

## Effect of organic vapour in diesel exhaust on nanoparticle formation

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### Abstract / Introduction

We investigated the nucleation in the exhaust of a modern light-duty diesel vehicle. The classical nucleation theory of homogenous nucleation of water/sulphuric acid underestimates the emissions of volatile nanoparticles. Other compounds are likely to be involved in nucleation. Organic compounds are suspected to play a key role in nucleation. We introduced two organic compounds directly into the diluted exhaust to study the influence on the nucleation process.

### Conclusions

These results emphasise the important role of volatile organic compounds for nucleation mode particle measurements in diesel exhaust. The hydrophilic methanol has a bigger potential than the lipophilic toluene to increase volatile nanoparticles. Condensation of the organic compounds on the existing particles is not the main contribution to the increase of nucleation. We propose that the investigated organic compounds are directly involved in the growth of the initial nucleation particles ( $D_p \sim 1$  nm) created by homogenous nucleation of water/sulphuric acid. The results implies that in absence of organic compounds only a small portion of the initial nucleation particles grows to the typically nucleation mode size range as observed in diesel exhaust.

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# Effect of organic vapour in diesel exhaust on nanoparticle formation



**Urs Mathis, EMPA**

# Motivation / Objectives

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- Organic compounds were found in volatile diesel nanoparticles

Tobias, H.J. et al. (2001). *Environmental Science and Technology* 35, 2233-2243.

Sakurai, H. (2003). *Atmospheric Environment* 37, 1199-1210.



- Organic vapour in diesel exhaust
  - effect on nucleation mode particles
  - effect of substance class
  - implication on the formation mechanism of nucleation mode particles

# Investigated vehicle

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- Light duty diesel vehicle
  - ∞ displacement: 1.9 l, diesel, TDI
  - ∞ max. power: 74 kW (4000 rpm)
  - ∞ max. torque: 240 Nm (1800 rpm)
  - ∞ fuel sulphur: 320 ppm



# Dilution conditions

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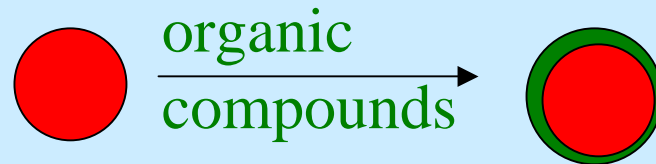
- Weak nucleation
  - sample temperature: 45 °C
- Strong nucleation
  - sample temperature: 36 °C

all other parameters such as humidity, dilution ratio, and residence time were constant

# What do we know about the composition of volatile nanoparticles?

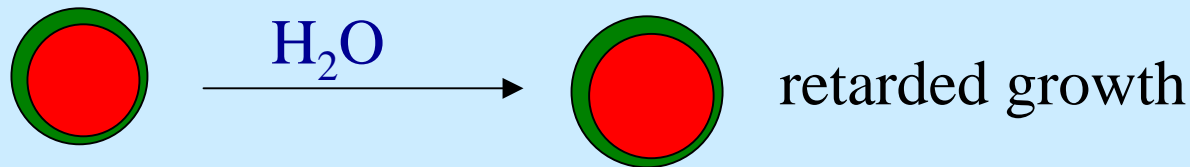
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Sulphuric acid droplets can be coated with organic substances



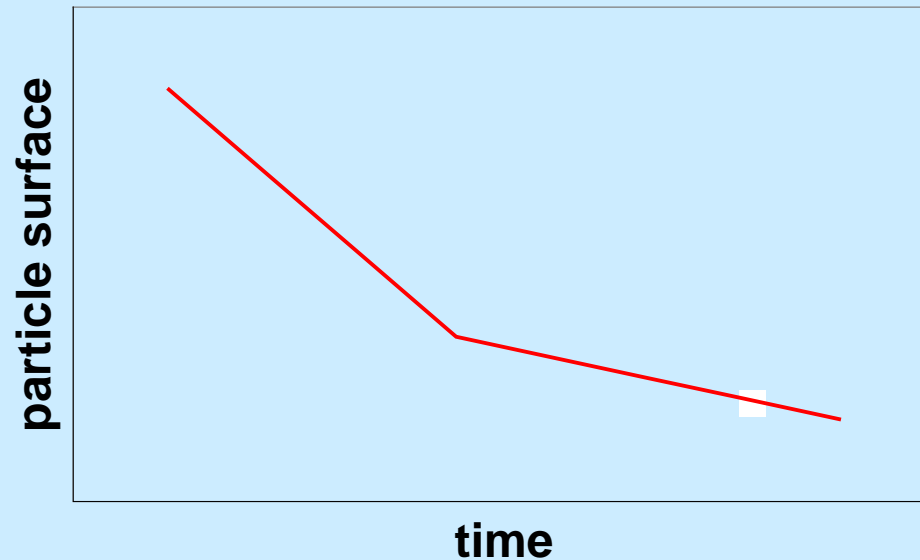
Niessner, R. et al. (1990). *Aerosol Science and Technology* 12, 953-963.

Hygroscopic growth of sulphuric acid droplets is retarded when they are coated with an organic film



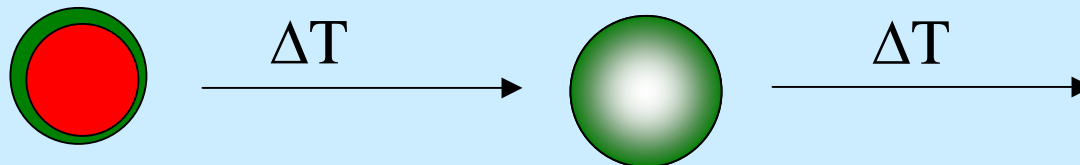
Xiong, J.Q. et al. (1998). *Environmental Science & Technology* 32, 3536-3541.

# Evaporation is divided in two stages



Frey, D.D. & King, C.J. (1986). Aiche Journal 32 (3), 437-443.

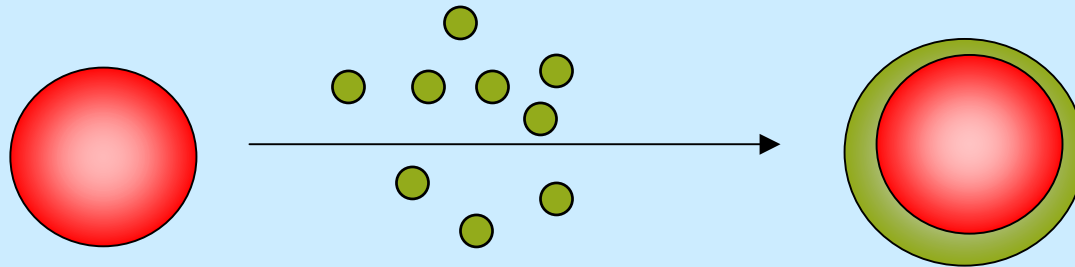
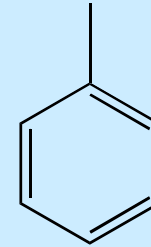
Shulman, M.L. et al. (1996). Geophysical Research Letters 23 (3), 277-280.



# Investigated organic compounds

- Toluene

- hydrophobic
- low water solubility:  $0.5 \text{ g l}^{-1}$
- boiling point:  $111 \text{ }^\circ\text{C}$



assumption:  
condensation is  
proportional to  
particle surface

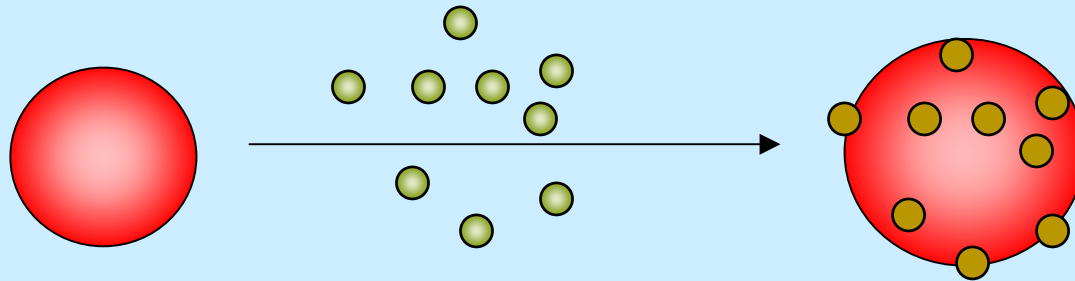


# Investigated organic compounds

- Methanol

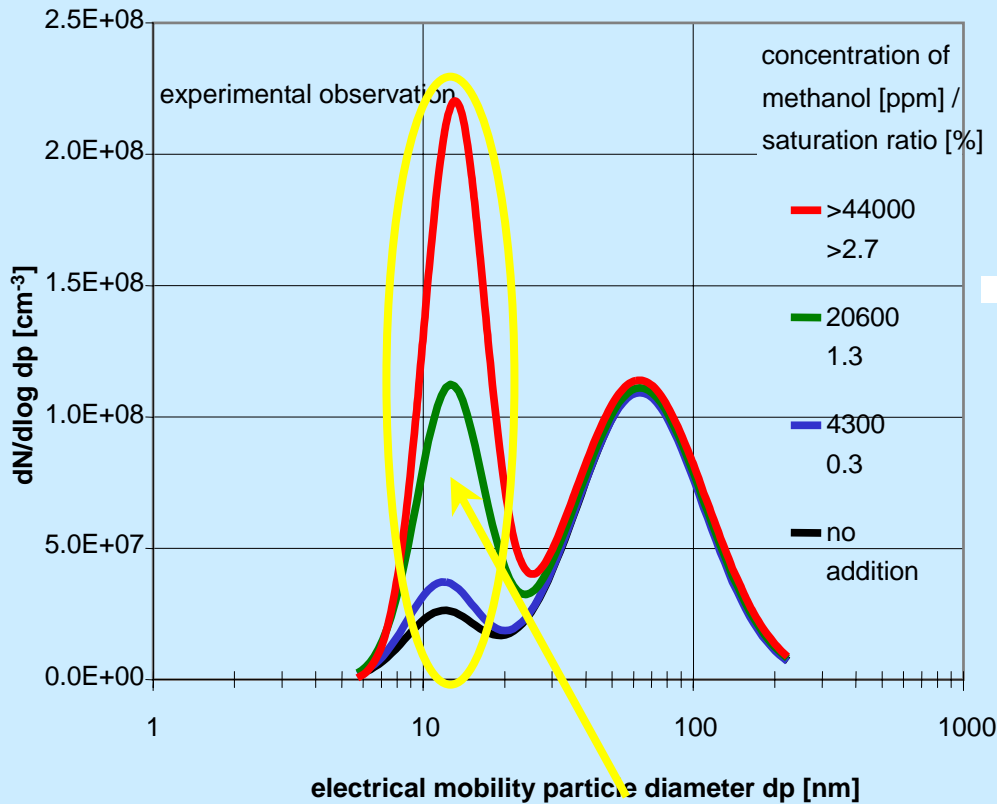
- hydrophilic
- water miscible
- soluble in organic compounds
- boiling point: 65 °C

— OH

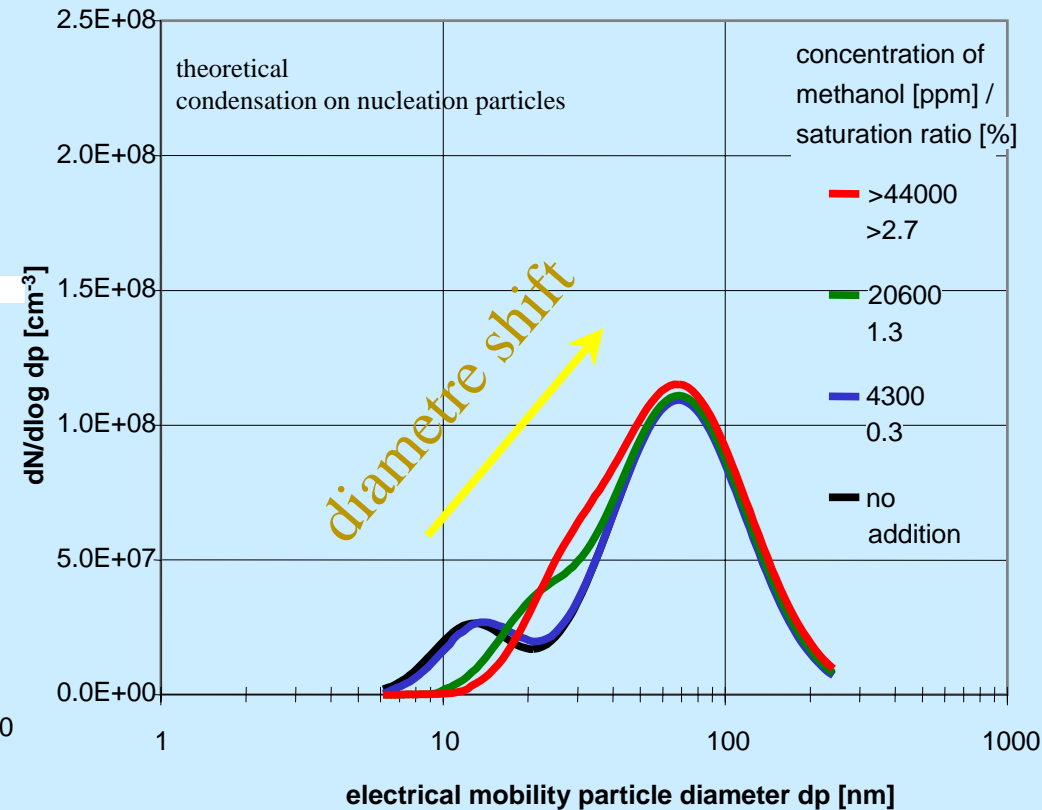


assumption:  
condensation is  
proportional to  
particle surface

# Effect of methanol on nucleation: Weak nucleation

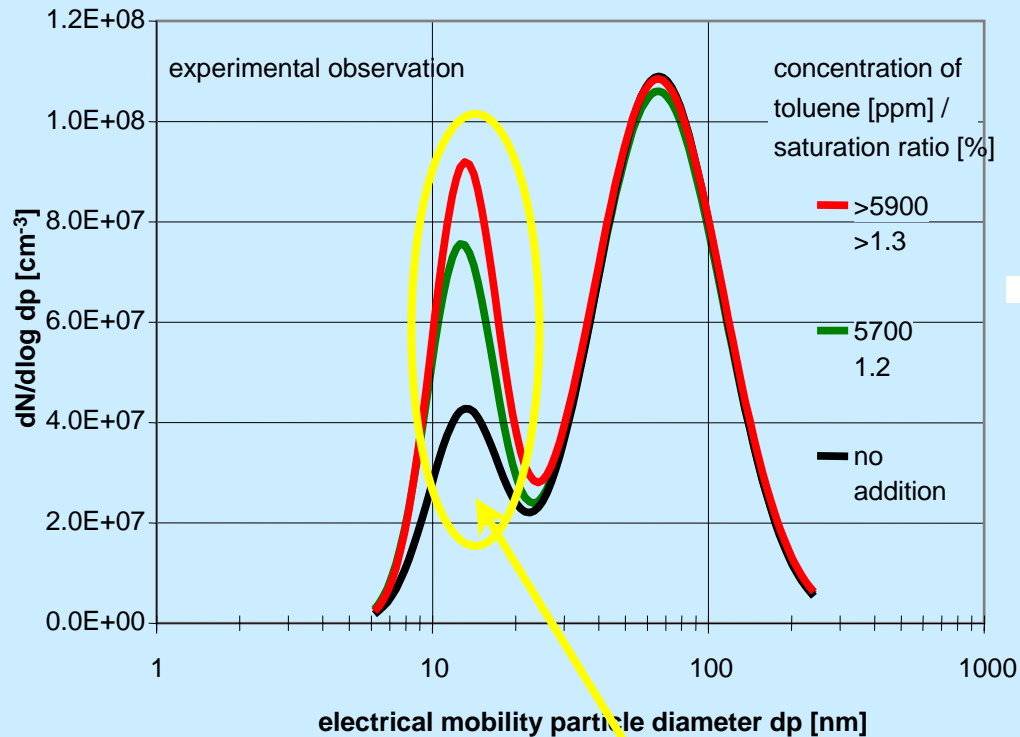


no diameter shift

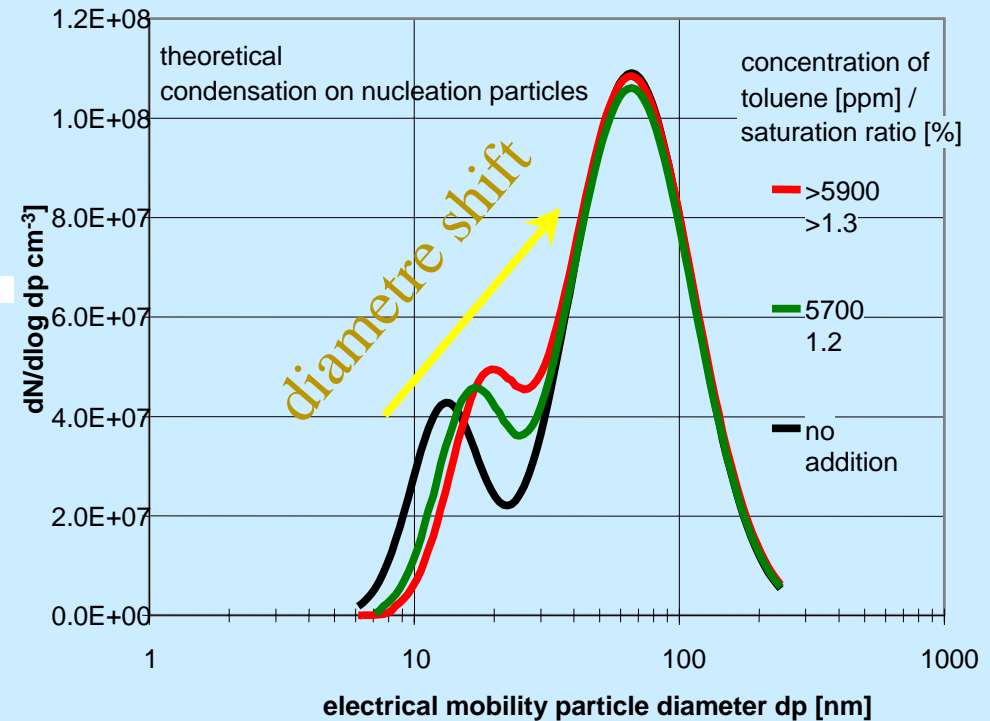


diameter shift

# Effect of toluene on nucleation: Weak nucleation

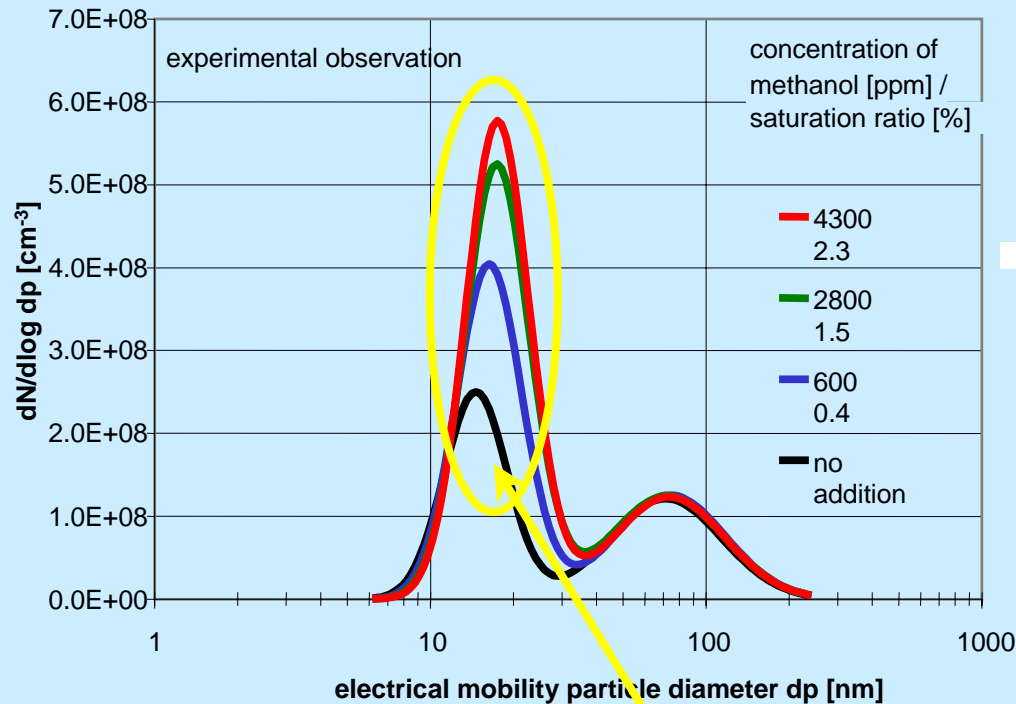


no diametre shift

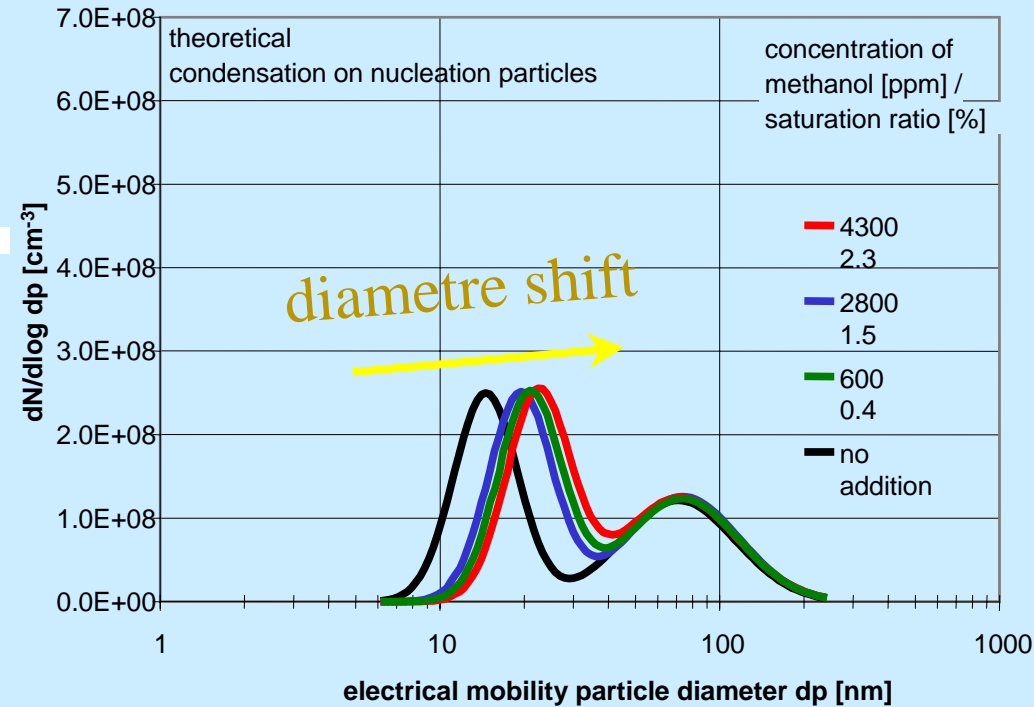


diametre shift

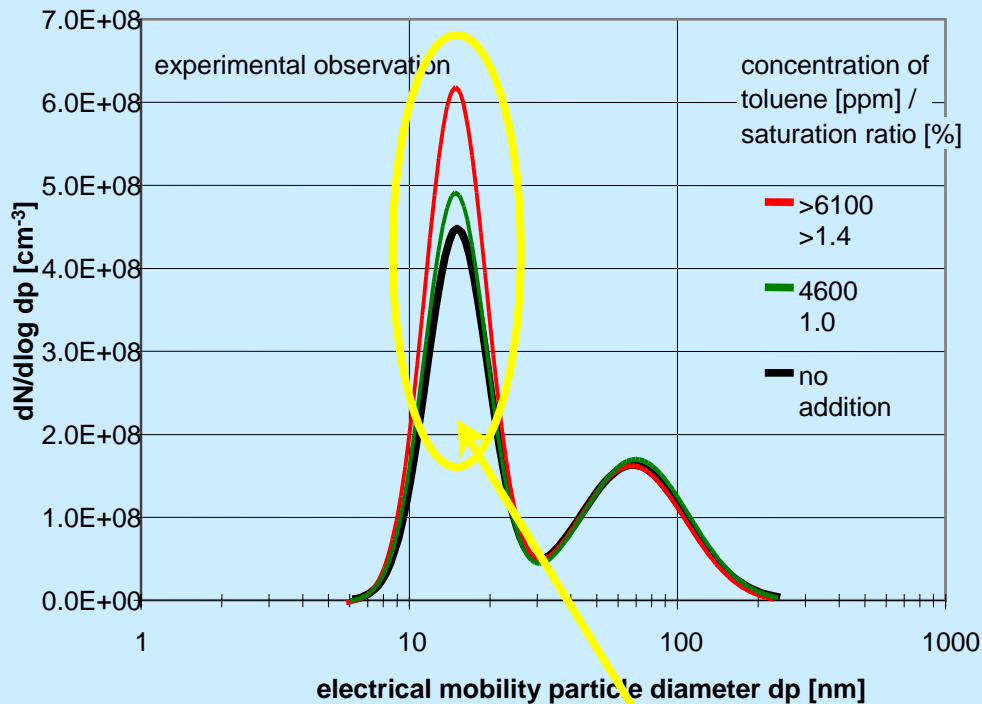
# Effect of methanol on nucleation: Strong nucleation



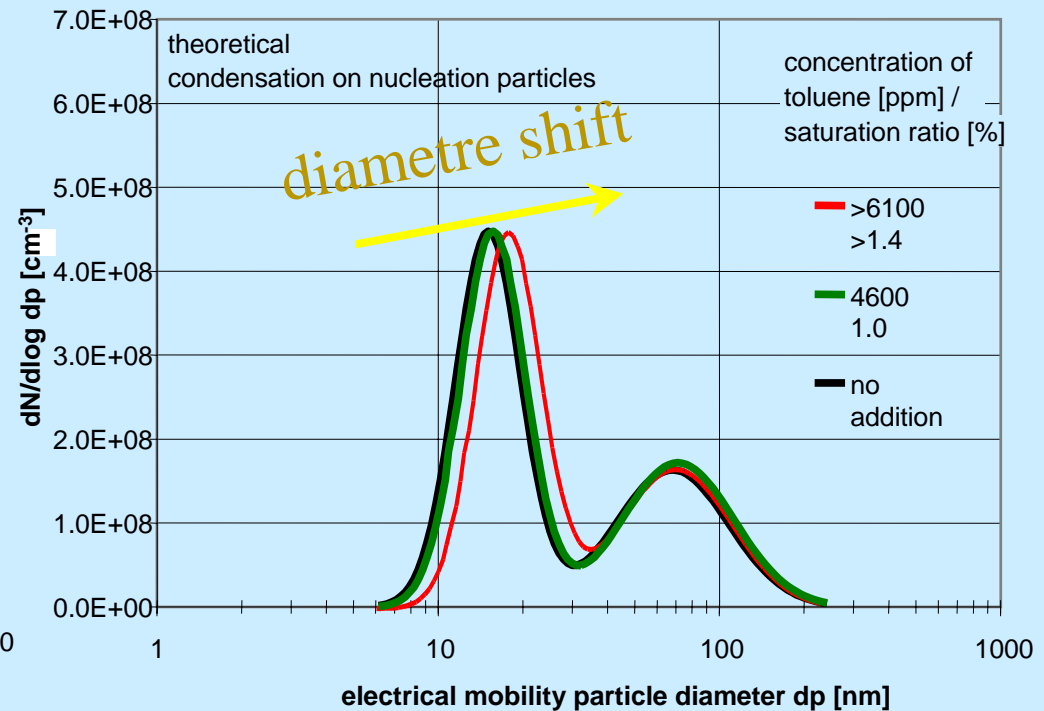
weak diametre shift



# Effect of toluene on nucleation: Strong nucleation



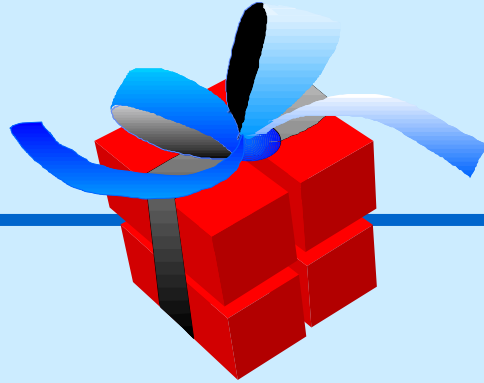
no diametre shift



# Conclusions

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- Organic compounds increased nucleation in diesel exhaust
  - hydrophilic and hydrophobic compounds
  - stronger effect on “weak” than “strong” nucleation
  - stronger effect of methanol than toluene



Thank you for your attention



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