Title: **The combustion-generated volatile "nanodroplets": What control their formation and concentration?**

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Abstract: The combustion-emitted volatile "nanodroplets" or nanoparticles (NPs) have received increasing attention due to their potential health effects. A mechanism of vehicular NP formation involving binary nucleation of H_2SO_4-H_2O followed by condensation growth of hydrocarbon has been suggested in the literature. We propose that ions generated in the combustor may also play an important role in the NP formation as the binary homogeneous nucleation of H_2SO_4-H_2O fails to explain many observed NP properties. Using an advanced aerosol dynamics model which simulates a size-resolved multi-component aerosol system involving both neutral and charged particles, we have investigated the key parameters controlling the formation of vehicular NPs. The predicted NP properties based on our ion-mediated nucleation of H_2SO_4-H_2O consistently explain the NP measurements in terms of total concentrations and their sensitivity to fuel sulfur contents, on-road vehicle speeds, and soot concentrations. Our study indicates that total number of NPs formed is very sensitive to ion concentrations. If the role of ions in vehicular NP formation is confirmed, new technique could be designed to reduce NP emission. The key uncertainty in our study is the concentration of ions in the engine exhaust. Some preliminary measurements of ions in motor engine exhaust will be presented.

Introduction

Present engine particulate emission standards are based on mass. Recently it has been pointed out that it is not sufficient to study only the particulate mass. The main concern is that, while nanoparticles (NPs, diameter ≤ 50 nm) contribute a small fraction to the mass concentration of the ambient aerosol, they may contribute disproportionately to its toxicity because of their high number concentration and surface area, high deposition efficiency in the pulmonary region, and high propensity to penetrate the epithelium. In view of the potential strong adverse health effects associated with NPs, future standards might be imposed on NP emissions and NP emissions from gasoline engines may also become a concern. Effective and least costly means of NP emission reduction must be based on a firm physical understanding of the formation mechanisms of NPs in vehicle exhaust.

Measurements of NPs in motor engine exhaust have been made both in the laboratory and in the atmosphere. Most of NPs are formed during exhaust dilution and the measured NP concentrations are very sensitive to dilution and sampling conditions. It has been shown that in motor vehicle engine exhaust only sulfuric acid is likely to become super-saturated enough for homogeneous nucleation during dilution [*Abdul-Khalek et al.,* 2000]. It has been found that the classical H_2SO_4-H_2O binary homogeneous nucleation (BHN) theory was not able to explain several key aspects of the observed properties of ultrafine particles (i.e., total concentrations [*Shi and Harrison*, 1999], sensitivity to Fuel Sulfur Concentrations [*Abdul-Khalek et al.*, 2000]). Other factors that have been observed to affect engine nanoparticle properties include transfer line residence time, on-road vehicle speeds, and soot concentrations.

Recently, *Yu* [2001, 2002] proposed that chemiions generated during fuel combustion might play an important role in the formation of these ultrafine particles. Preliminary study indicates that the chemiion theory can explain the observed dependence of ultrafine particles on some key parameters.

We have studied the key processes and parameters controlling formation and evolution of NPs in vehicle exhaust through model simulations and comparisons with measurements. The detailed aerosol dynamics are simulated with an advanced particle microphysics (APM) model that simulates a size-resolved multi-component aerosol system via a unified collisional mechanism involving both neutral and charged particles down to molecular sizes [Yu and Turco, 2001].

Abdul-Khalek, I. S., D. B. Kittelson, and F. Brear (2000). *SAE Technical Paper Ser. No. 2000-01-0515.*

Shi, J. P., and R. M. Harrison (1999). *Environ. Sci. Technol., 33,* 3730-3736.

Yu, F. and R. P. Turco (2001). *J. Geophys. Res*., 106, 4797- 4814.

Yu, F. (2001). *Geophys. Res. Lett.,* 28, 4191-4194.

Yu, F., (2002). *Geophys. Res. Lett.*, 29(15), 10.1029/2002GL015004.

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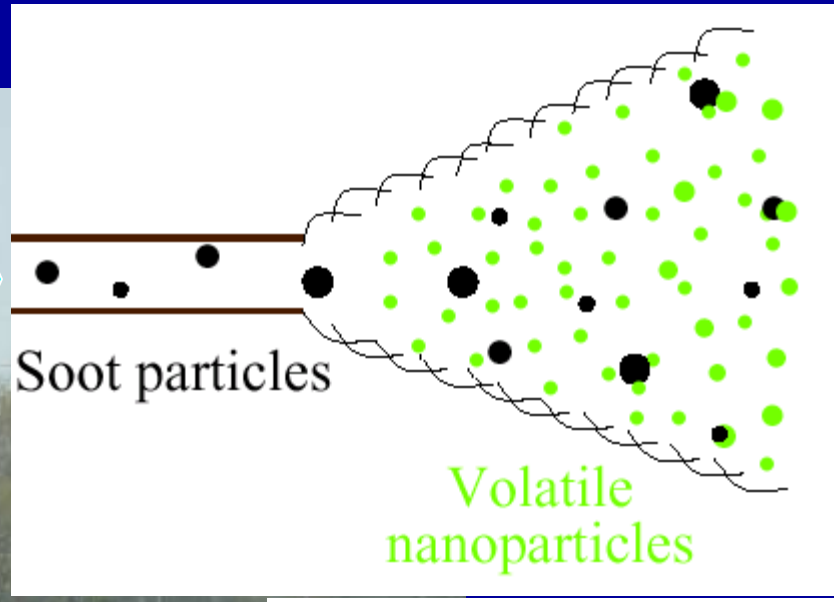
State University of New York at Albany

Funding: US NSF and NYSERDA

Nanoparticle formation mechanism

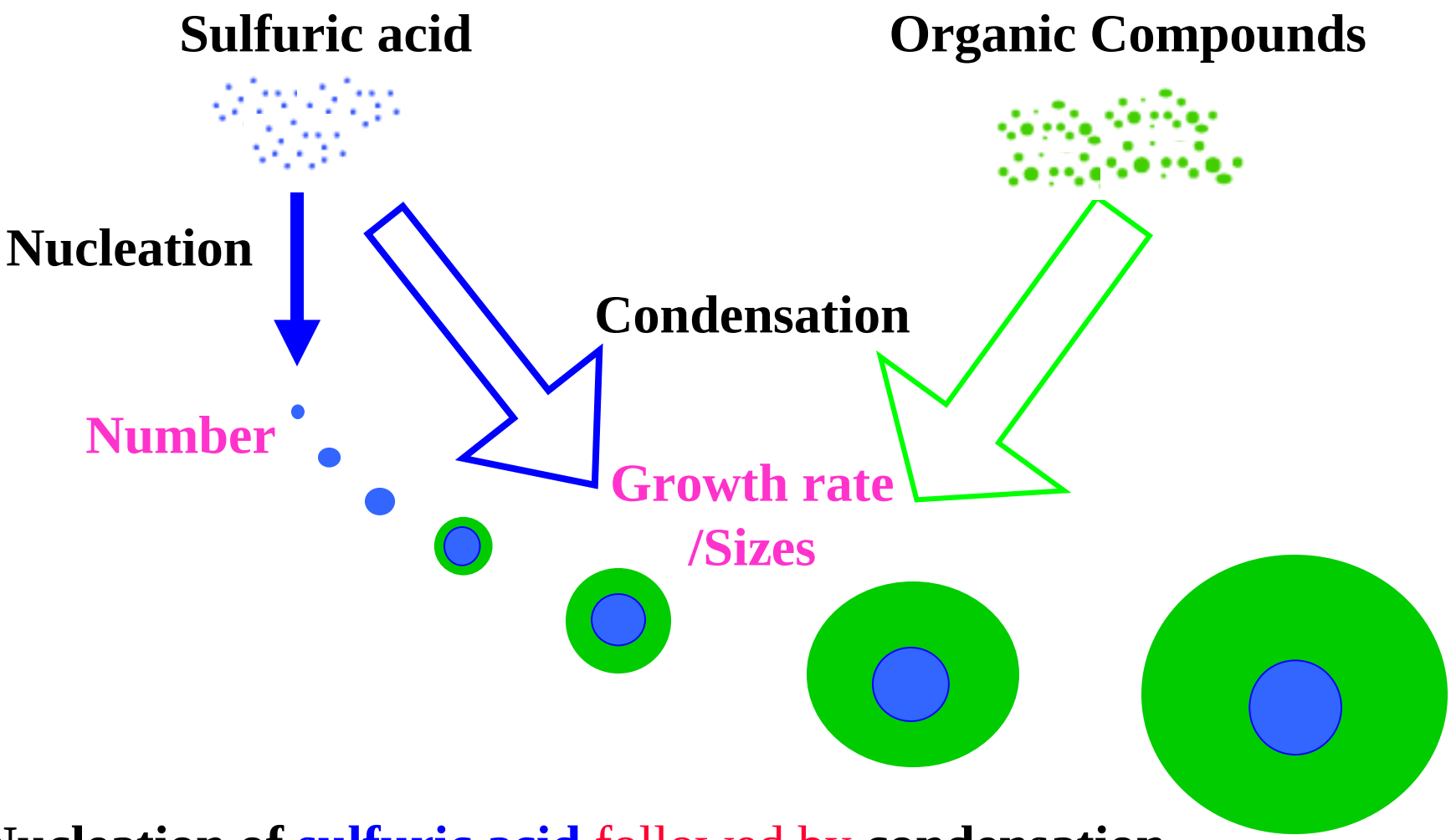


Main compositions:
Sulfuric acid,
Organic compounds

- Only sulfuric acid is likely to become supersaturated enough for homogeneous nucleation during dilution [*Abdul-Khalek et al.*, 2000]

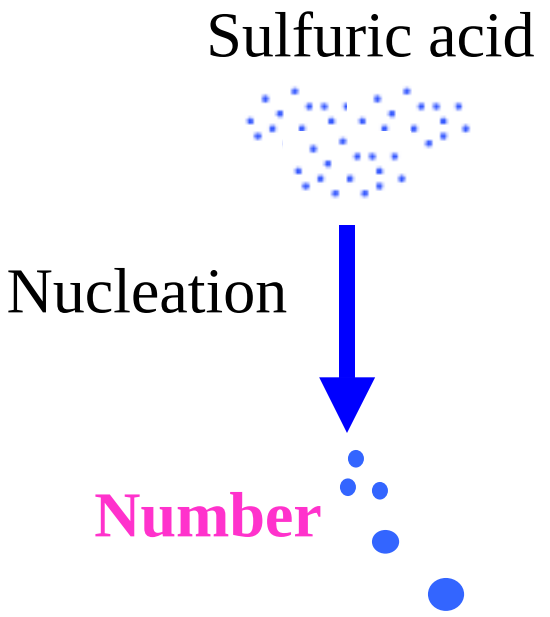
- It is unlikely that organic compounds alone are nucleating [*Tobias et al.*, 2001].

Nanoparticle formation mechanism



Nucleation of sulfuric acid followed by condensation growth of organic compounds [*Shi and Harrison*, 1999; *Abdul-Khalek et al.*, 2000; *Tobias et al.*, 2001].

Nanoparticle formation mechanism

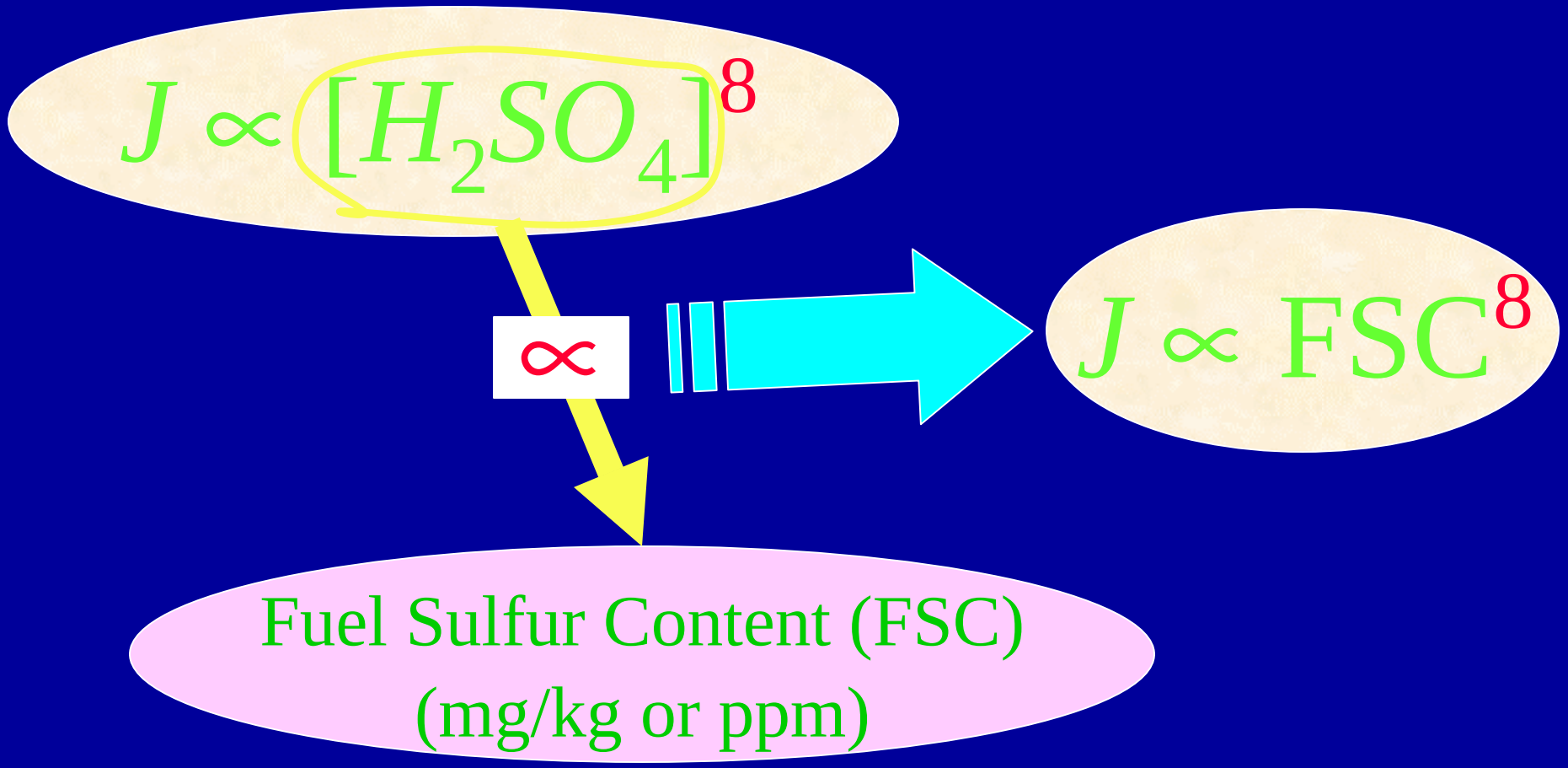


Binary homogeneous nucleation (BHN) theory has been applied to predict nanoparticle formation in engine exhaust [*Shi and Harrison*, 1999; *Abdul-Khalek et al.*, 2000]**.**

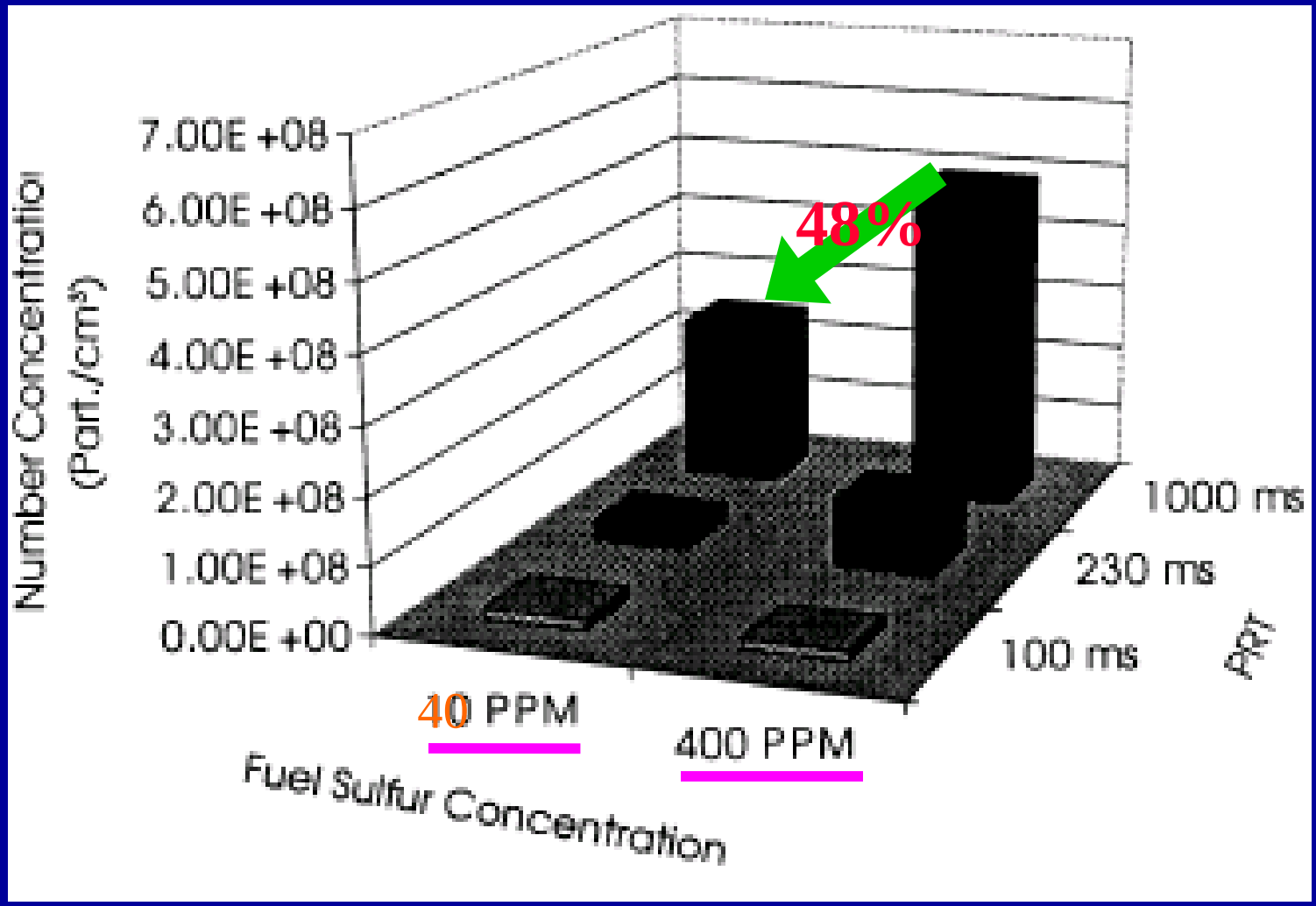
However, as we will show below, BHN theory is not able to explain some important observed NP properties.

Nanoparticle Concentration and FSC

Binary homogeneous nucleation (BHN) theory

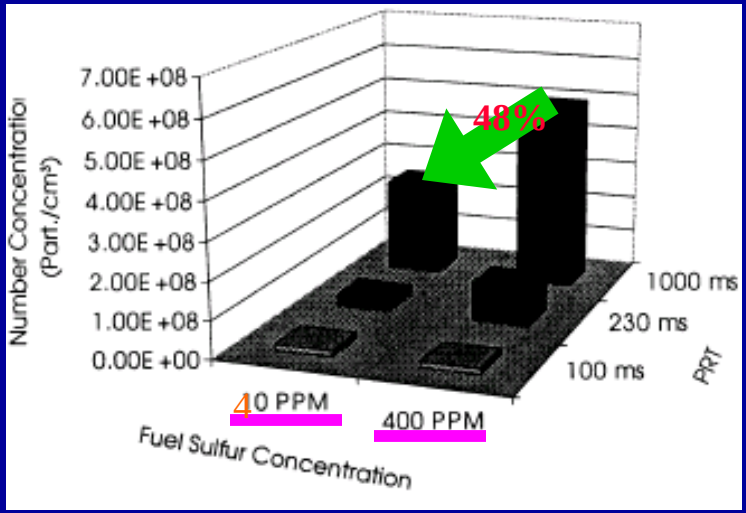


Observations: Influence of fuel sulfur content on number size distributions



From Abdul-Khalek et al., 2001.

Observations: Influence of fuel sulfur content on number size distributions



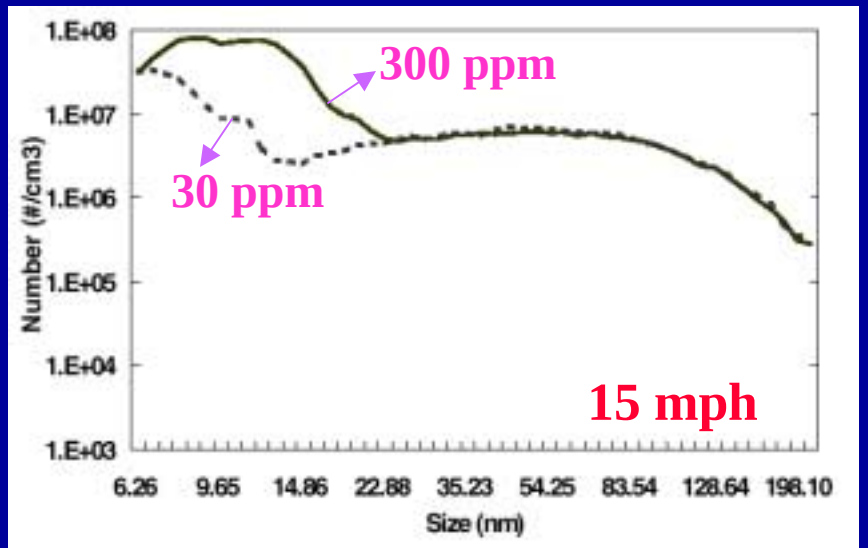
From Abdul-Khalek et al., 2001.

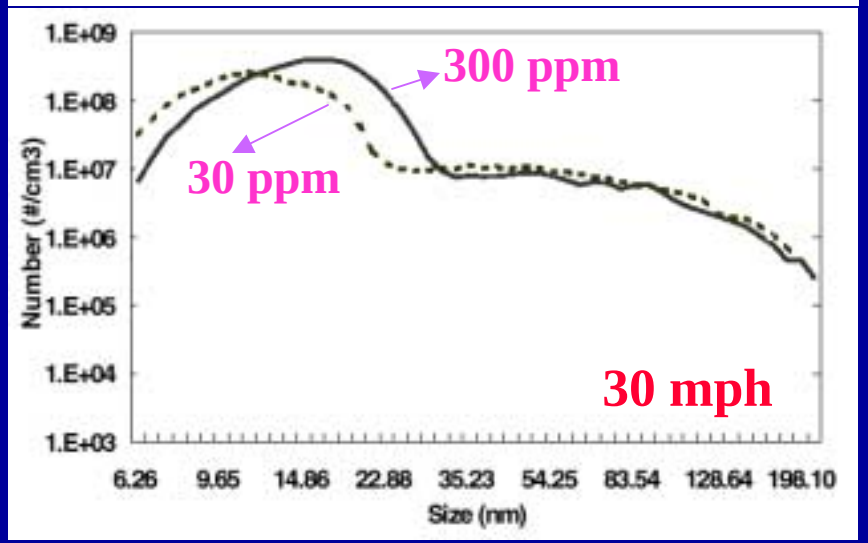
Integrated particle/NO_x concentration ratios.

Source	Campaign	Particles/NO_x (cm^{-3}/ppb)
Diesel	1999 (500 ppm)	839 ± 17
Diesel	2000 (50 ppm)	367 ± 11
Petrol	1999–2000	395 ± 9

56%

From Wåhlin et al., 2001.





Adapted from Lanni et al., 2001.

Aircraft nanoparticle emissions and fuel sulfur content

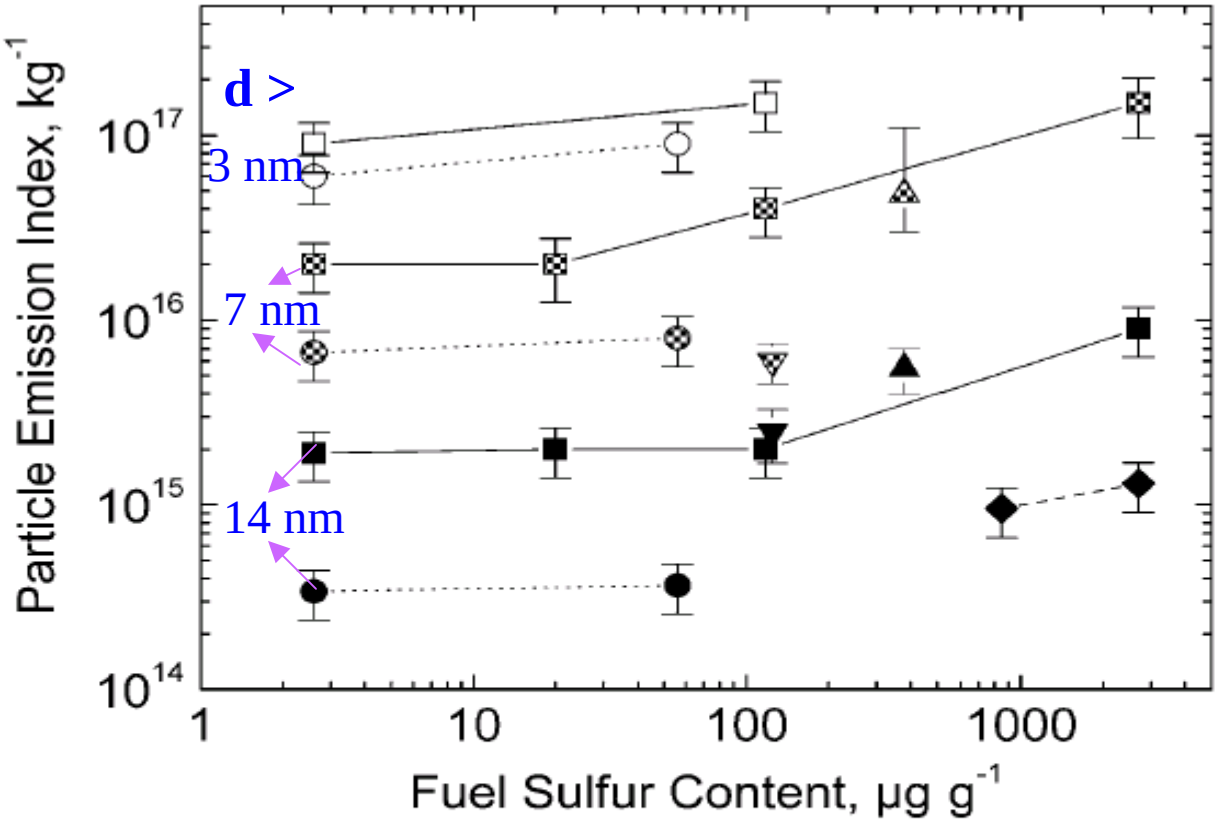
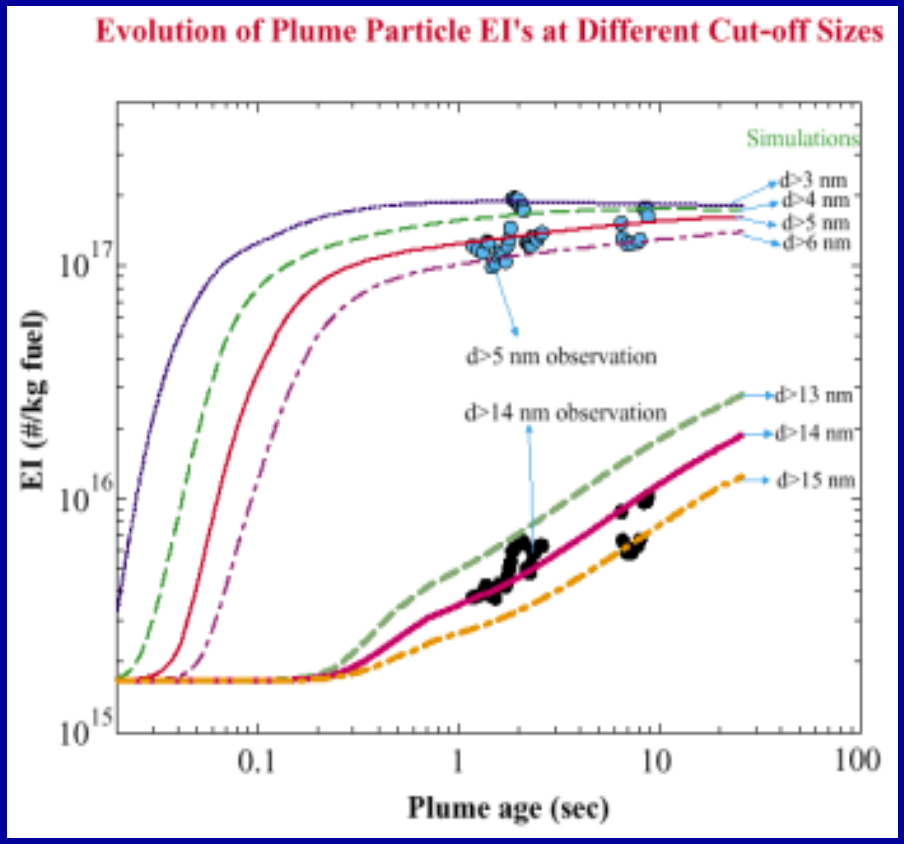


Figure 6. Emission index of the number of detectable volatile particles versus FSC in plumes without contrail formation, for various aircraft, lower detection limits d of particle diameters (open symbols: $d = 3$ nm; gray symbols: 5 nm; black symbols: 14 nm), and plume ages. ATTAS (squares) from S5, 7–9 s, and from S6, 0.5–7 s; B737 (circles) from S6, 0.4–0.6 s; A340 (upward pointing triangle) from S7, 0.5–1.5 s; and B707 (downward pointing triangle) from S7, 0.4–1.2 s. Note that the ATTAS values are higher than all others mainly because of the larger plume age.

From Schumann et al, 2002.

Aircraft nanoparticle emissions

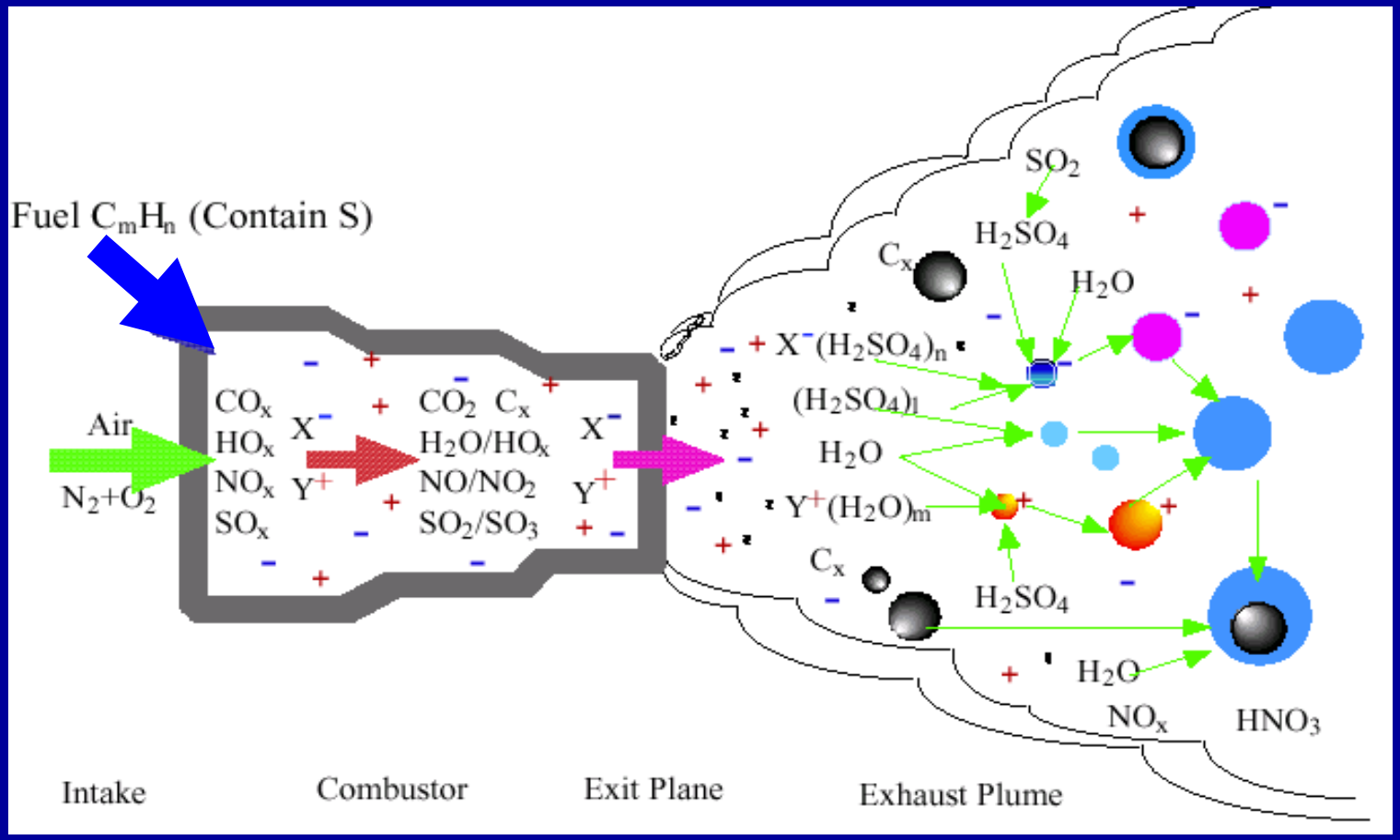
From Schroeder et al, 2001.



From Yu et al, 1999.

Ions and aircraft nanoparticle emissions

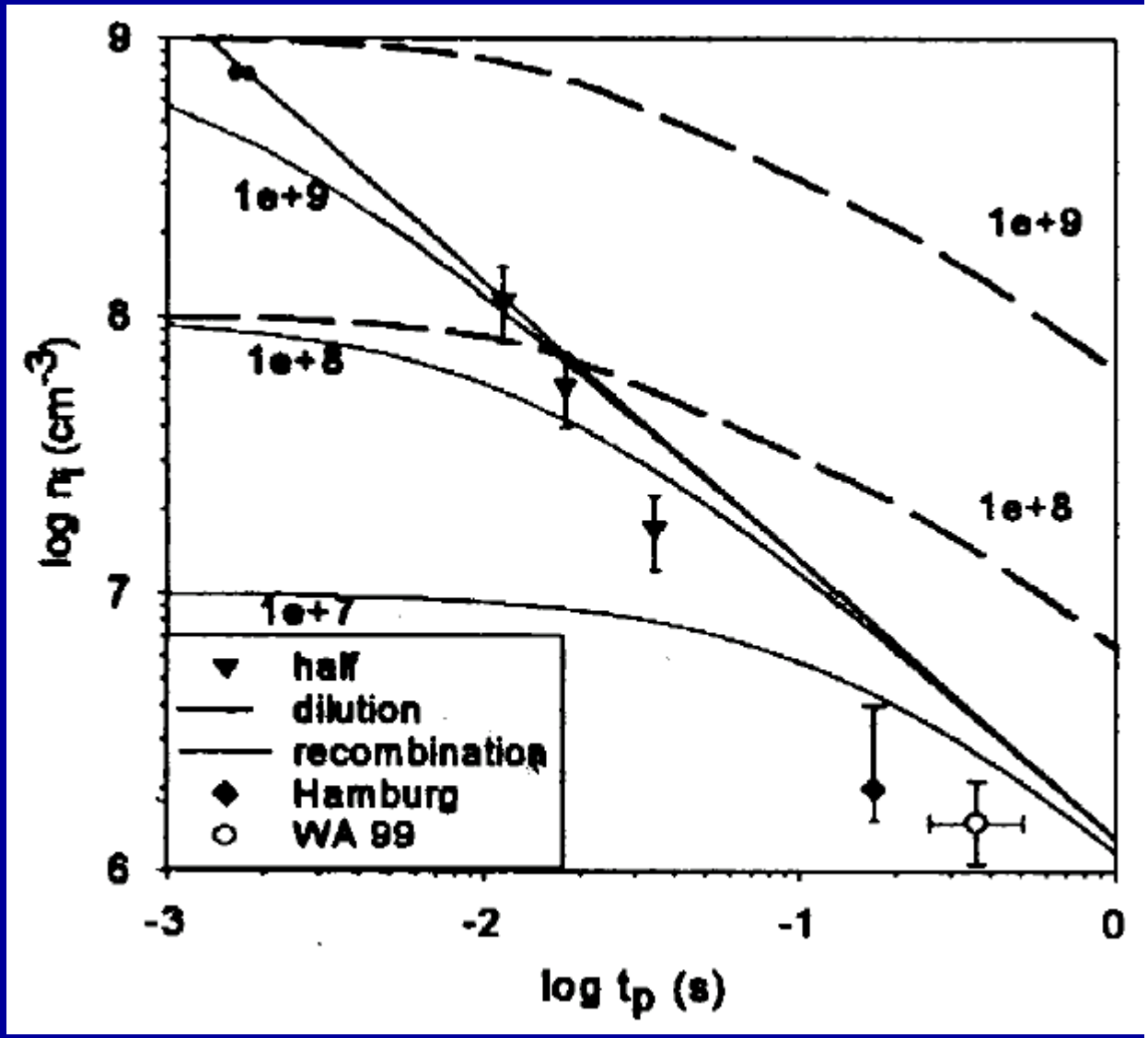
- It has been demonstrated that chemiions generated during combustion play an important role in the formation of nanoparticles in aircraft wakes.



Yu and Turco, 1997, 1998.

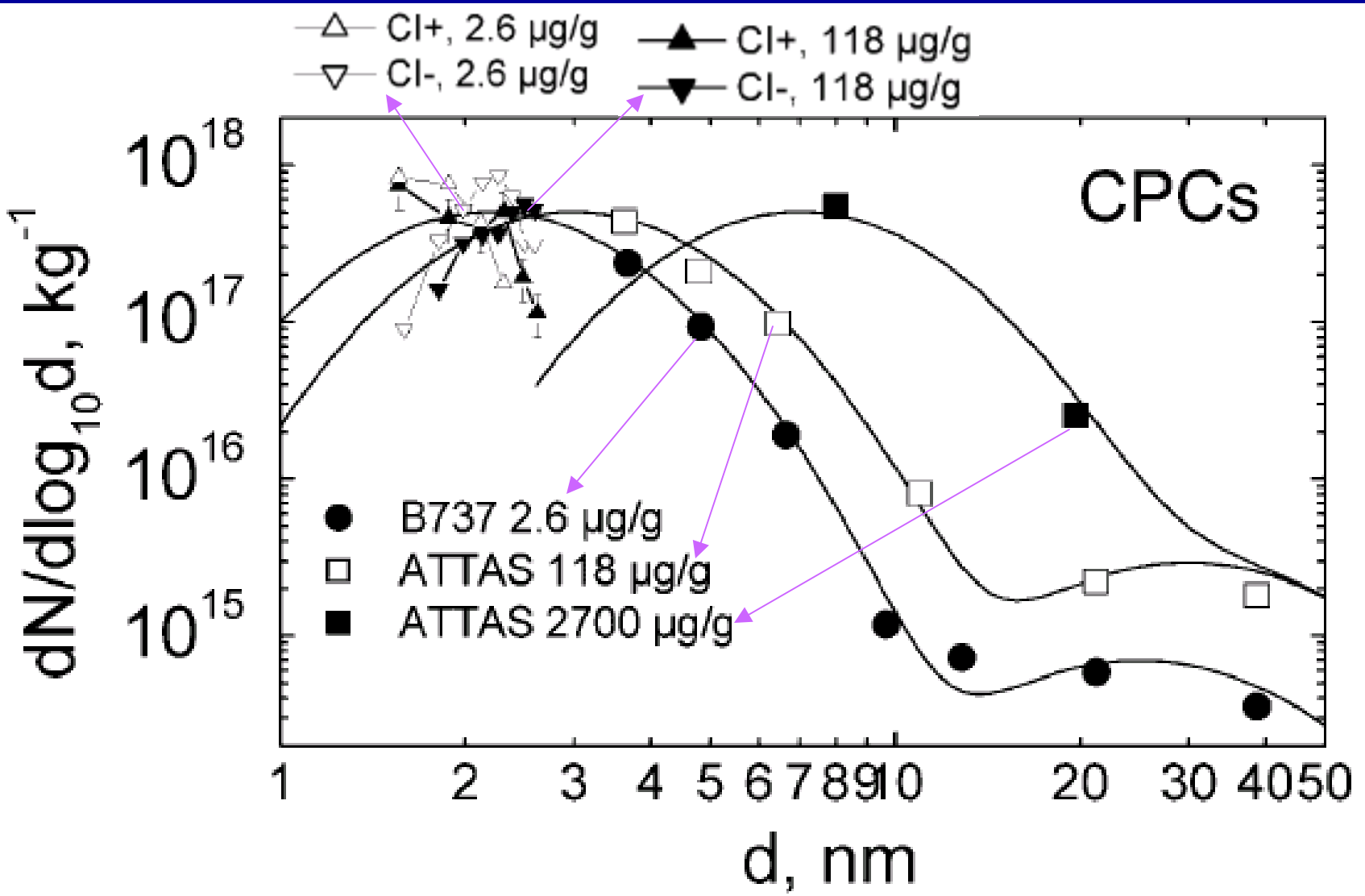
Measurements of chemiions in aircraft wake

Arnold et al. [2000] have detected a positive CI concentration of ~1.6x10^8/cm^3 at a distance 1.39 m behind the jet engine and concluded that positive CI concentration at the exit plane should be at least 1x10^9/cm^3.



From Arnold et al., 2000.

Aircraft nanoparticle emissions



From Schumann et al, 2002.

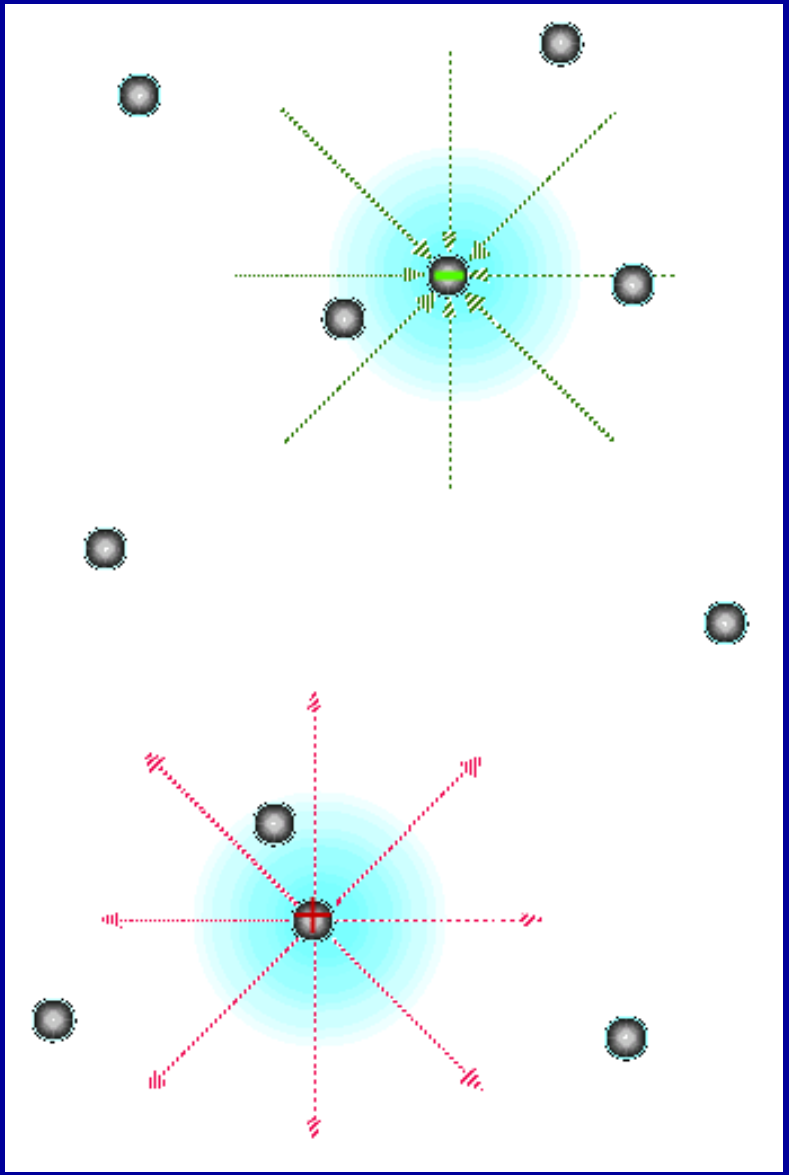
Ion-mediated nucleation (IMN)

- Charged molecular clusters are much more stable and can grow significantly faster than neutral clusters, and thus can preferentially achieve observable sizes.

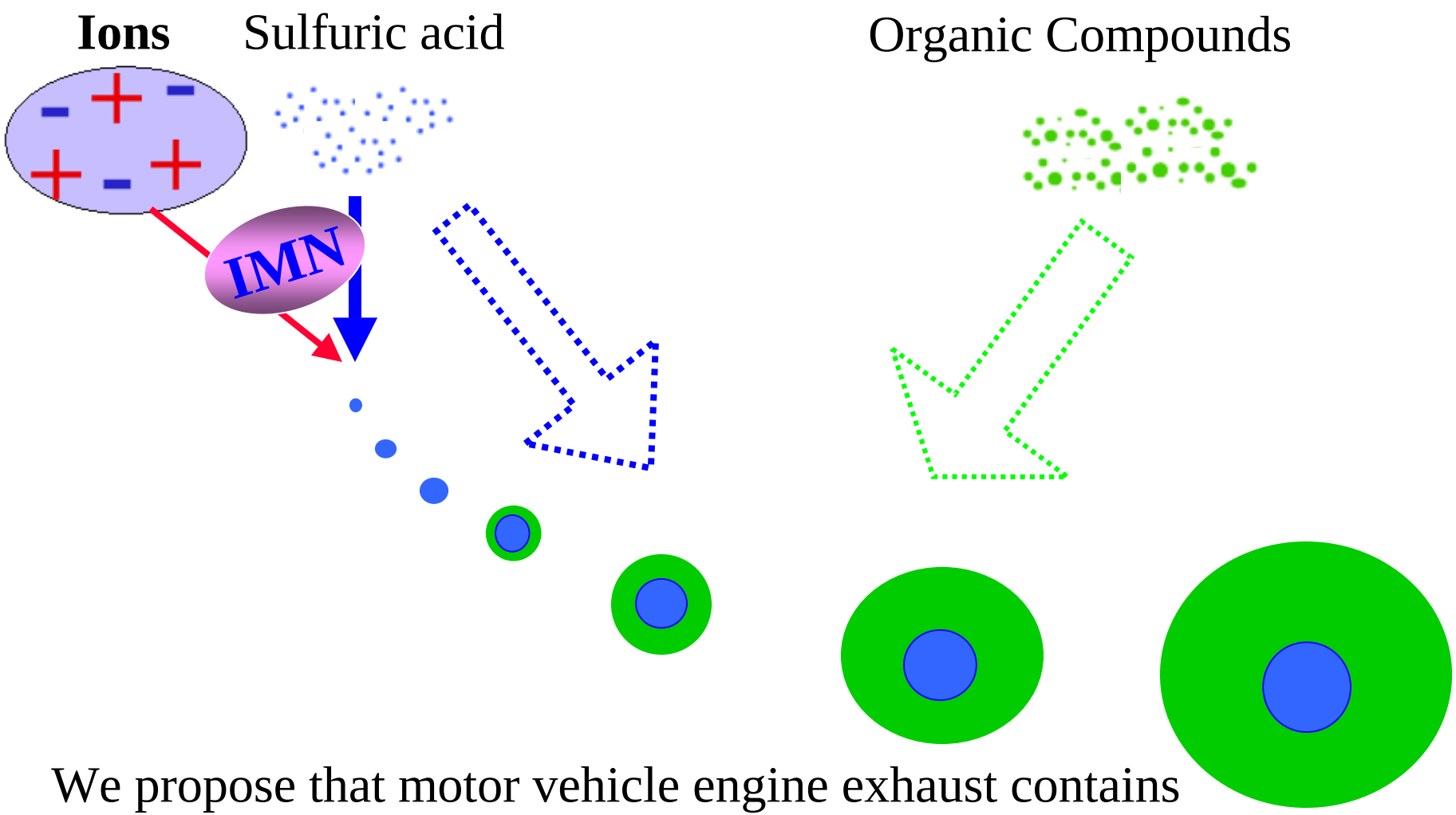
$$E=e/r^2$$

$E = 10^8$ volts/m at r = 1 nm

$E = 10^6$ volts/m at r = 10 nm

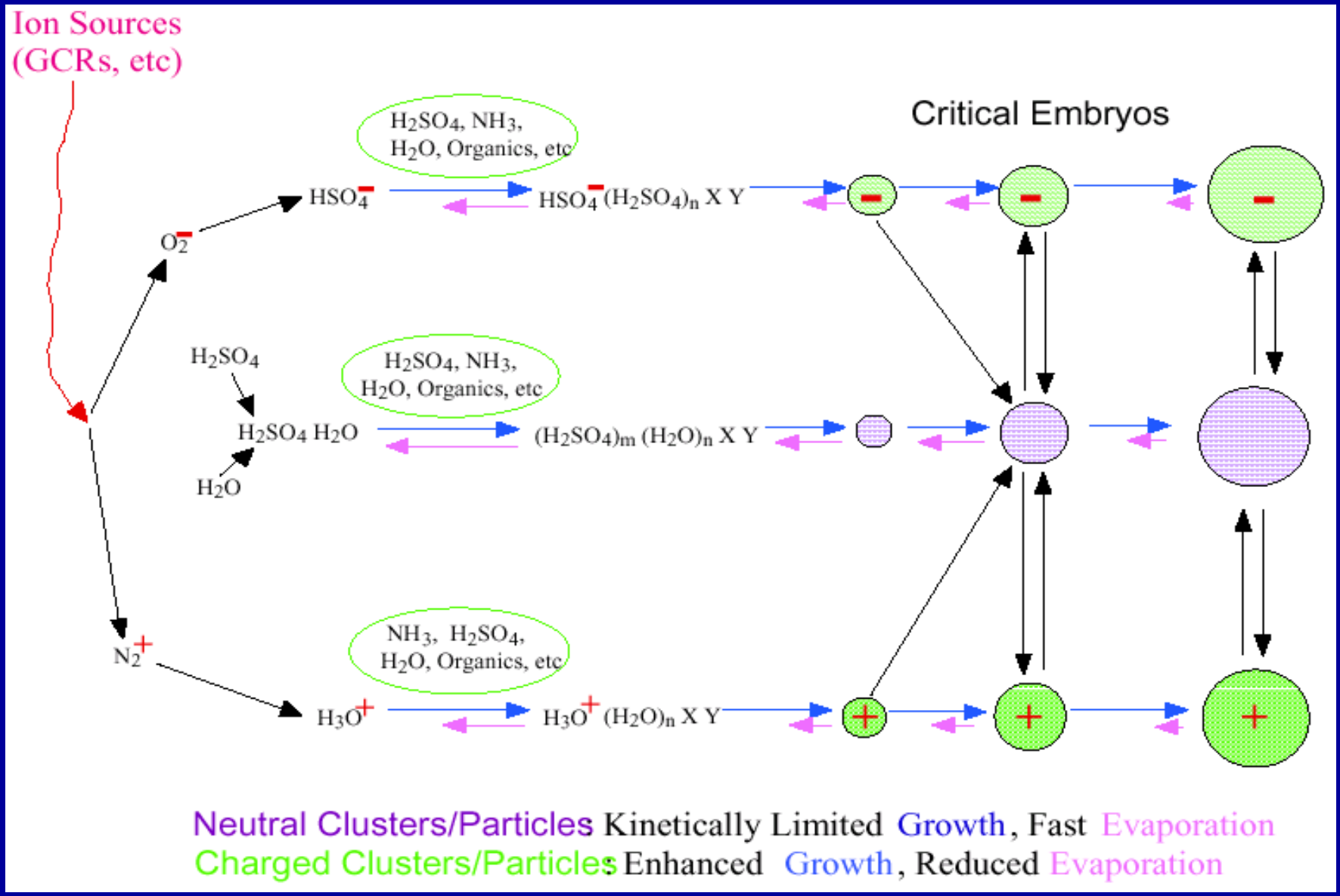


Nanoparticle formation mechanism



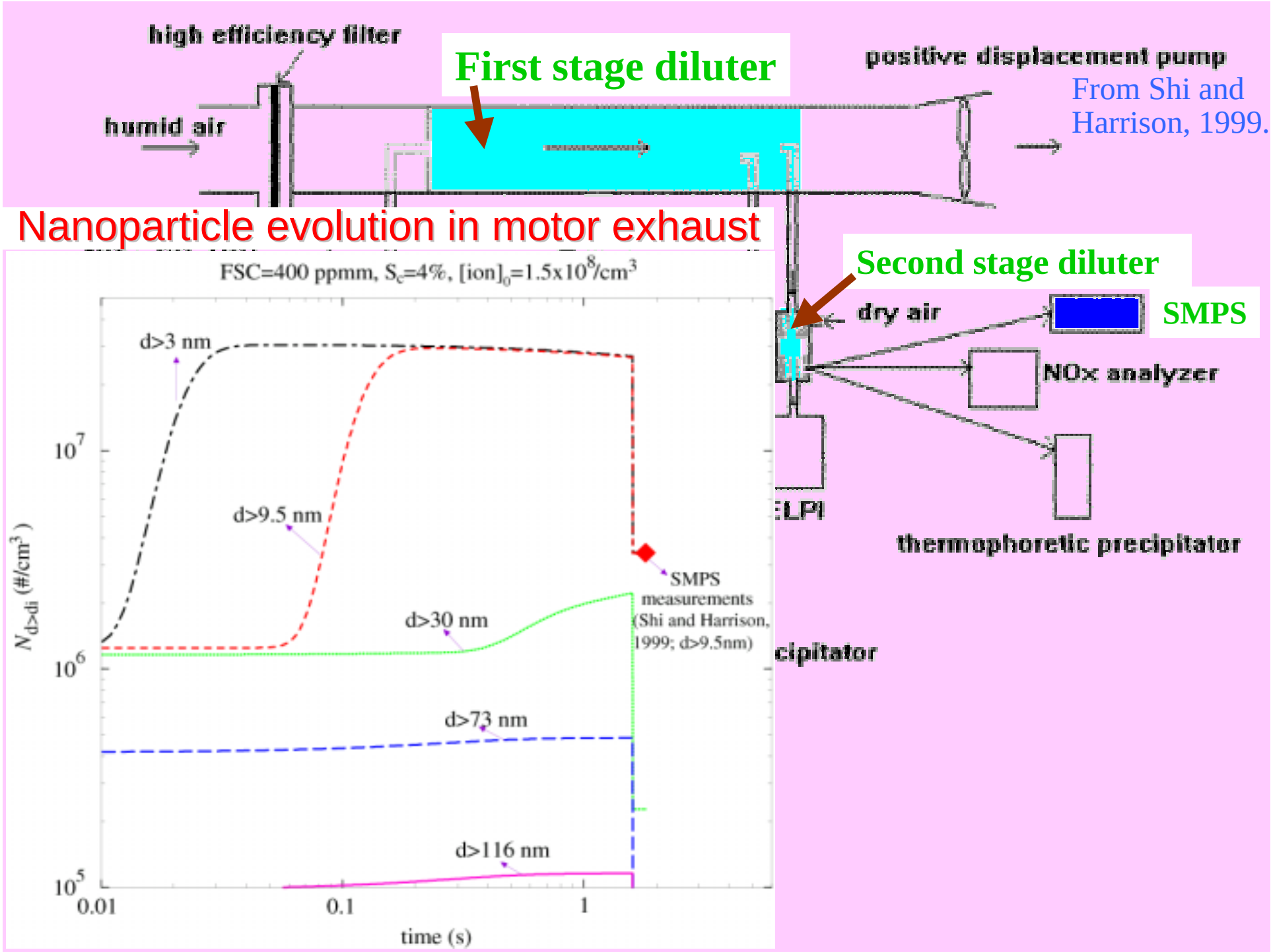
We propose that motor vehicle engine exhaust contains **chemiions**, and these ions **play an important role** in the formation of observed vehicular nanoparticles.

Ion-mediated nucleation (IMN)

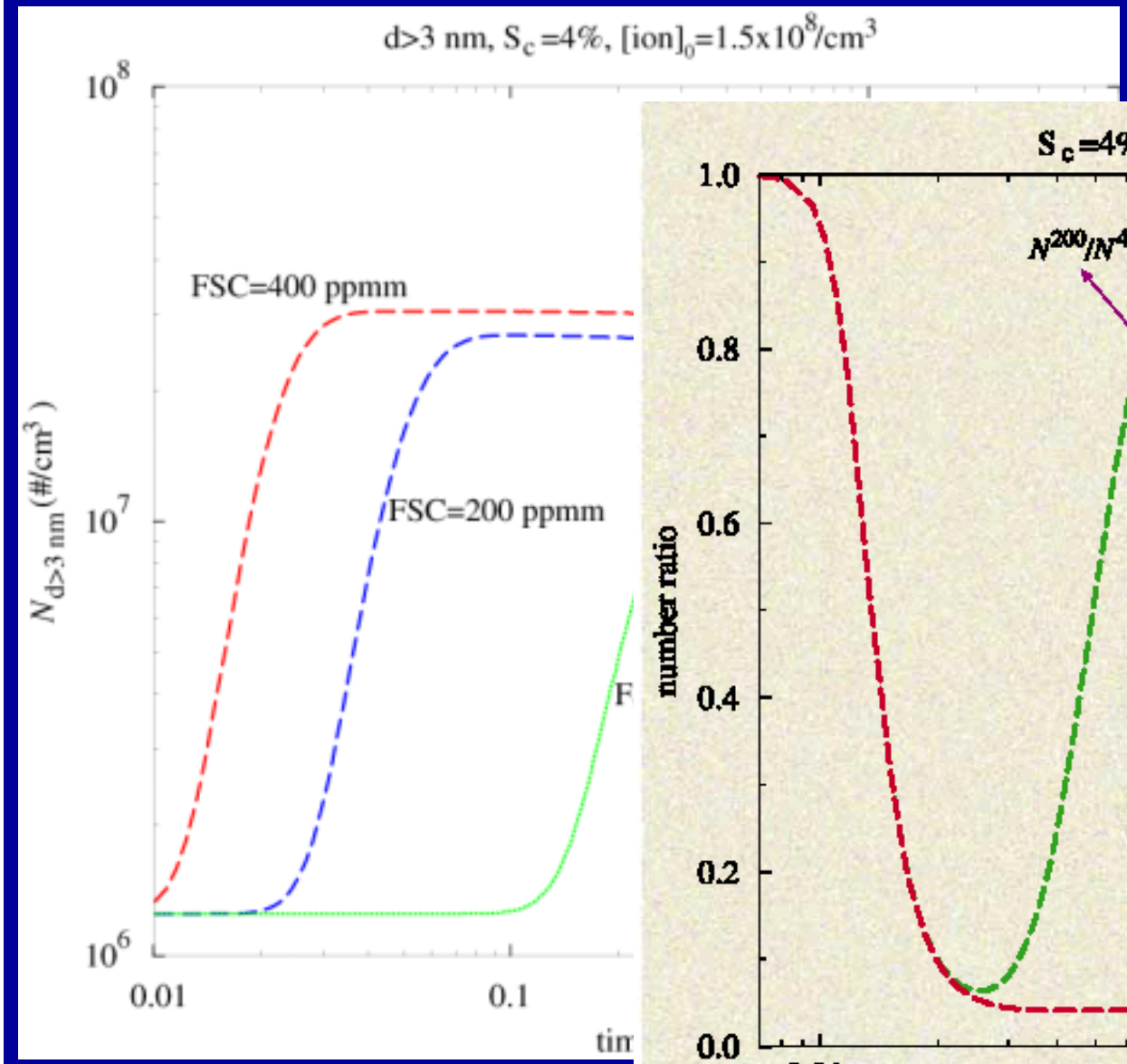


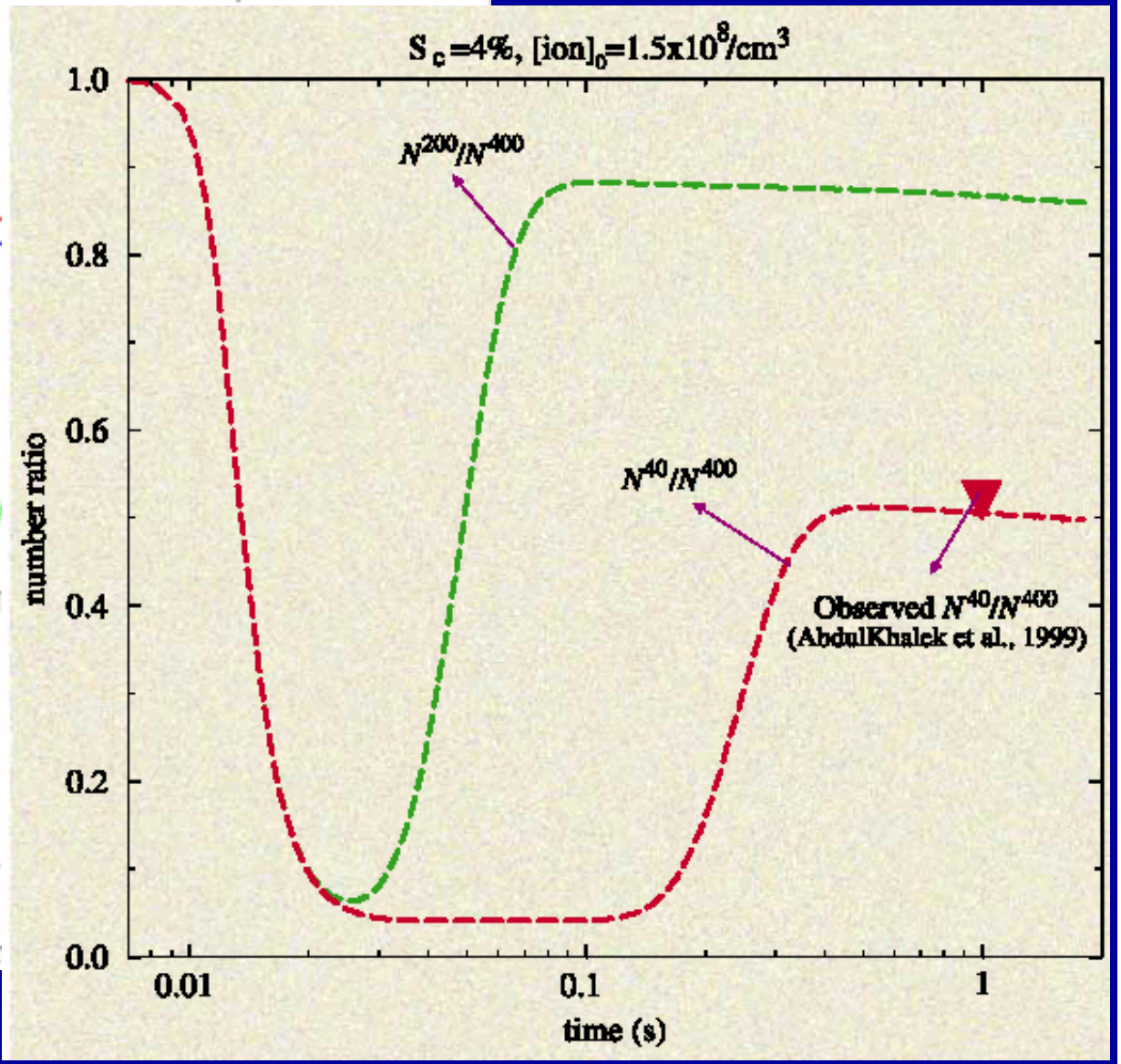
From Yu and Turco, 2001.

Nanoparticle evolution in motor exhaust

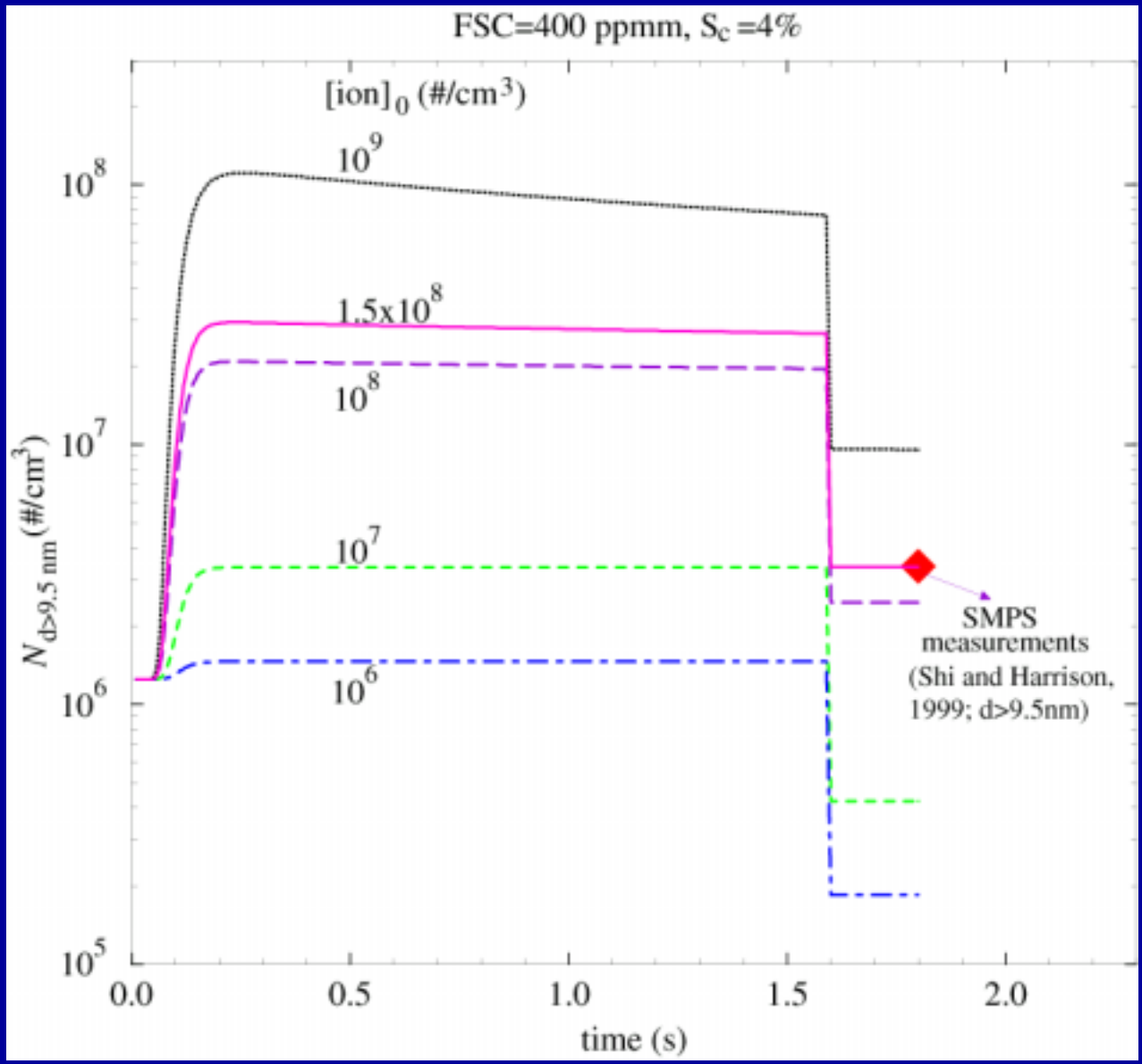


FSCs and motor nanoparticle emissions

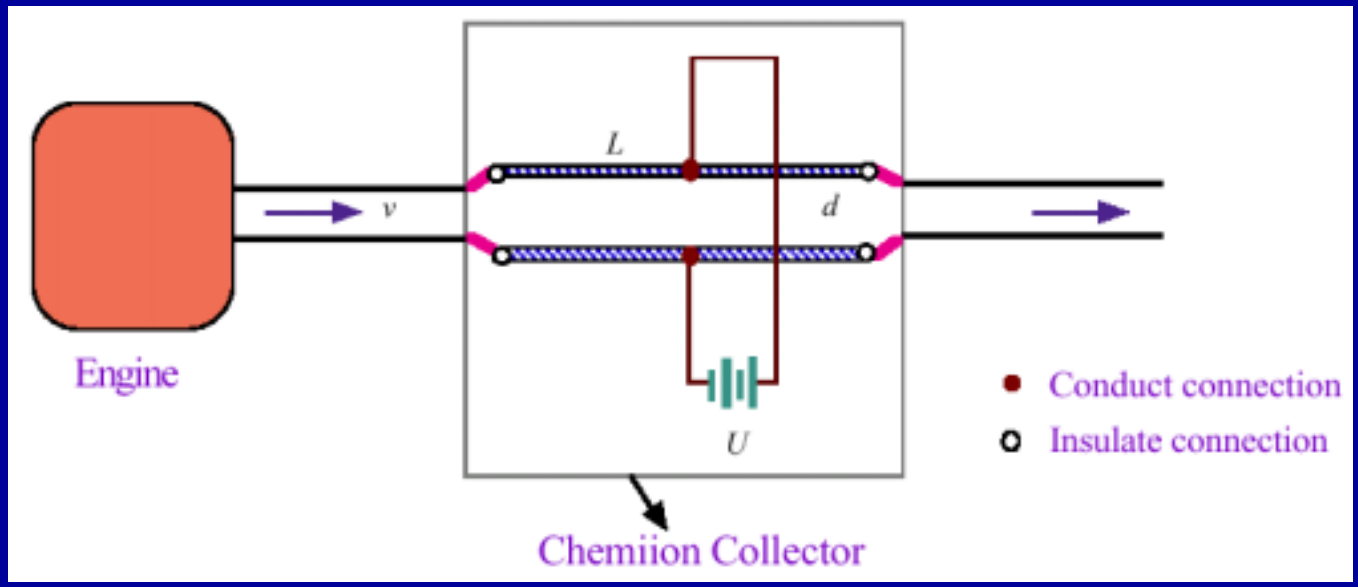




$[ion]_0$ and motor nanoparticle emissions



An efficient method for reducing vehicle nanoparticle emissions

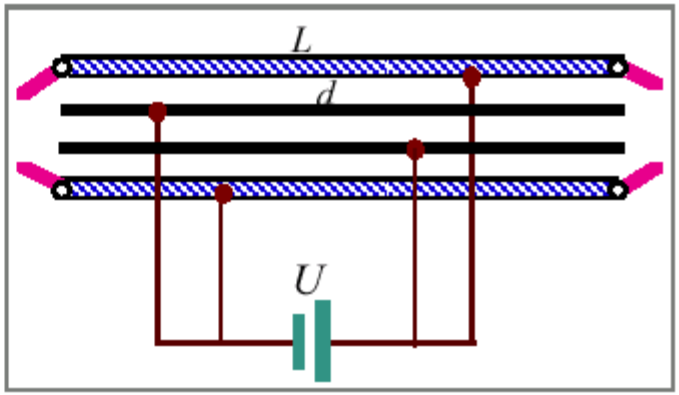


U can be reduced by reducing d with multiple parallel collecting plates

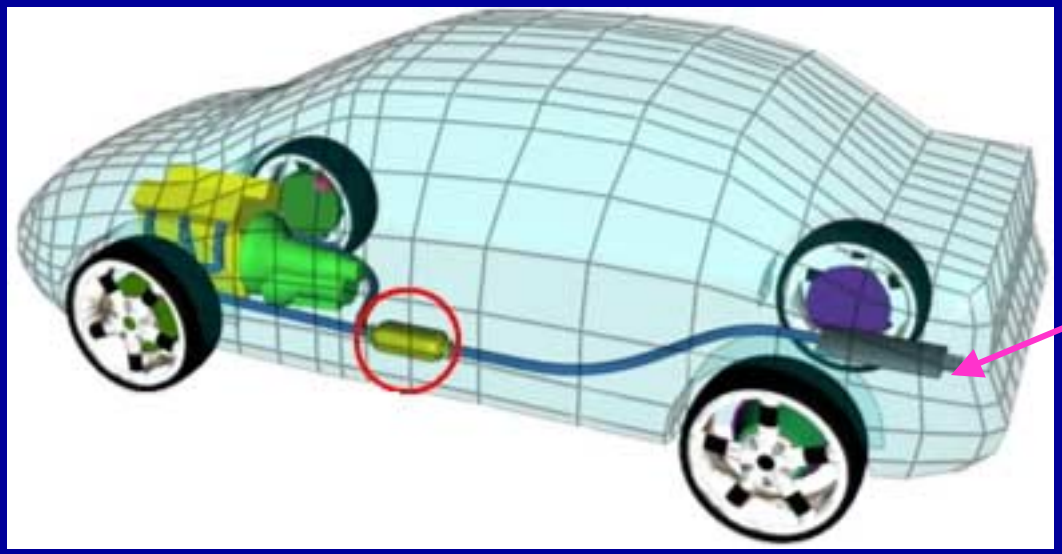
If d is reduced by a factor of 3

U = 11 volts for 46 amu ions

U = 28 volts for 500 amu ions



Chemiion concentration at tailpipe exit $[ion]_0$



$$[ion]_0 = \frac{[ion]_{engine}}{[ion]_{engine} K_r \tau (e^{t_0/\tau} - 1) + e^{t_0/\tau}}, \qquad \frac{1}{\tau} = \frac{1}{\tau_s} + \frac{1}{\tau_{wall}}$$

$[ion]$ at engine exit

Recombination coefficient

Time inside tailpipe/tube

Loss to soot

Loss to wall

$[ion]_0$ and aftertreatment systems

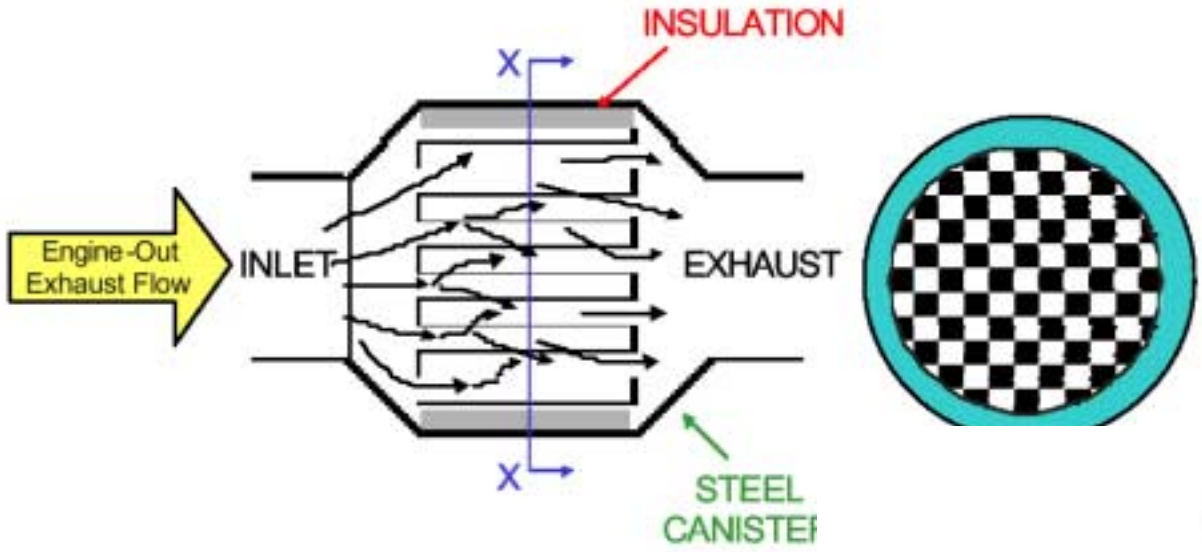


Figure 12. Catalyzed Diesel P

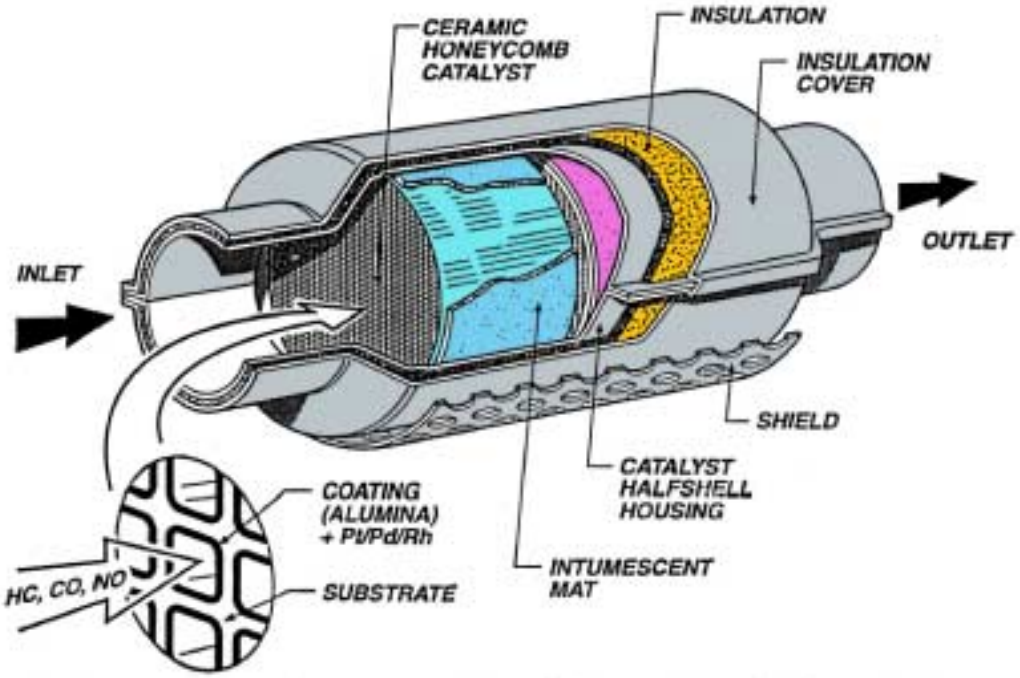
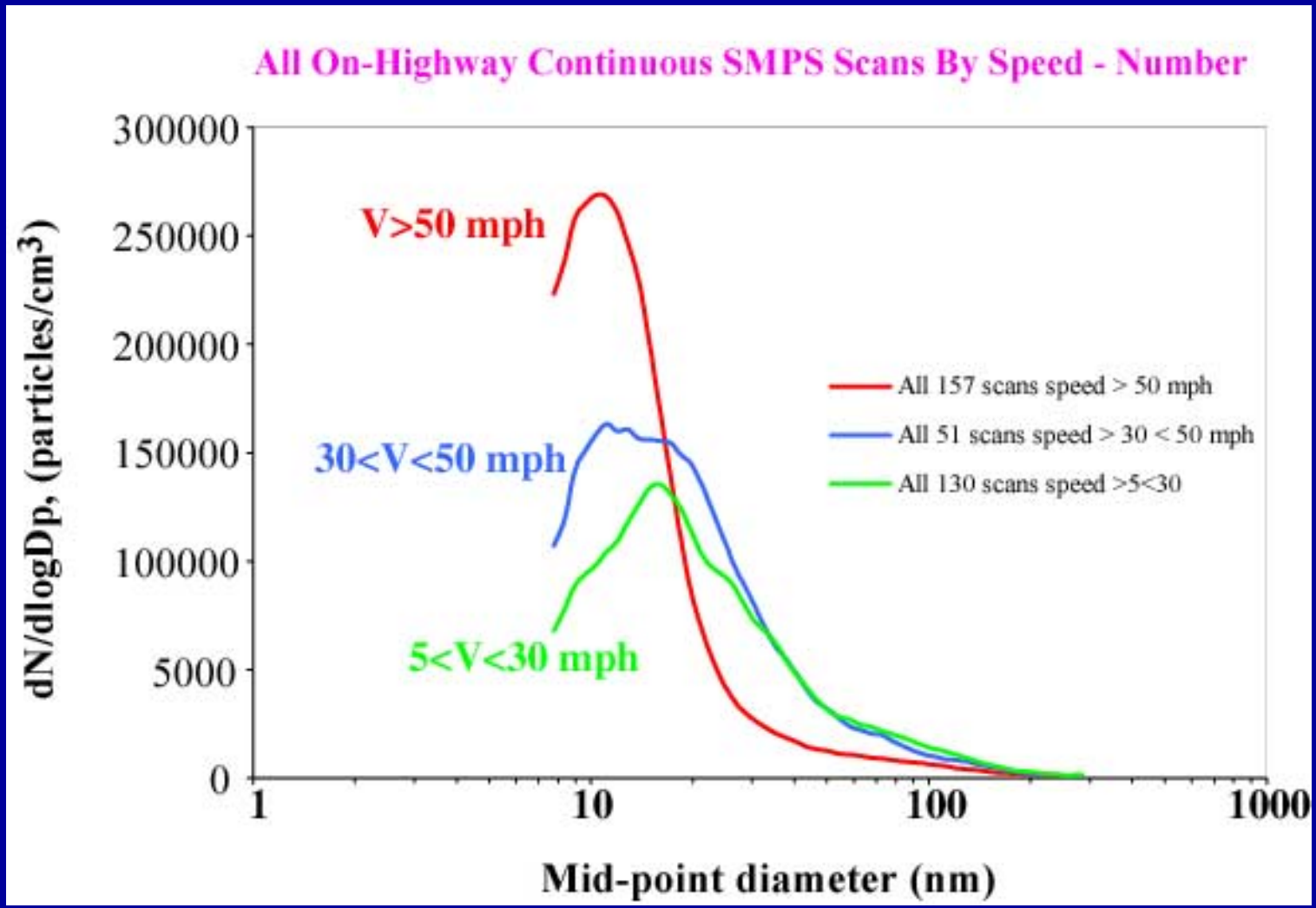


Figure 13. Automotive (Gasoline) Catalytic Converter (Three-Way Catalyst Design)

From Eberhardt, 2000.

Observations: Influence of vehicle speed on number size distributions



Adapted from Kittelson et al., 2001.

Laboratory Measurements

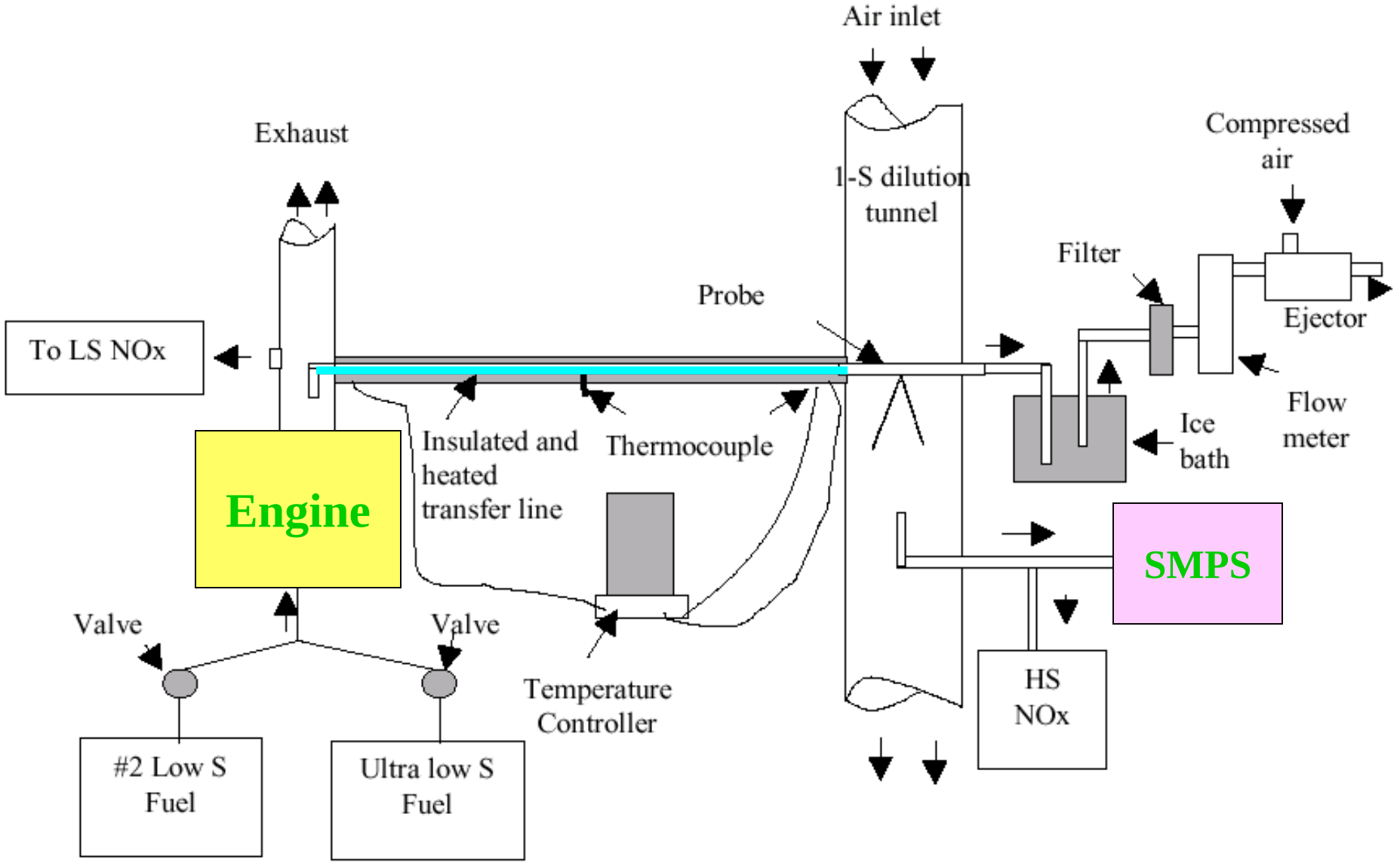
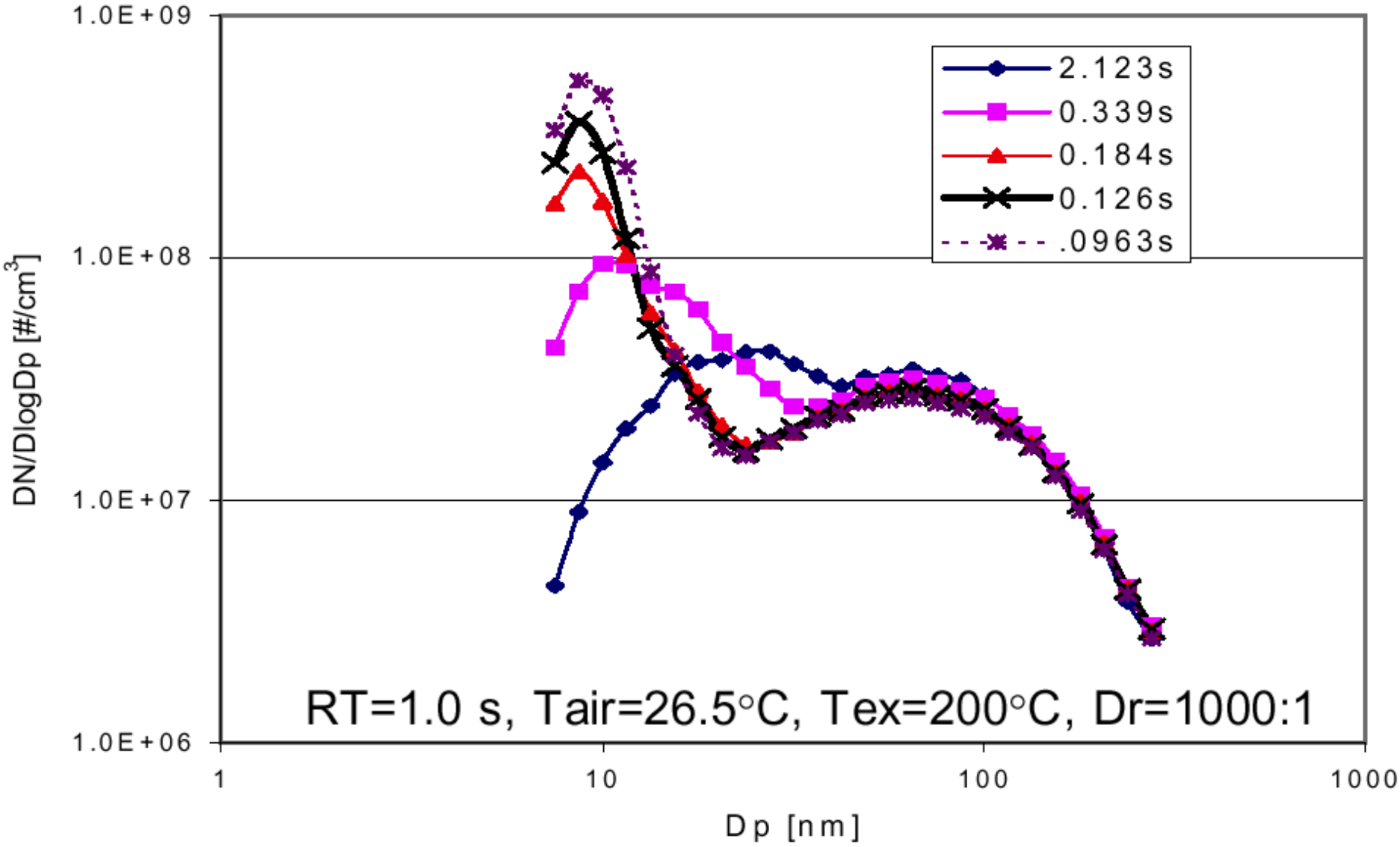


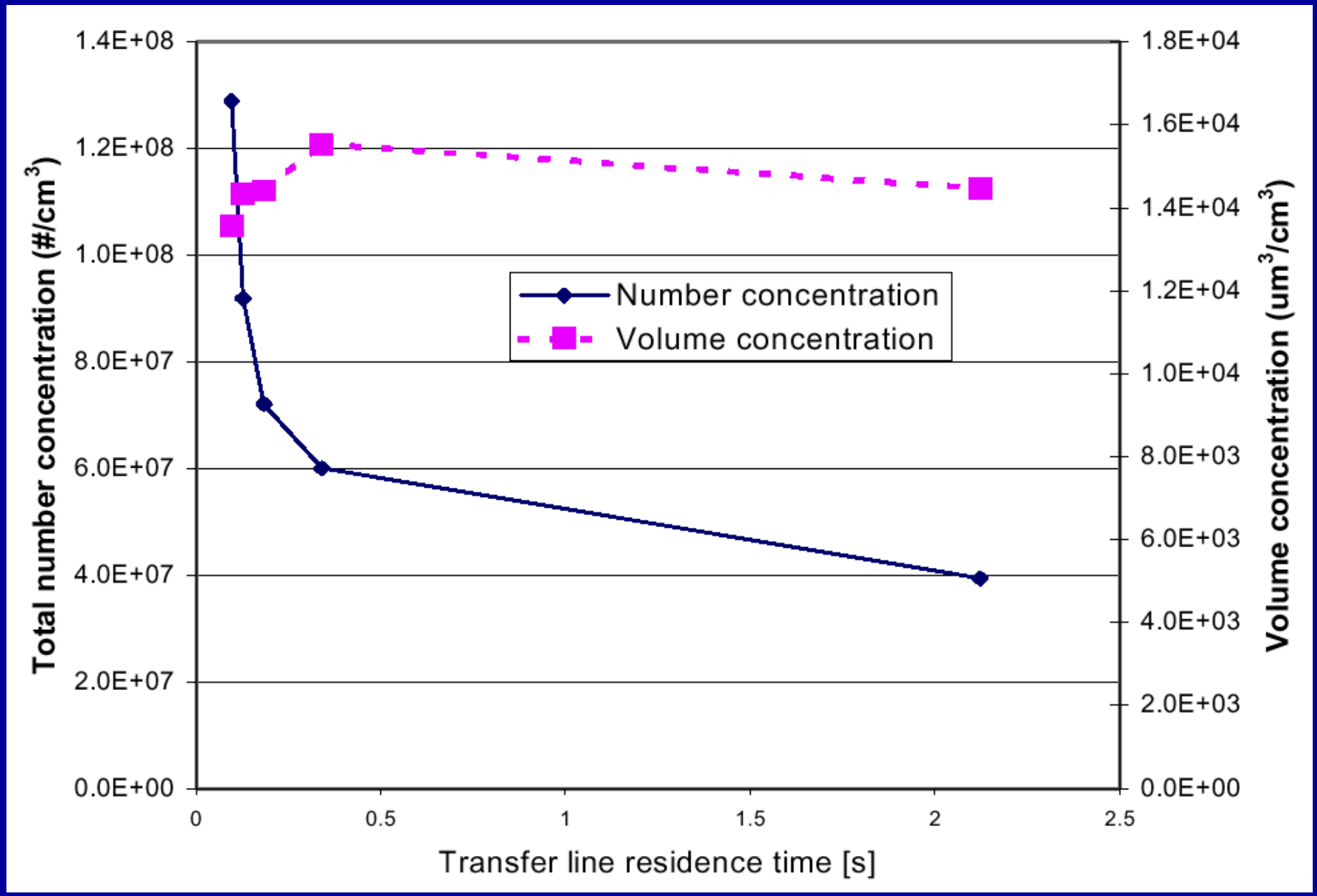
Figure 3. A schematic of experimental setup From Wei, Kittelson, and Watts, 2001.

Effect of transfer line



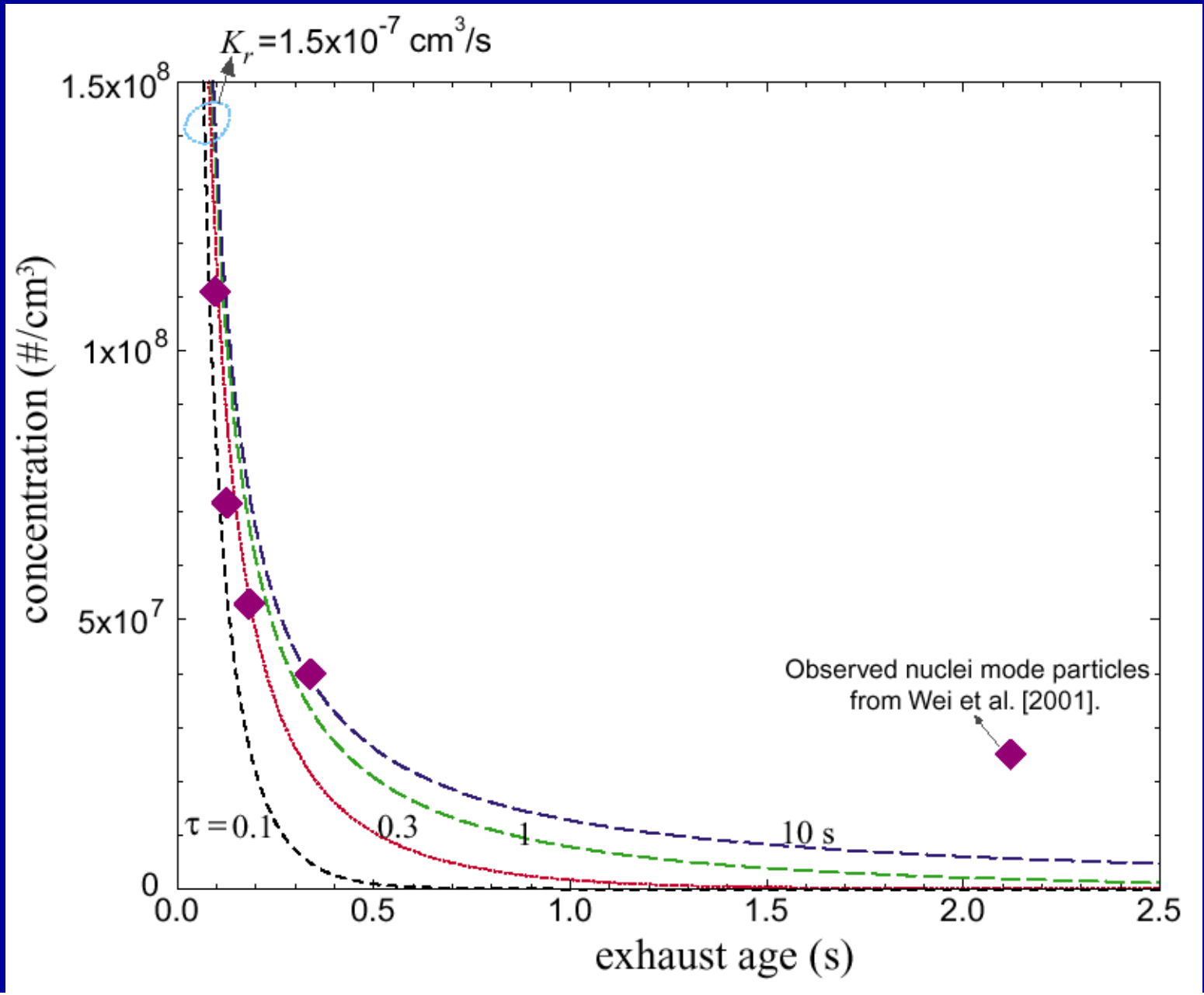
From Wei, Kittelson, and Watts, 2001.

Effect of transfer line

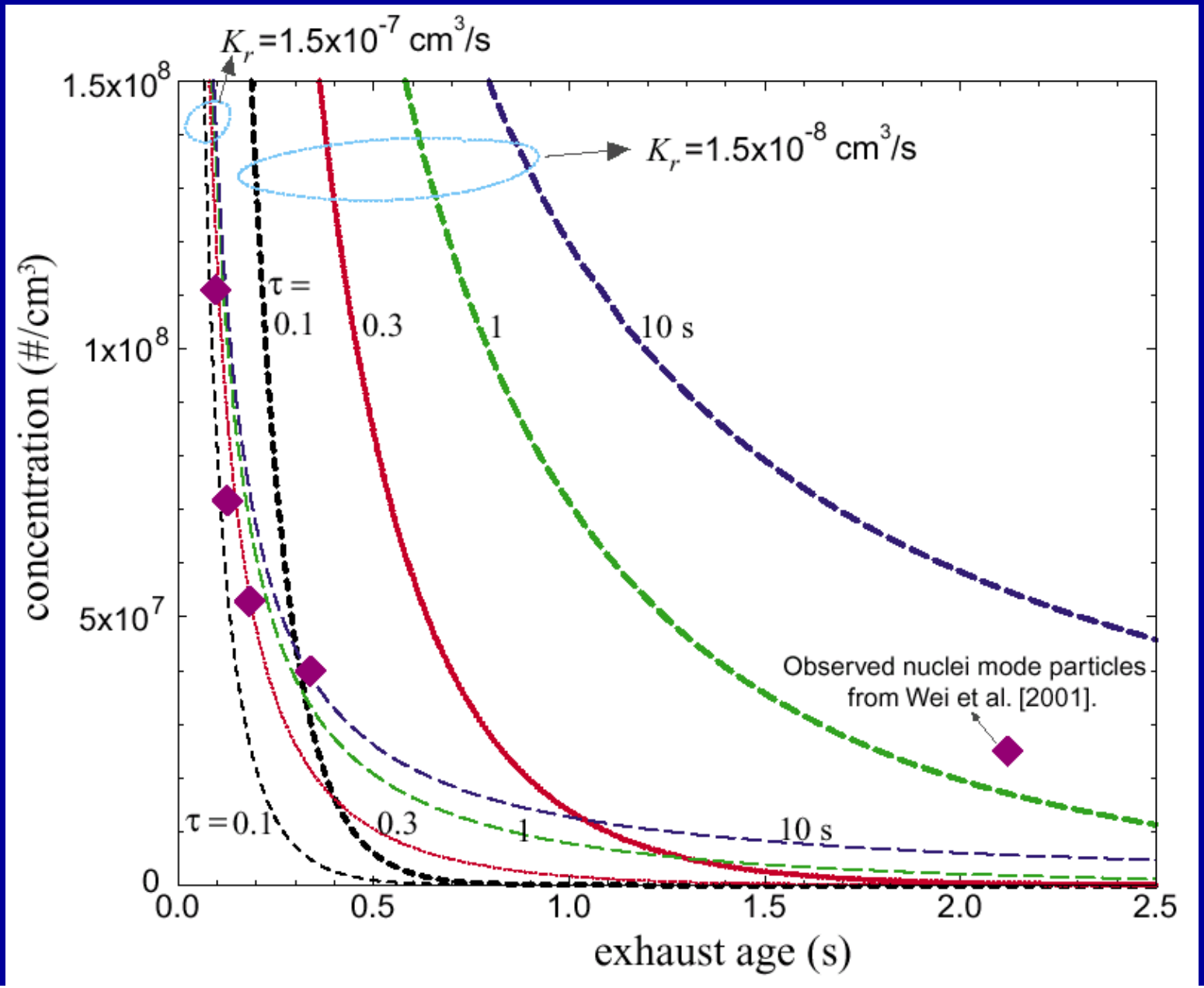


From Wei, Kittelson, and Watts, 2001.

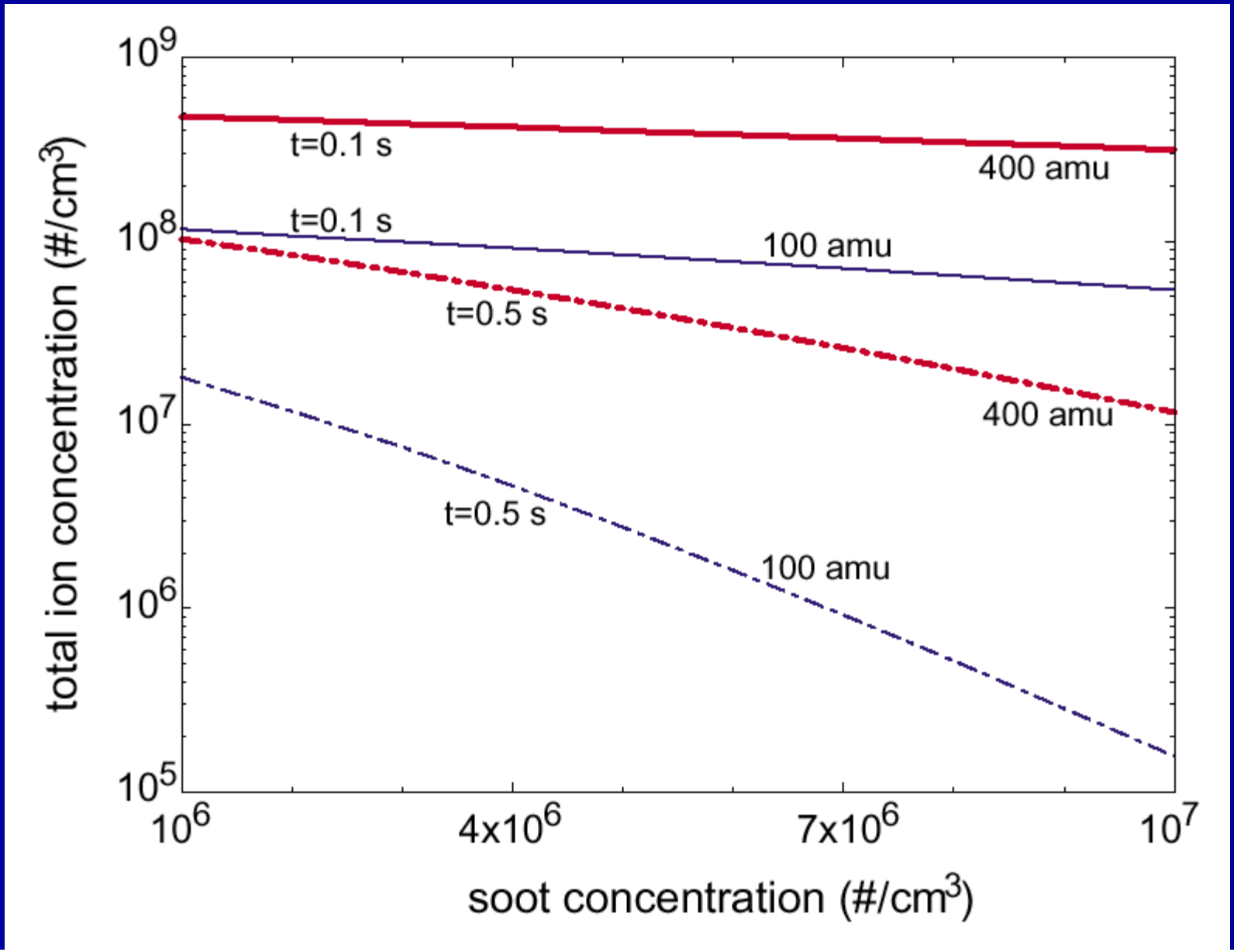
Chemiion evolution under different τ and K_r



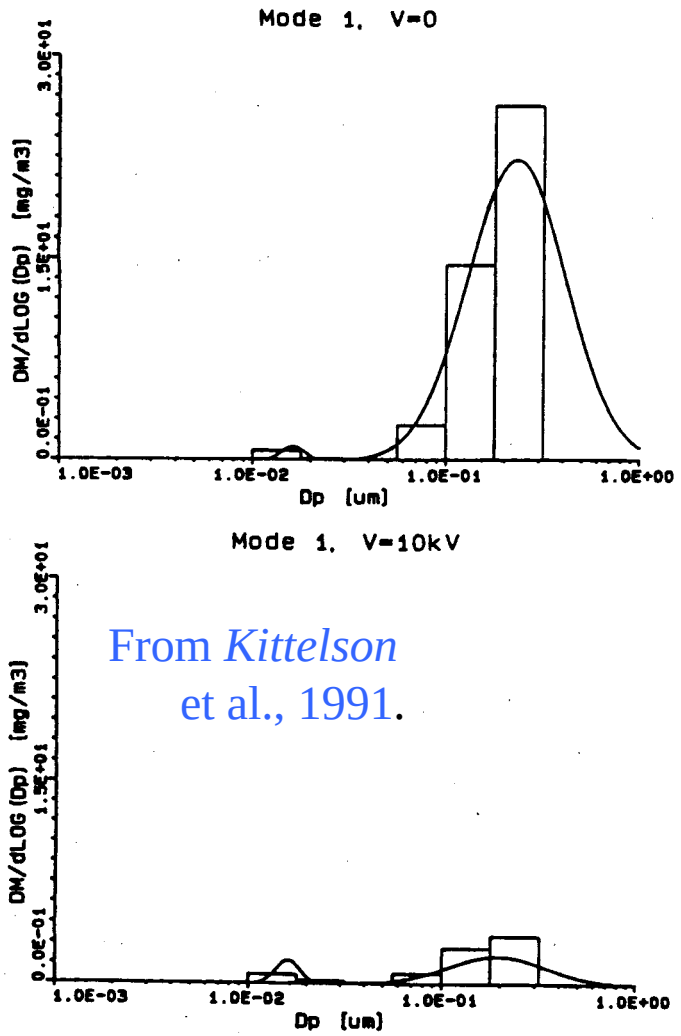
Chemiion evolution under different τ and K_r



Effect of soot concentrations



Measurements Relevant to Chemiion Theory



From *Kittelson* et al., 1991.

Figure 14 - Charged Fraction Test Results, Precipitator Voltage On and Precipitator Voltage Off, Engine Mode 1, obtained by EAA, Volume Distribution.

Our calculations suggest that about 20-70% of the fresh nuclei mode particles should be charged.

Earlier measurements by Kittelson et al. [1991] indicated that nuclei mode particles were mainly uncharged.

Possible explanation:

1. Most of nuclei mode particles are smaller than 10 nm.
2. Charged particles were lost in the sample line.

Measurements of Ions in engine exhaust

From *Collings* et al., 1988.

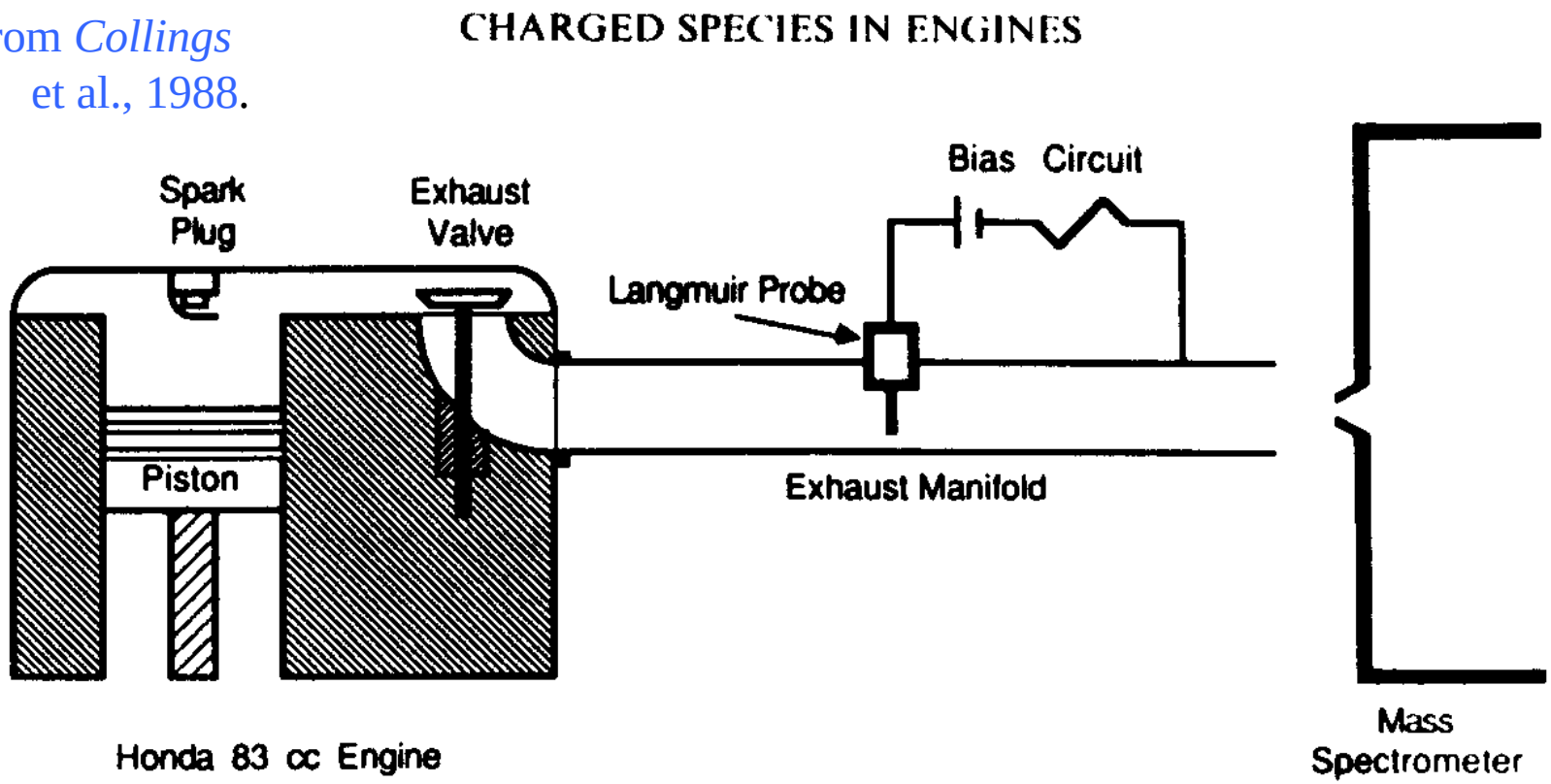
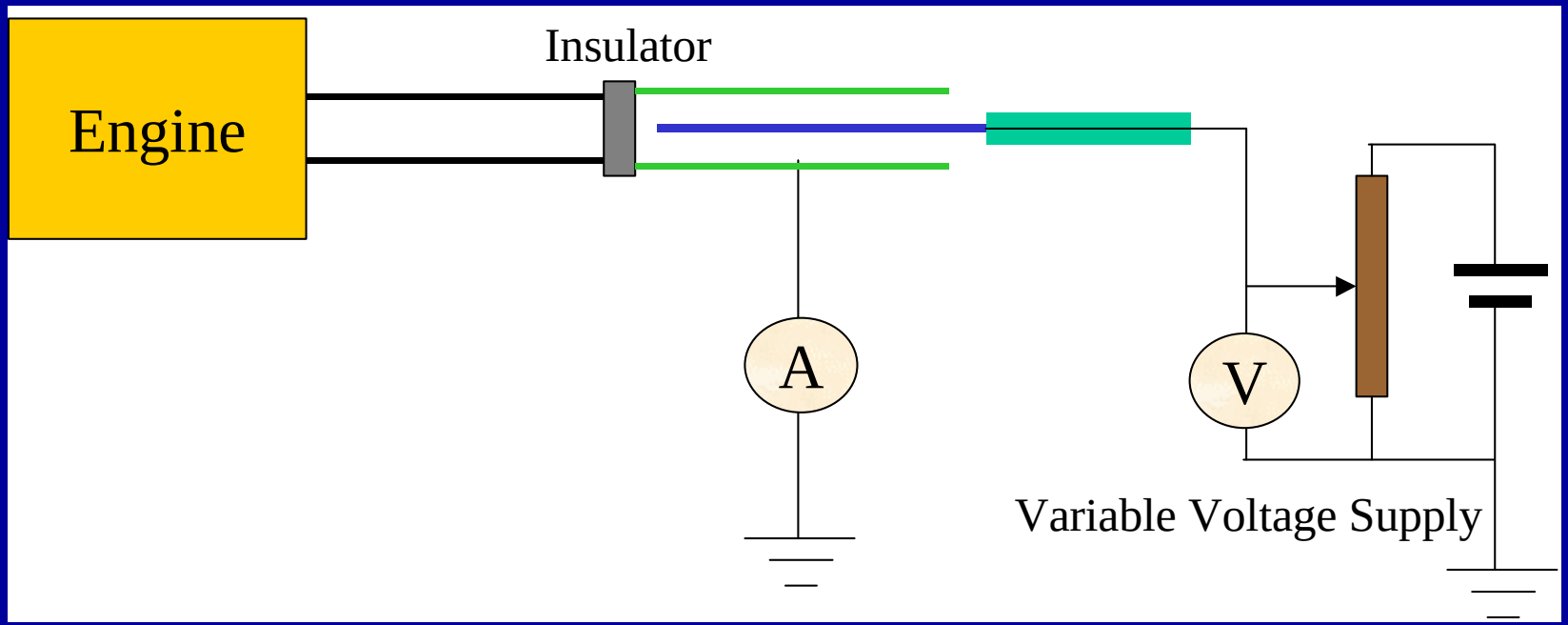


FIGURE 1 Overall schematic of apparatus.

Peak ion concentrations in the exhaust are of the order of 10^7–10^8 ions/cm^3.

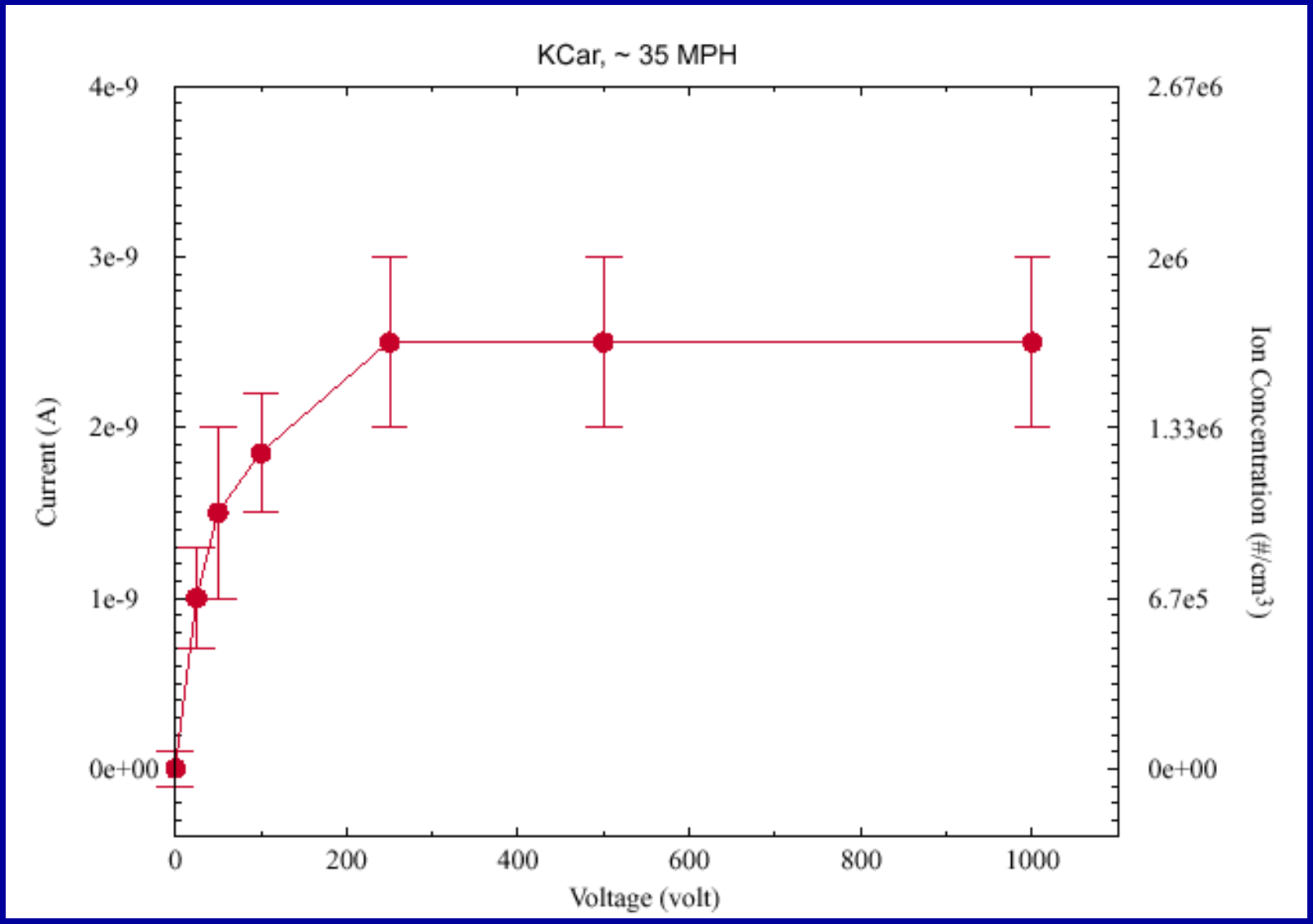
Measurements of Chemiion Concentration



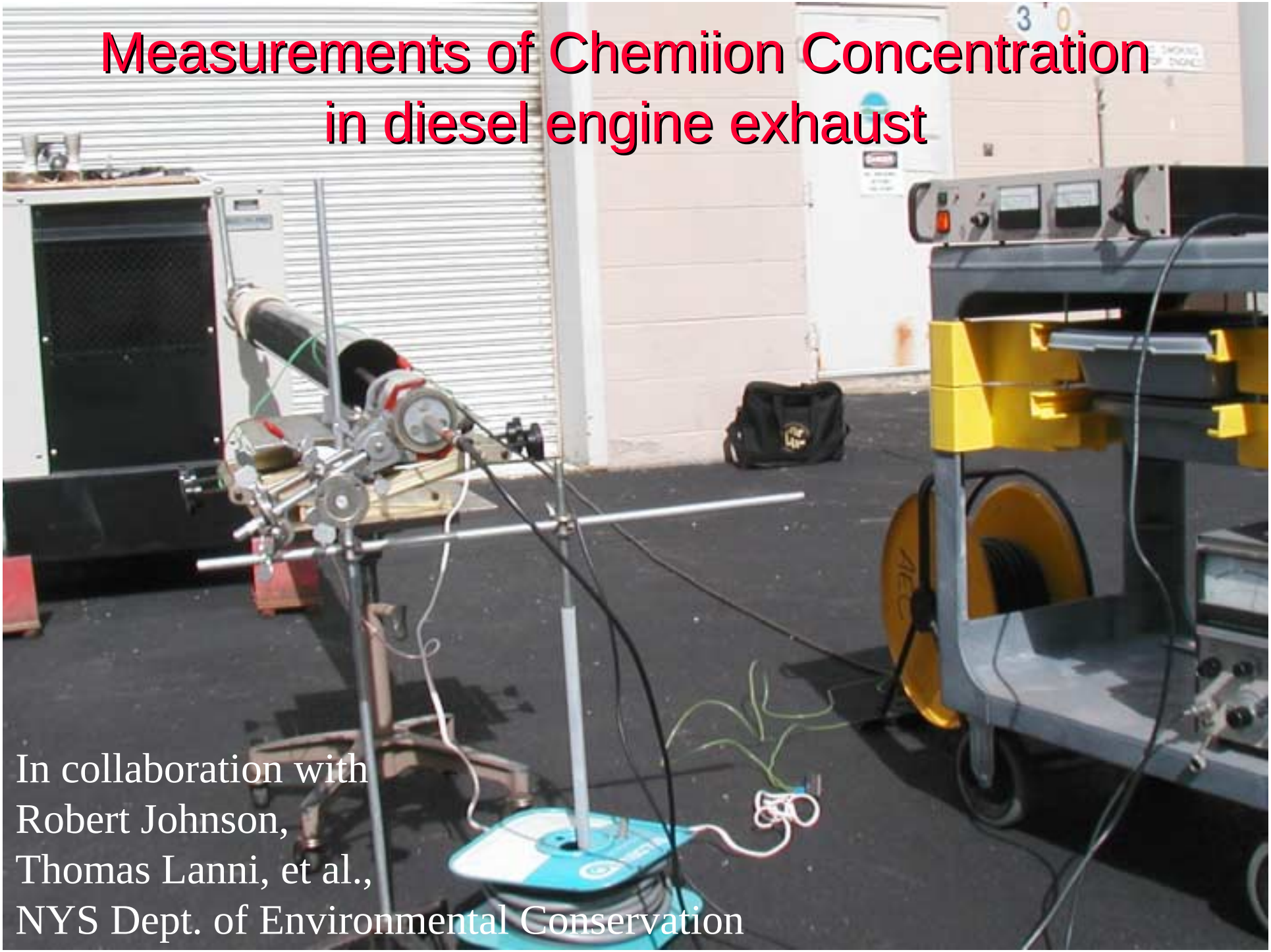
Measurements of Chemiion Concentration in gasoline engine exhaust

In collaboration with
Robert Johnson,
Thomas Lanni, et al.,
NYS Dept. of Environmental Conservation

Measurements of Chemiion Concentration in gasoline engine exhaust

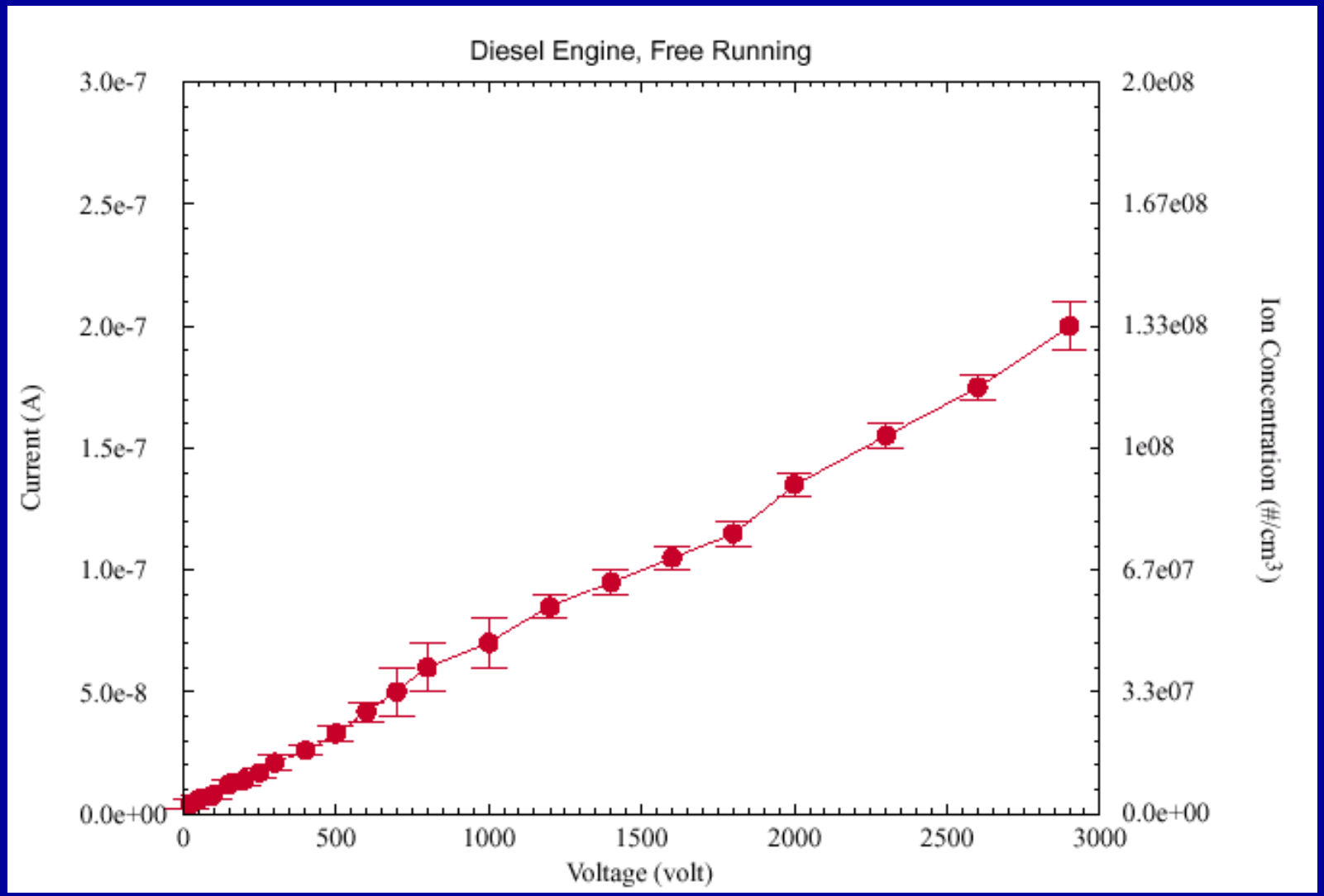


Measurements of Chemiion Concentration in diesel engine exhaust

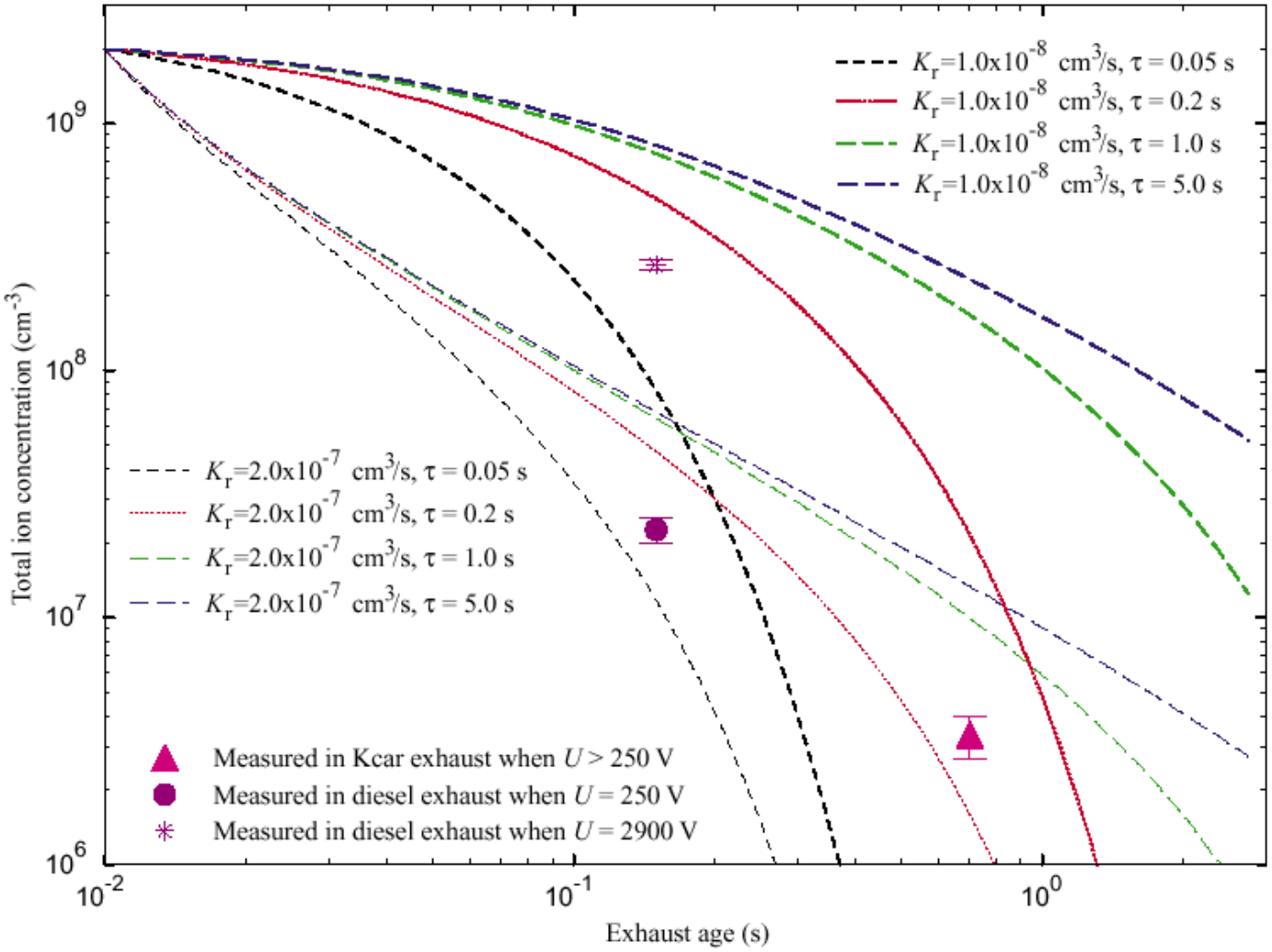


In collaboration with
Robert Johnson,
Thomas Lanni, et al.,
NYS Dept. of Environmental Conservation

Measurements of Chemiion Concentration in diesel engine exhaust



Chemiion Measurements vs Calculations



Summary

- Chemiions may play an important role in the formation of the nanoparticles in motor vehicle exhaust.
- The predicted nanoparticle properties based on our chemiion theory consistently explain the measurements in terms of total number concentrations, and their sensitivity to fuel sulfur contents, transfer line residence time, on-road vehicle speeds, and soot concentrations.
- Number of nanoparticles formed is very sensitive to chemiion concentrations.
- Preliminary measurements in the exhaust of a gasoline vehicle and a diesel engine reveals the presence of ions of various mass.