In-Situ Mass Spectrometric Analysis of Diesel Exhaust Particles

U. Kirchner, V. Scheer, and R. Vogt

Ford Forschungszentrum Aachen GmbH, Süsterfeldstraße 200, D-52072 Aachen, Germany

J. Schneider, N. Hock, S. Weimer, and S. Borrmann

Max Planck Institute for Chemistry, Cloud Physics and Chemistry Department, D-55020 Mainz, Germany

Abstract

Size-resolved measurements of the chemical composition of the volatile and semi-volatile fraction of diesel exhaust particles were performed using the Aerosol Mass Spectrometer (AMS, developed by Aerodyne Inc.). The instrument can be operated in two modes: The bulk analysis mode which is used for total chemical composition measurement, and the time-of-flight mode, in which the size selective mass loadings of individual species can be measured (slide 3). A diesel car with a standard oxidation catalyst was used on a chassis dynamometer (slides 4 & 5). At low power settings, the mass distribution peaks at 40 nm aerodynamic diameter and the composition is dominated by organic species. At high load (45 kW), corresponding to an uphill slope of 6% at 120 km/h, the maximum of the mass distribution shifts to about 100 nm and agrees very well with the mobility diameter measured by an SMPS system simultaneously (slides 6 - 8). The composition is dominated by sulfate, which is most likely due to the conversion of SO_2 into SO_3 inside the oxidation catalyst. The SO_3 reacts fast to H_2SO_4 which nucleates or condenses on pre-existing particles.

Comments to the presentation

With increasing engine load at high speed, e.g. 120 km/h, a steadily rising mode of nucleation particles was observed on a chassis dynamometer (slide 7). These particles consist mainly of sulfate, which was rising from 5 µg m^{-3} at 6 kW load to 160 µg m^{-3} at 40 kW, whereas a simultaneously appearing organics mode was smaller and nearly constant at 10-20 µg m^{-3} (slide 8). This leads to an increasing sulfate/organics ratio (slide 9).

A significant mode of 80 - 100 nm particles (mass size distribution) consisting of organics was observed during measurements in ambient air close to the German Autobahn A4 (slides

10-12). In control measurements at a rural background site these particles were not observed, the levels of sulfate, nitrate, ammonium and organics > 300 nm aerodynamic diameter were similar at the Autobahn and the background site (slide 12).

To further investigate this difference real world emissions were measured in individual car chasing experiments, where dilution of exhaust is different as compared to a chassis dynamometer (slide 13). Again nucleation particles were consisting of sulfate and were observed only when 360 ppm sulfur fuel was used and the car was driven at high speed, i.e. high engine load (slide 14). No nucleation particles appeared with low engine load, e.g. 50 km/h, or with low sulfur fuel (slides 14 & 15). Therefore, the origin of nucleation mode particles, which consist of organic material and are observed in the vicinity of busy roads such as an Autobahn is still unclear. Heavy duty diesel trucks seem to be probable emitters of organic nucleation particles.

Conclusions and summary

- AMS confirms chemical bulk analysis: ratio of sulfate / organics in particles increases with engine load.
- Highway experiment showed small organics mode, which is due to traffic.
- Chasing experiment with passenger diesel vehicle showed small sulfate nucleation mode in correspondence with chassis dynamometer tests.
- Oxidation catalyst leads to efficient conversion of organics and some sulfate formation.
- Difference between autobahn and chassis dynamometer / passenger car chasing: Are heavy duty diesel VOF emissions larger than passenger diesel VOF?

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IN-SITU MASS SPECTROMETRIC ANALYSIS OF DIESEL EXHAUST PARTICLES

U. KIRCHNER[2], V. SCHEER[2] and R. VOGT[2]
J. SCHNEIDER[1], N. HOCK[1], S. WEIMER[1], S. BORRMANN[1]

[1]Max Planck Institute for Chemistry, Cloud Physics and Chemistry Department, D-55020 Mainz, Germany

[2]Ford Research Center Aachen, Environmental Science, D-52072 Aachen, Germany

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Outline

Introduction

The Aerosol Mass Spectrometer (AMS)

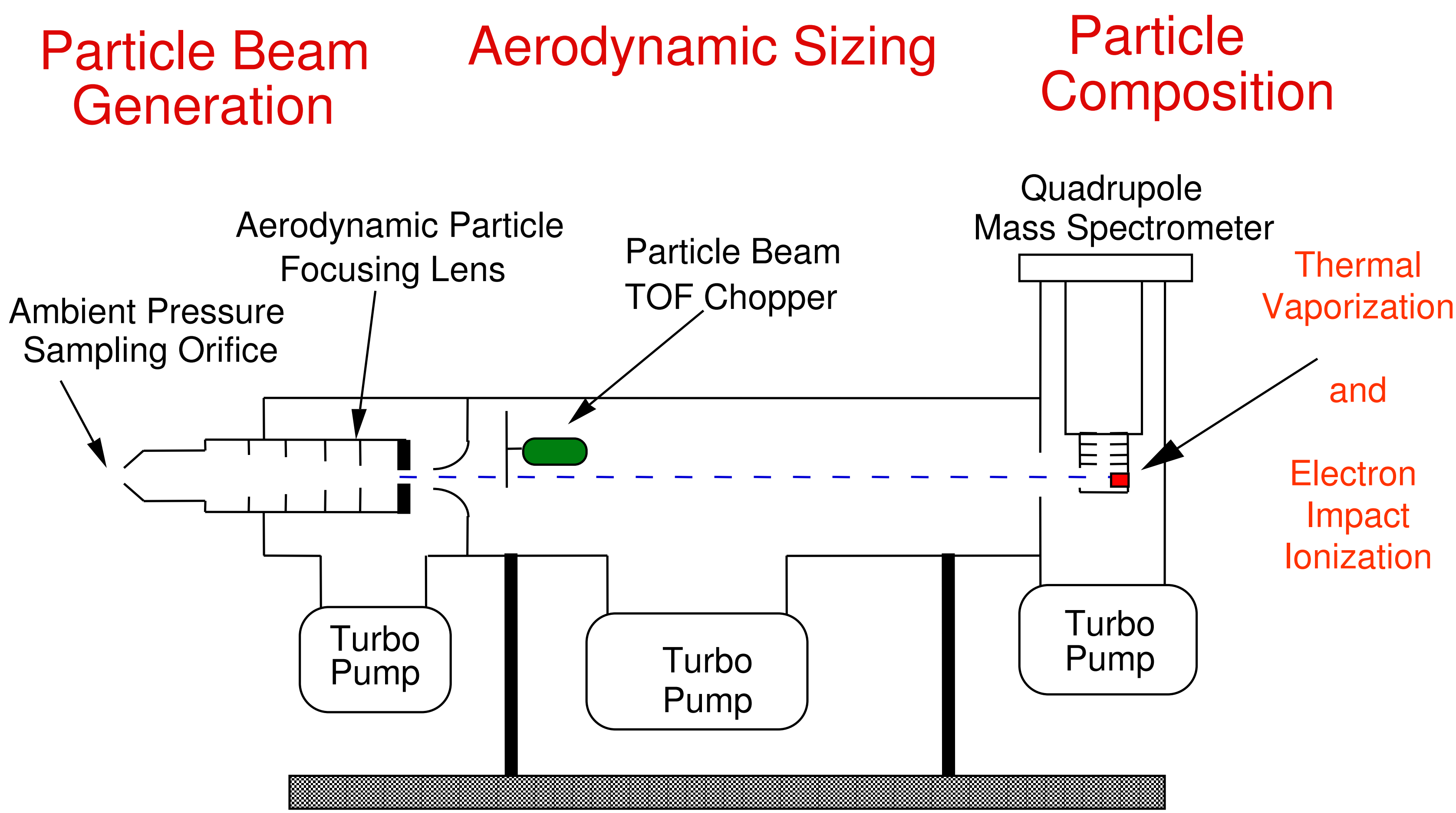
Measurement Results:

- Chassis dynamometer
- Freeway (Autobahn)
- Individual car chase

Discussion

Summary / Conclusions

Aerosol Mass Spectrometer (AMS)



Aerodyne Research, Inc.

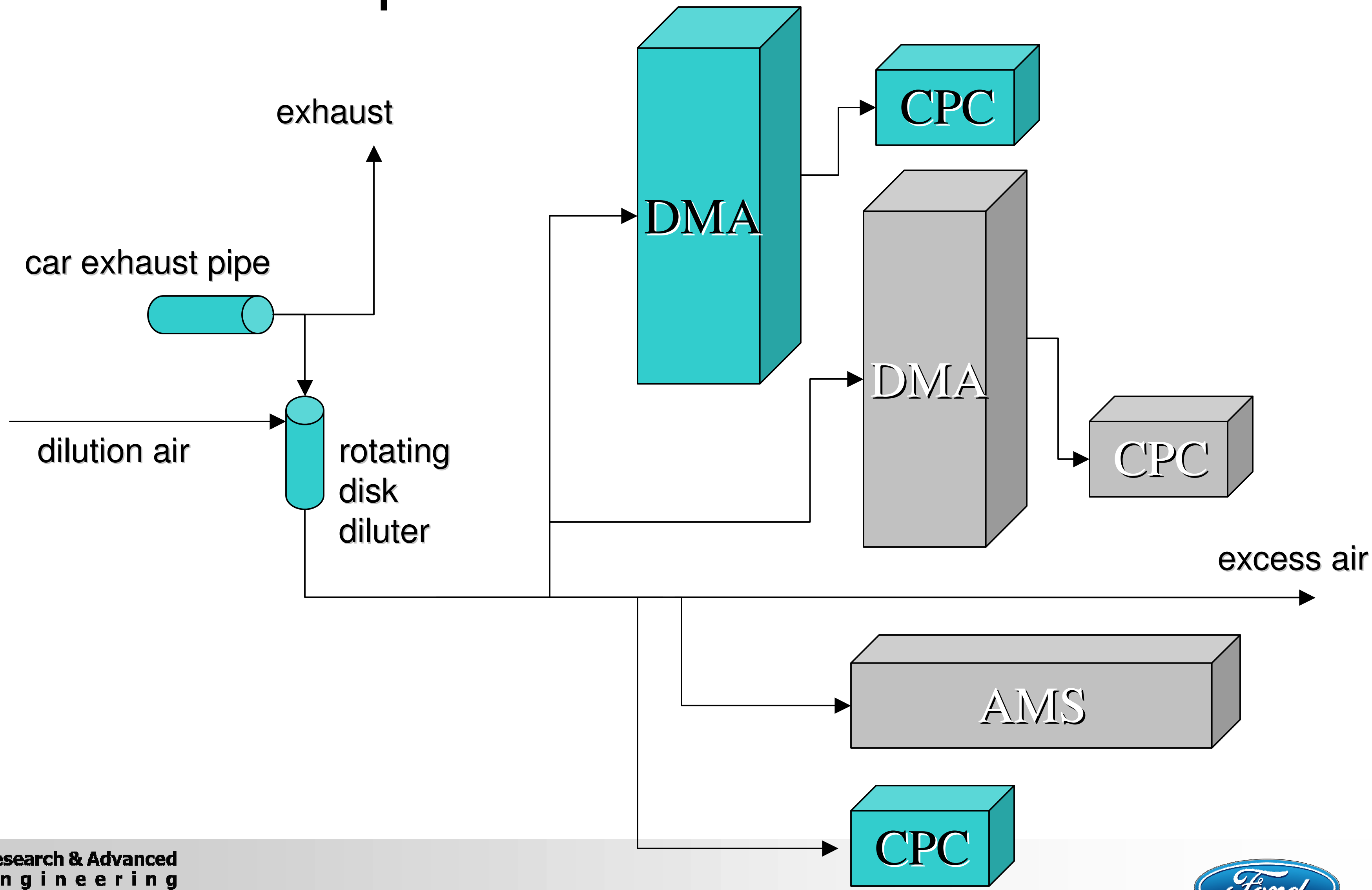
Chassis Dynamometer Measurements

Chassis dynamometer at Ford Research Center Aachen (FFA):

- 48" (1.22 m) diameter role
- Max. 186 kW break power
- Max. speed 200 km h^{-1}
- Loss compensation

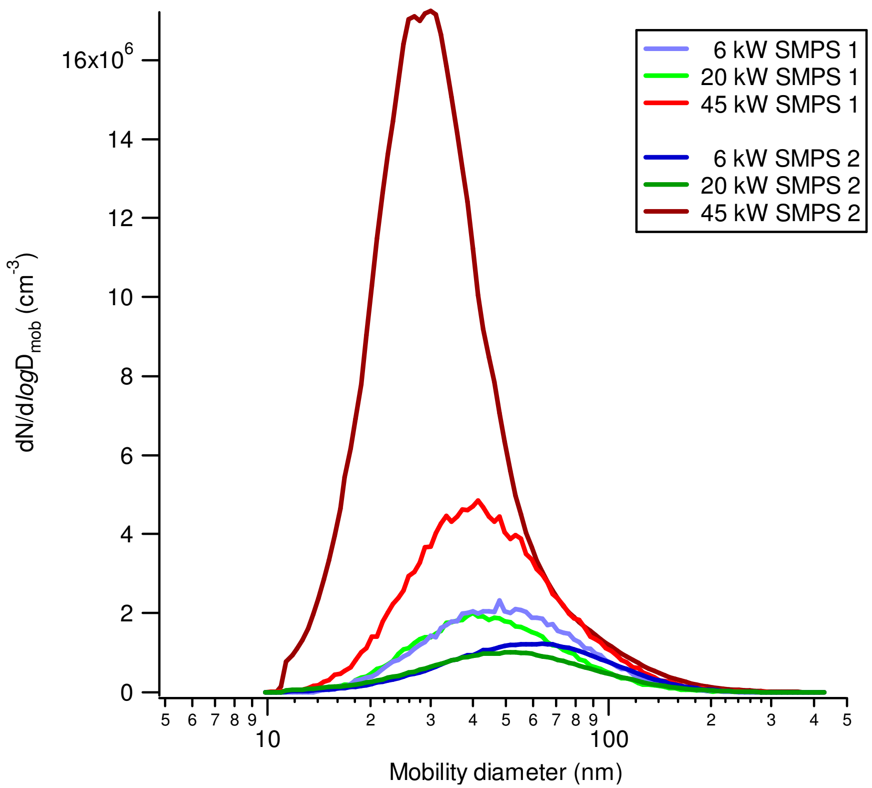
- Passenger diesel car (euro III), 1.8 L, 66 kW (90 hp),
- 50 ppm / 350 ppm S fuel.
- Turbo charger, direct injection, exhaust gas recirculation, oxidation catalyst.

Setup

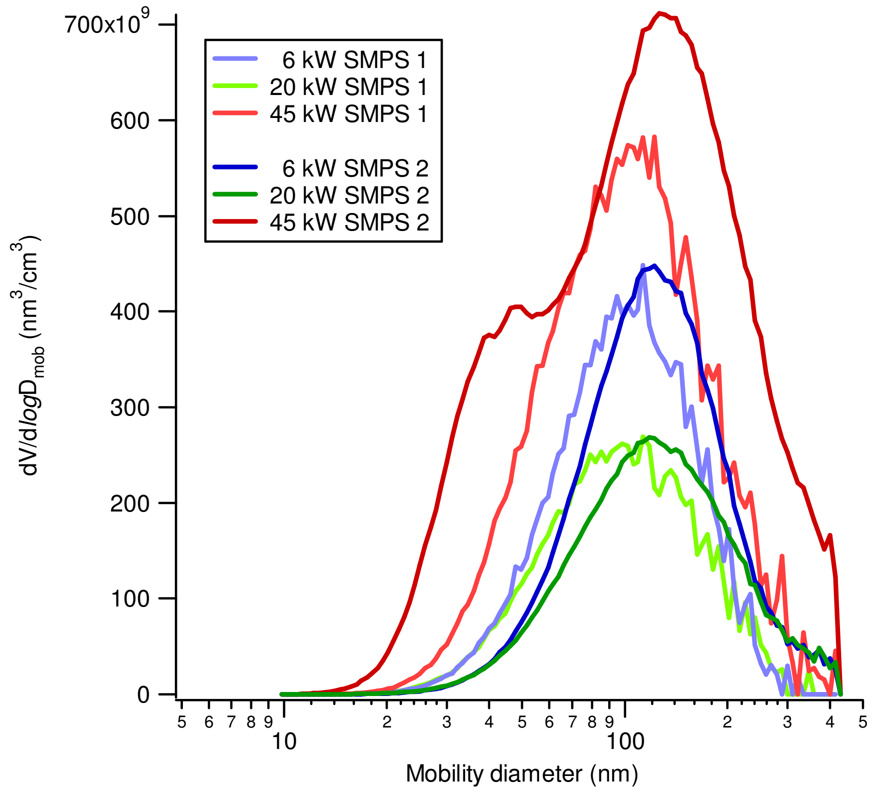

exhaust
car exhaust pipe
dilution air
rotating
disk
diluter
DMA
CPC
DMA
CPC
excess air
AMS
CPC

const. speed 120 km/h:

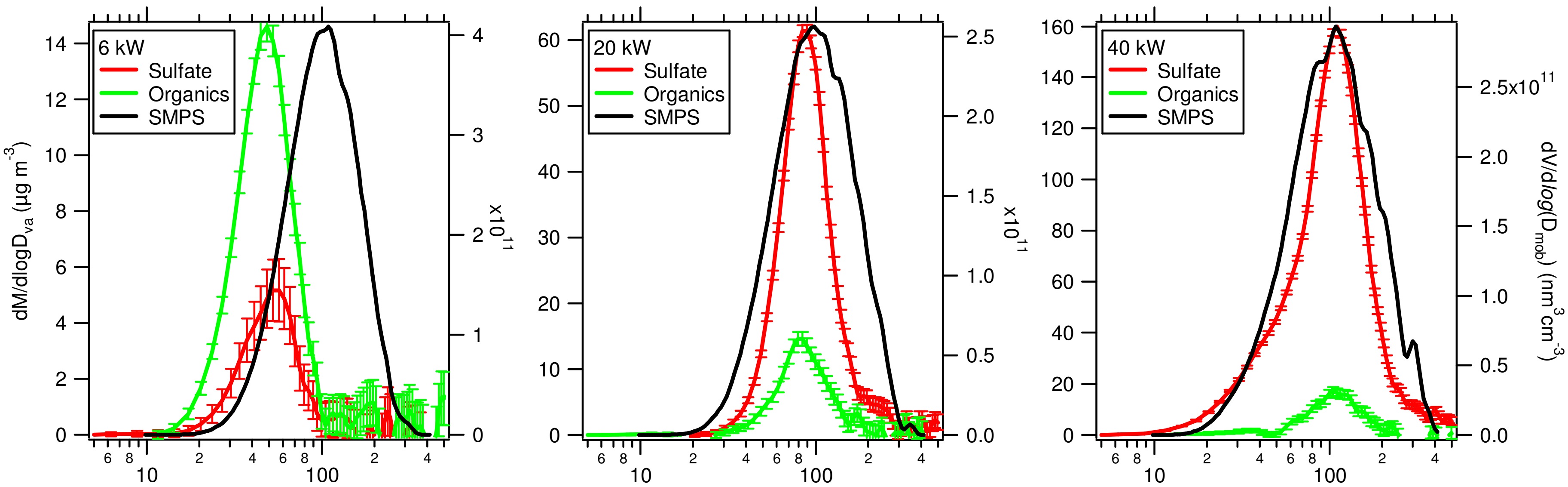
Number distribution



Volume distribution



Size distributions at different engine loads



low load: more organics, aerodynamic diameter smaller than mobility diam. => density < 1.

high load: more sulfate, density ≥ 1, larger particles.

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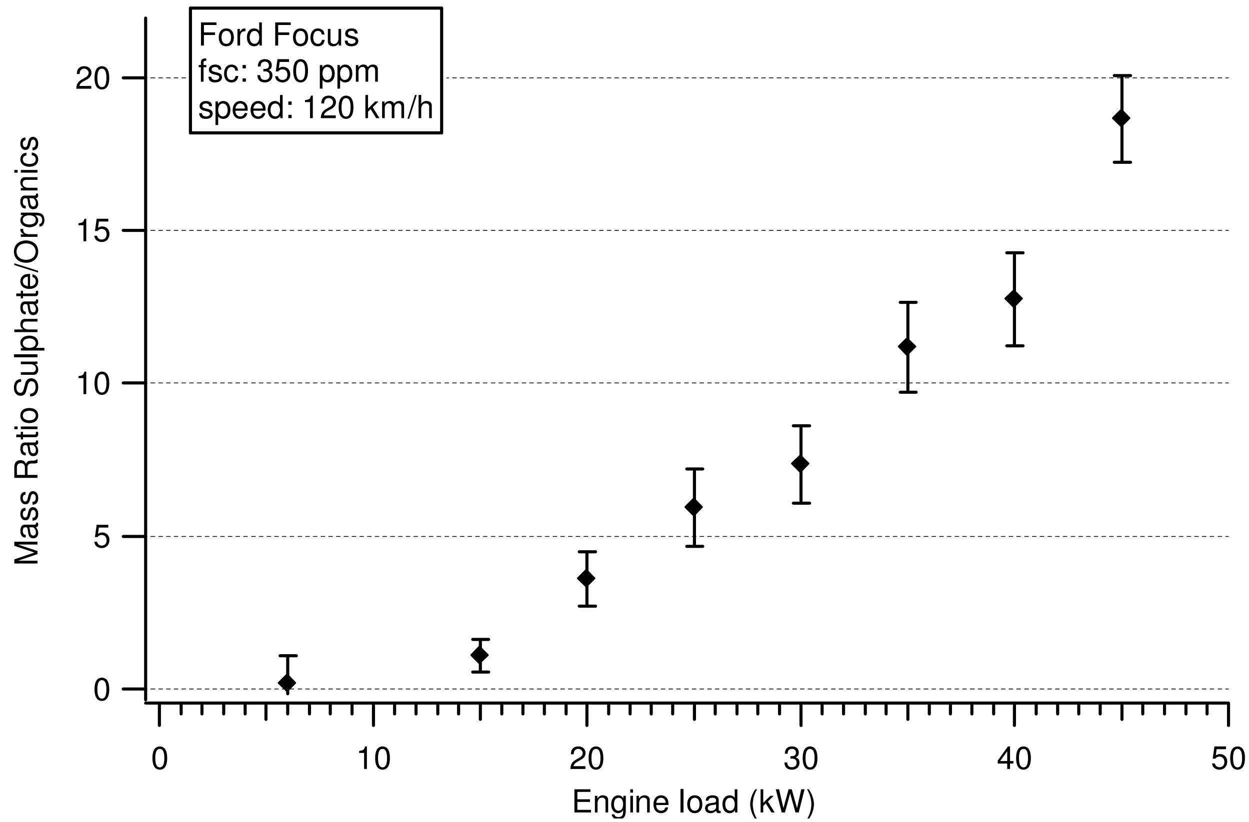
Mass ratio of sulfate to organics vs. engine load



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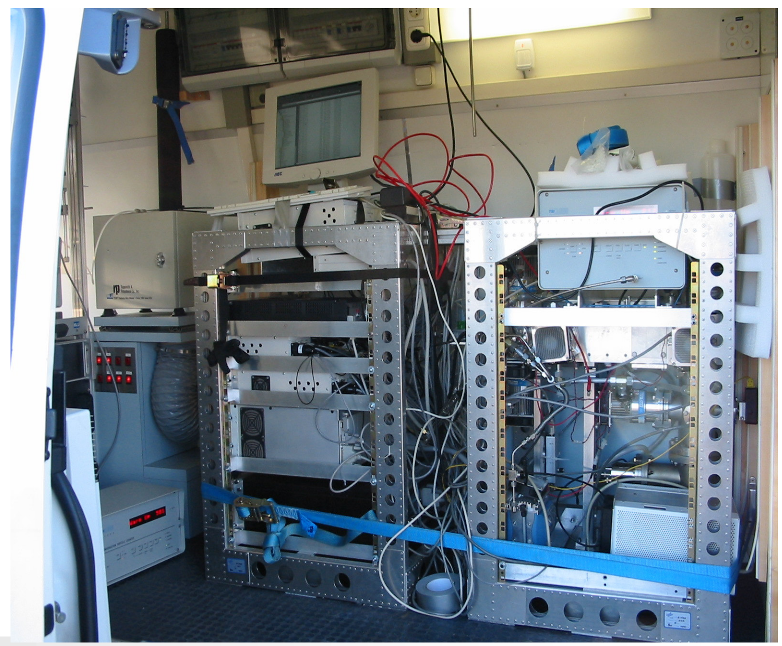
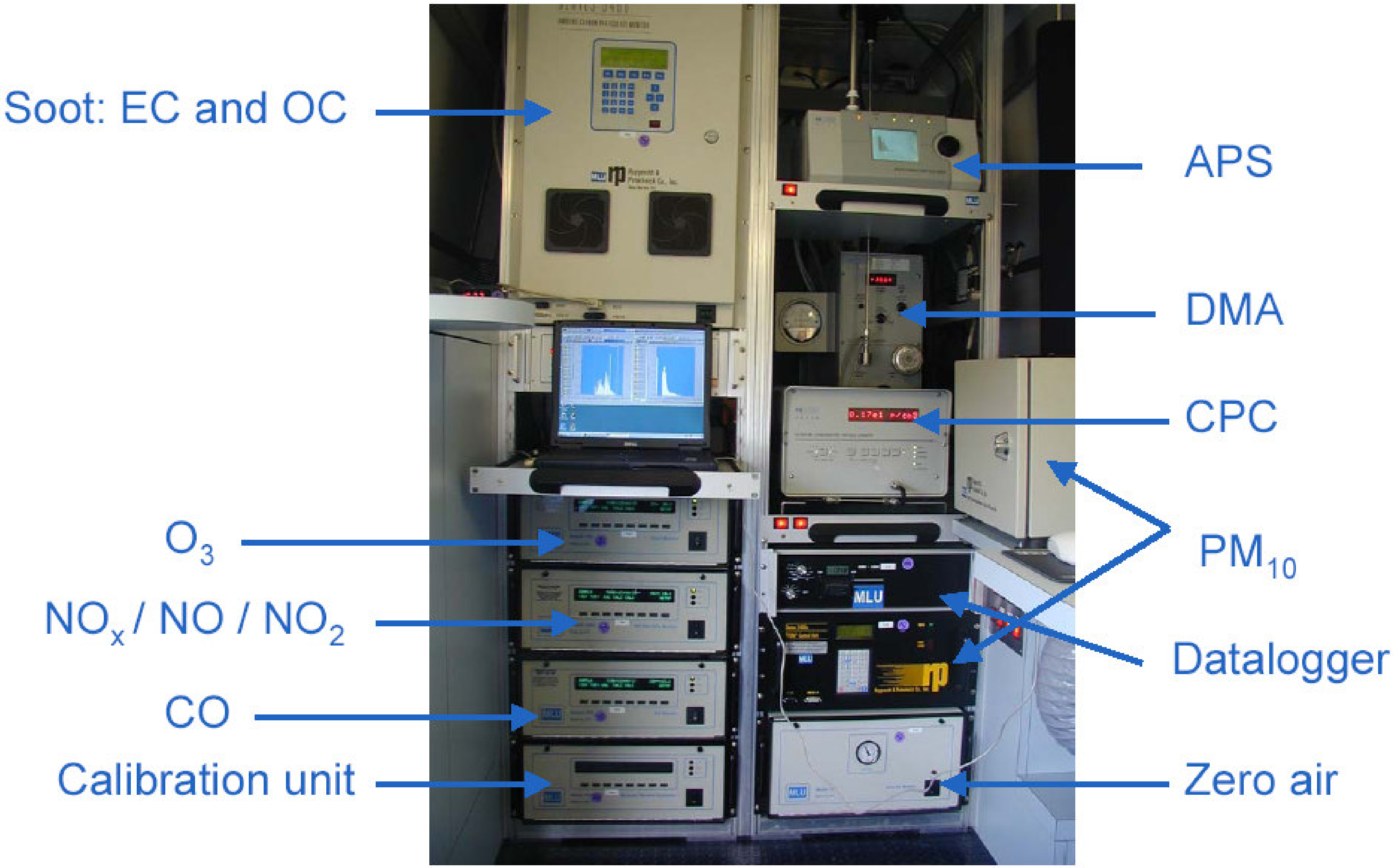
Motorway and rural background Experiment

(A4, near Aachen, Germany)



Instrumentation of Ford Mobile Laboratory



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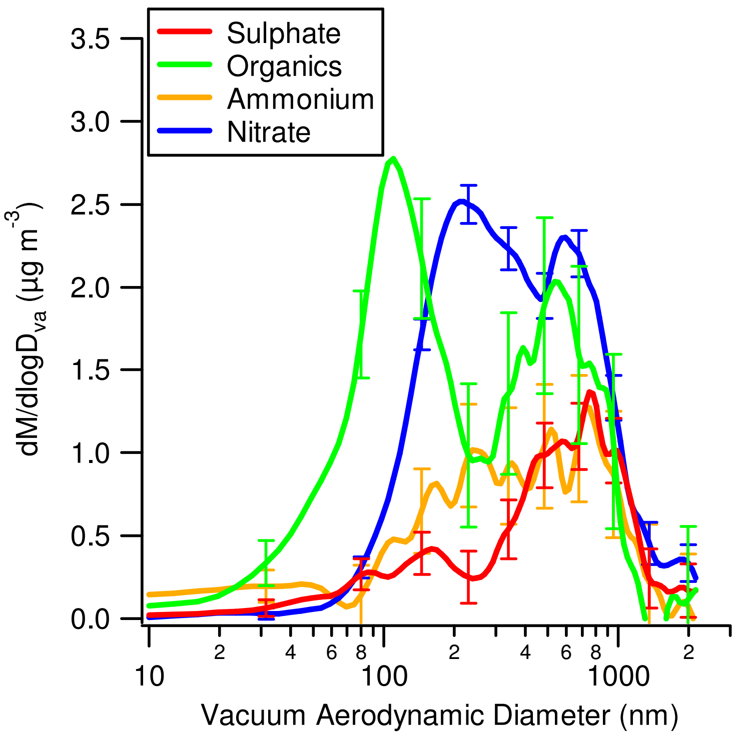
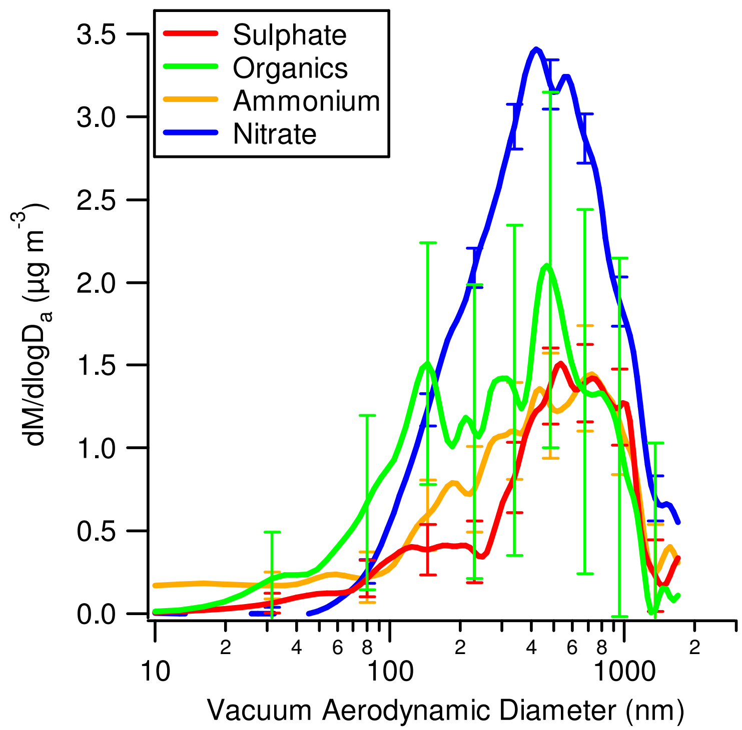
Mass distributions

near highway



rural background site



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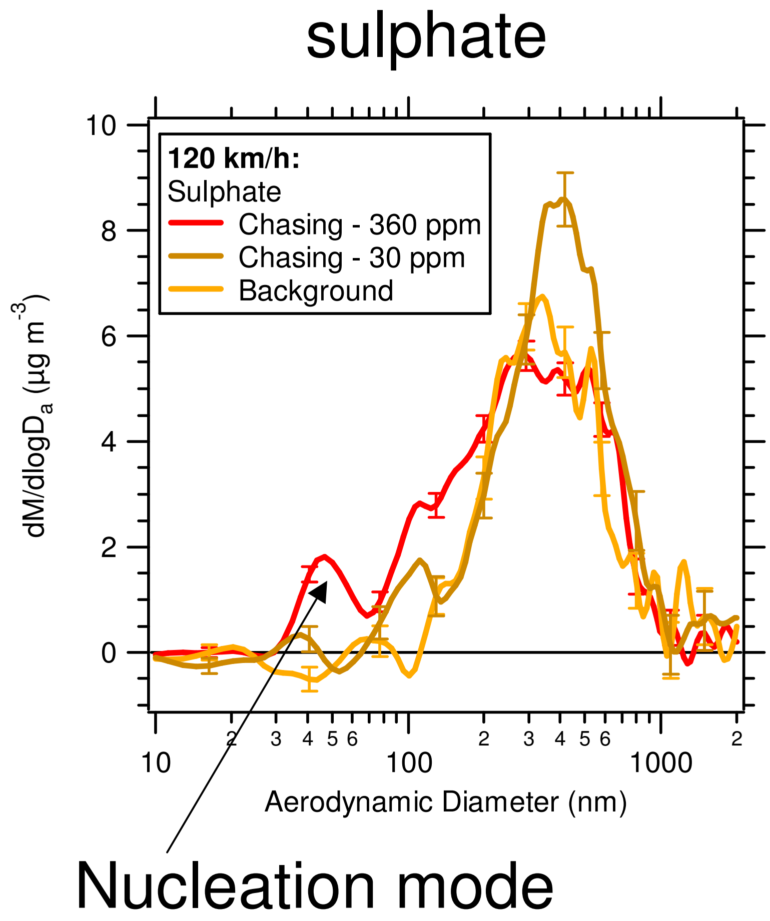
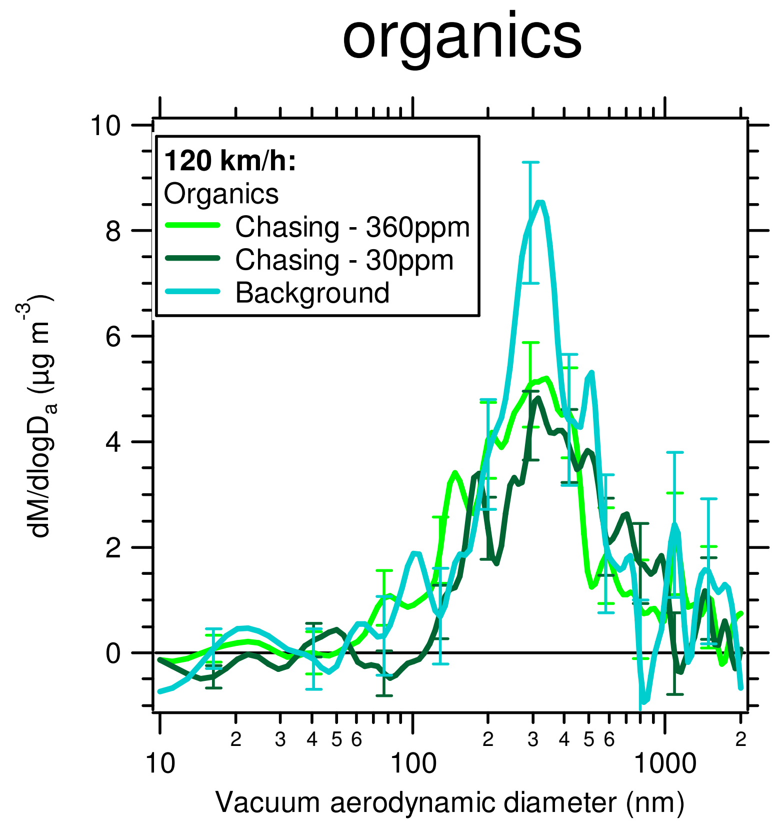
Car chasing experiment

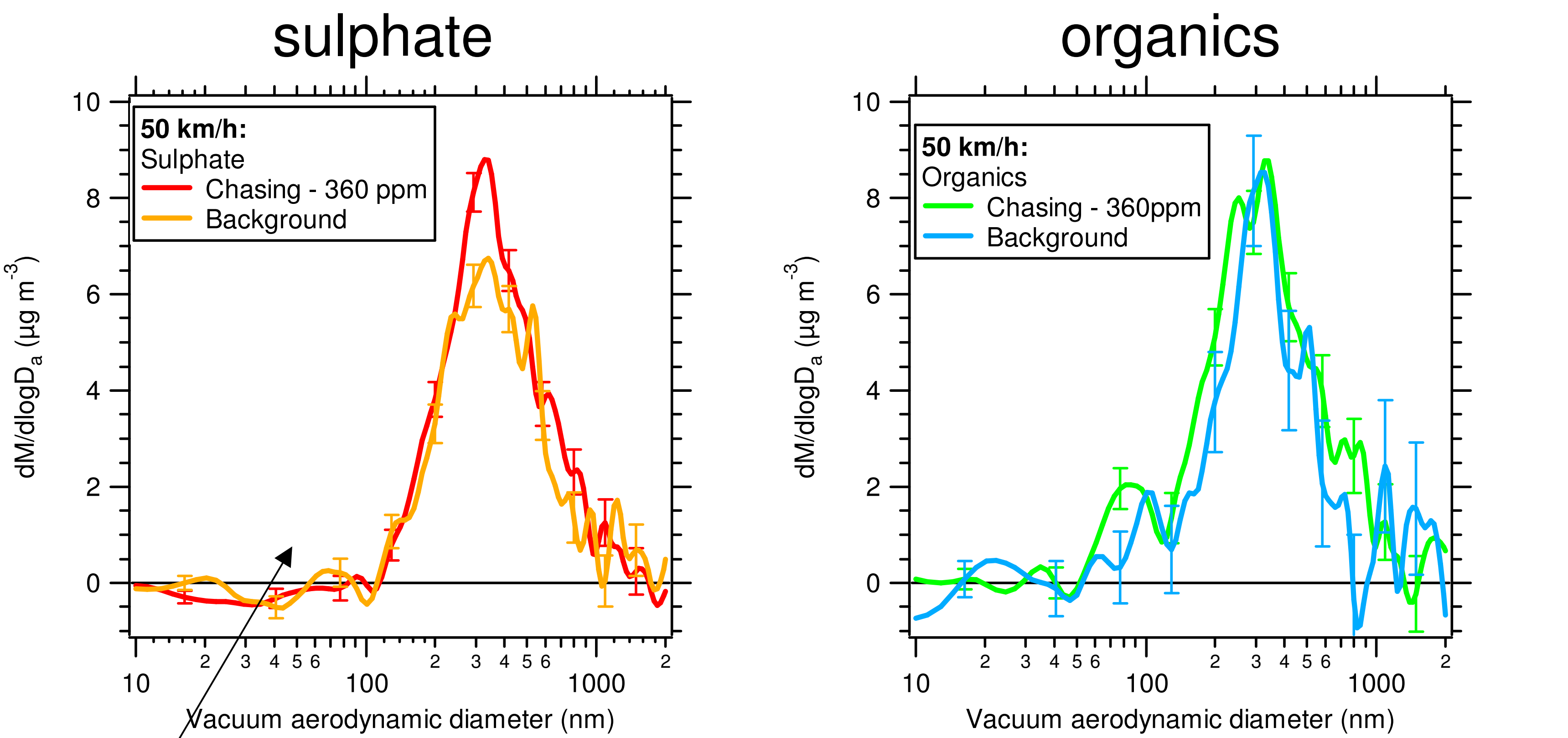
- Diesel passenger car, same as on the dyno
- Fuel sulphur content: 30 and 360 ppm
- speeds 50, 100, and 120 km/h
- Distance: 10 m

120 km/h with different fuel sulfur content





50 km/h with 360 ppm sulfur fuel



No nucleation mode

Summary

- AMS confirmes chemical bulk analysis: ratio sulfate / organics of particles increases with engine load.
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