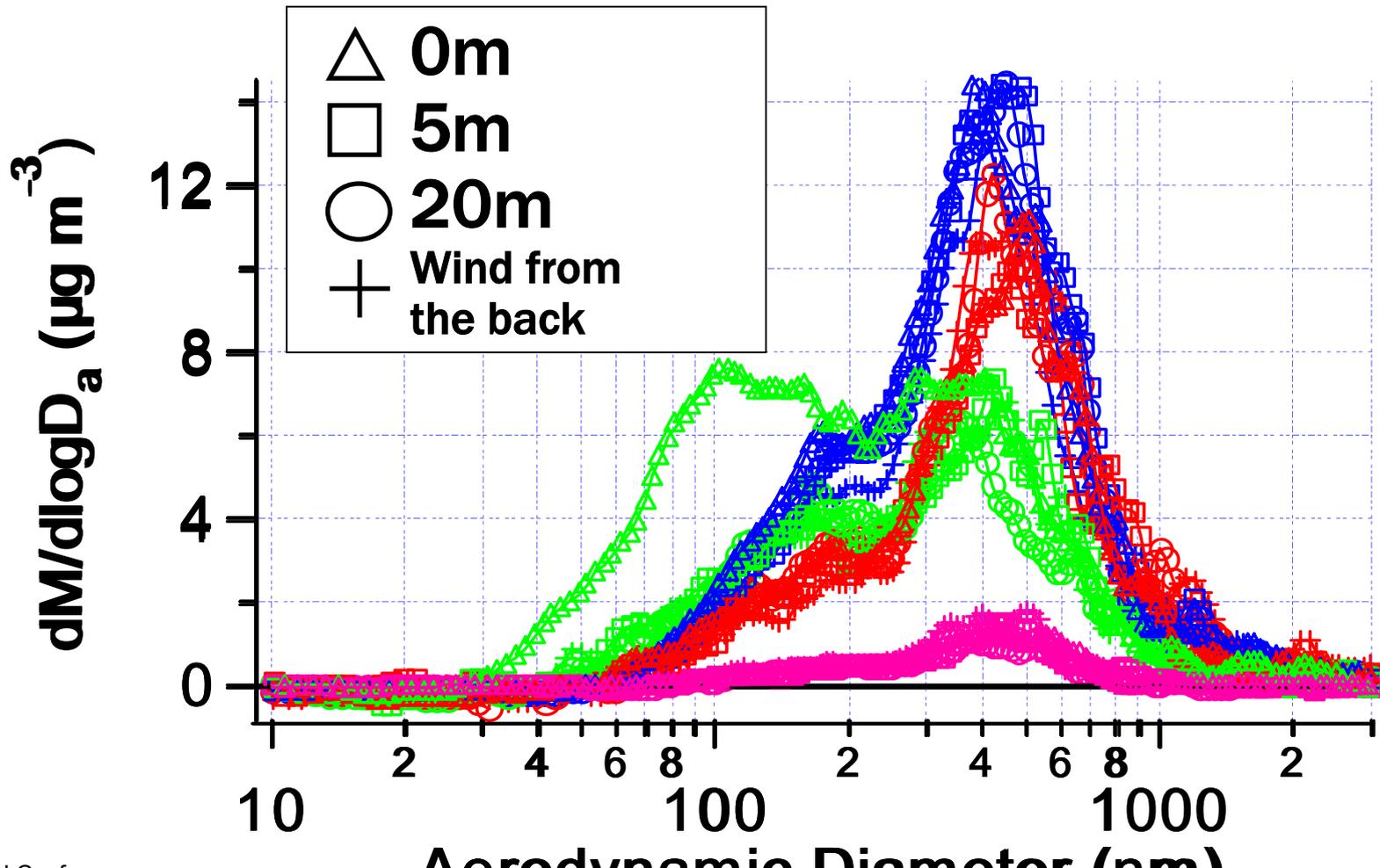
Particle Size Distributions by Chemical Component

Distribution pattern of Organic Compound alone varies with distance from the road.



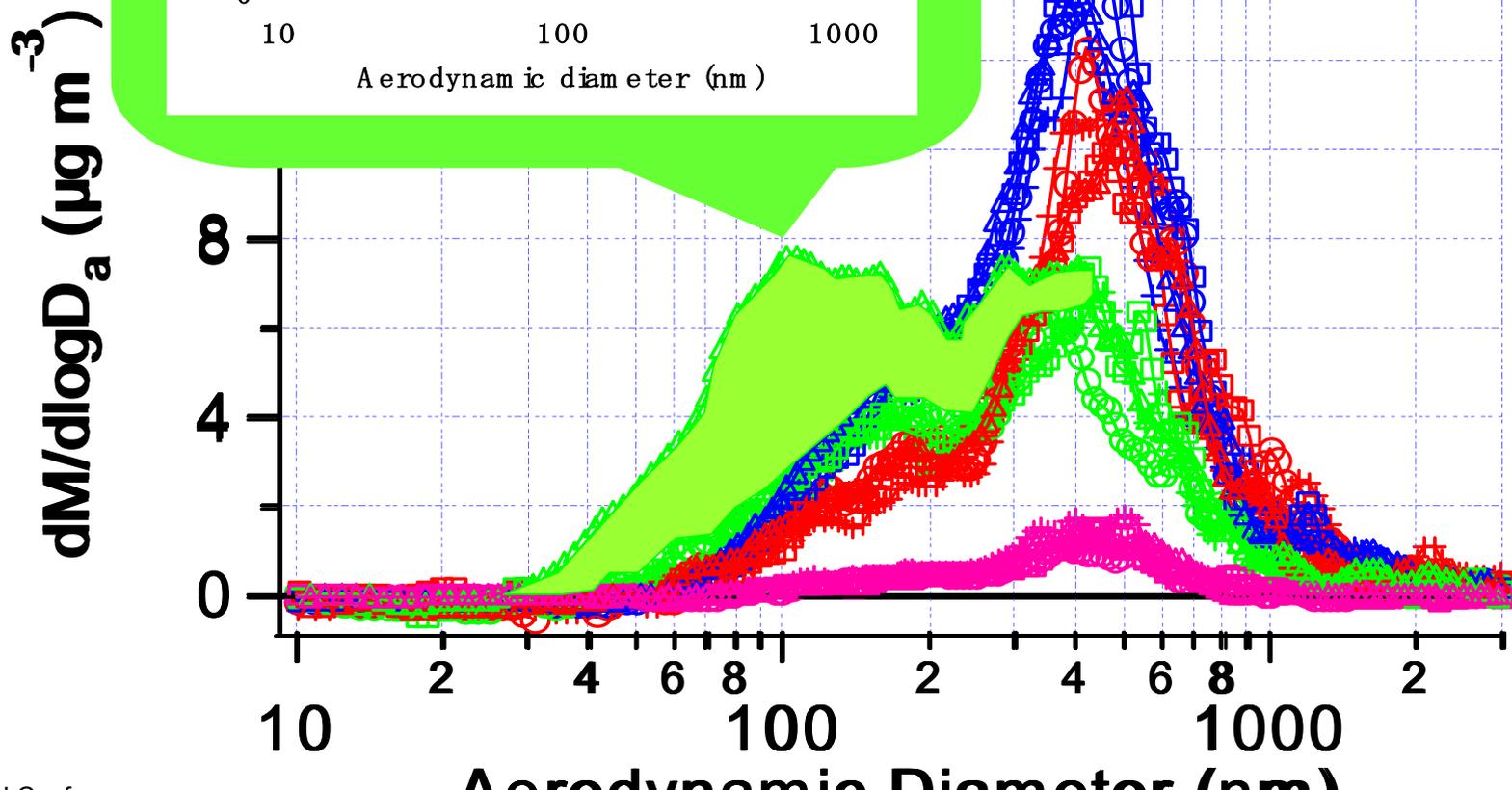
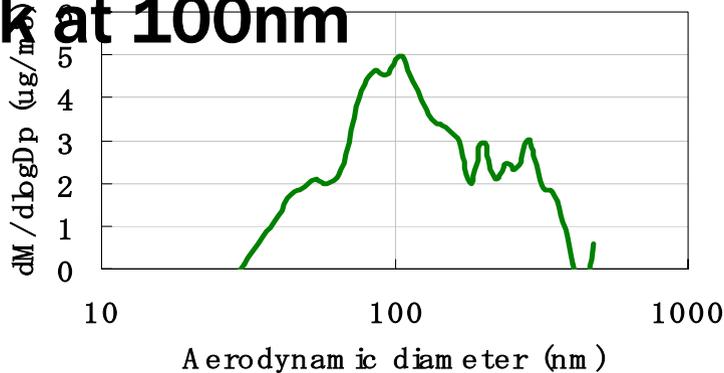
Particle Size Distributions by Distance

Inorganic chemicals and larger mode of organics show no difference in concentrations.

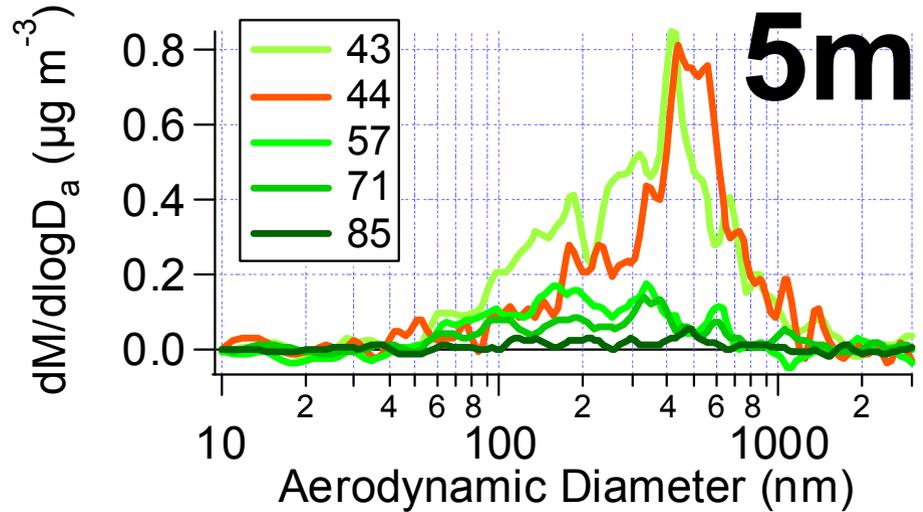
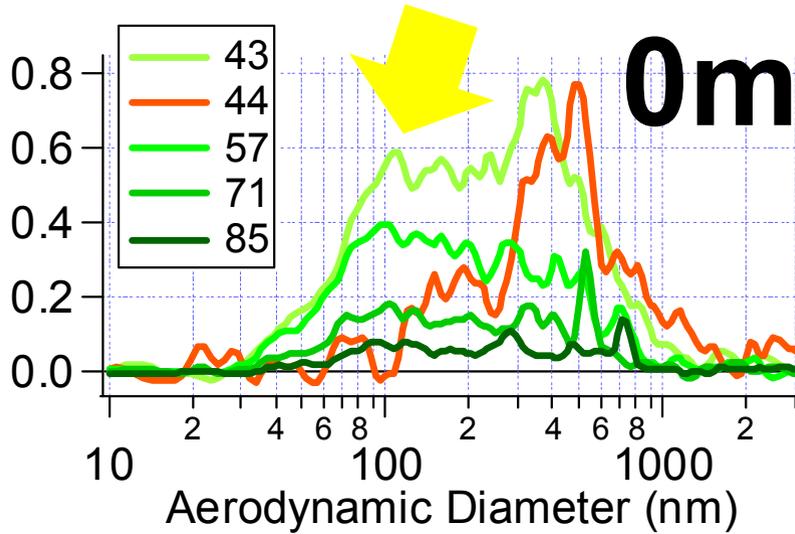


Particle size distributions for components

Effect of the road on Organic Compound:
Peak at 100nm



Particle Size Distribution by Sampling Point (m/z)



Smaller mode (100nm):
non-Oxygenated organics

Changes concentrations with distance from the road.

Larger mode(400nm):
Oxygenated organics

43: $C_3H_7^+$, $C_2H_3O^+$

44: CO_2^+

57: $C_4H_9^+$

71: $C_5H_{11}^+$

85: $C_6H_{13}^+$

Summary

Findings obtained through field observations using AMS

Organic compound concentrations of particles 100nm in diameter show a strong relationship with the distance from the Road.

Main chemical component of particles 100nm in diameter at roadside is suggested Non-oxygenated hydrocarbons.