Volatile nano particle formation by diesel cars equipped with modern catalytic filter systems: New Insights from First Gaseous Sulphuric Acid Measurements

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Talk given at 10 ETH conference on *"Combustion Generated Nano Particles"* , Zürich, 21-23 August 2006

Abstract. Gaseous sulfuric acid (GSA) is thought to represent an important if not the most important nucleating gas present in modern diesel automobile exhaust. It triggers the formation of new aerosol particles which grow by condensation and coagulation. Here we report on the first measurements of gaseous sulfuric acid in automobile exhaust. Two experiments have been made: Experiment 1 was a feasibility study involving a stationary passenger diesel car (operated in very low engine load conditions) equipped with a catalytic diesel particle filter system (CDF). Experiment 2 involved systematic measurements with a heavy duty diesel truck engine on a test bench at MAN Nutzfahrzeuge company in Nürnberg (Germany).

In experiment 1 the diesel fuel used had an ultra-low fuel sulfur content FSC of only 5 mg/kg. Here the exhaust leaving the tail pipe was passed through a tunnel where it experienced natural dilution with ambient air.. Measured GSA number concentrations reached up to $1x10^9$ $cm^{-3.}$ Freshly nucleated particles with diameters larger than 3 nm which were also measured. reached concentrations of up to $1x10^5$ cm^{-3} . They were positively correlated with GSA for GSA exceeding a threshold value in the range of $5x10^7$ – $2x10^8$ cm^{-3}. This suggests that GSA was involved in the formation of new volatile particles. However particle growth was strongly increased by condensation of condensable organic molecules (COM).

In experiment 2 two different FSC (7 and 36 mg/kg) were alternatively used. Engine load EL was systematically varied (25., 50, 75, and 100%). Three after treatment scenarios were investigated: CDF,

OXICAT without filter, and no after treatment. It was found that exhaust GSA increases with increasing FSC. GSA also increases with increasing EL. GSA increased very markedly when a catalyst was used.

Also experiment 2 indicates that particle formation by nucleation is driven by GSA while particle growth is driven not only by GSA but also by COM.

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Background Information

Sulphuric Acid Molecule H_2SO_4

- Represents powerful aerosol precursor
- Is also emitted by combustion of sulphur-containing fossil fuels

SULFURIC ACID MOLECULE H_2SO_4

- Most important property : large **GA**

→ proton transfer to other molecule with large **PA** (Atmosphere : **H_2O**)

→ Gas-Phase Hydrates **$H_2SO_4(H_2O)_n$**

→ **Nucleation** **$(H_2SO_4)_a(H_2O)_w$** cluster

SULFURIC ACID MOLECULE
H_2SO_4

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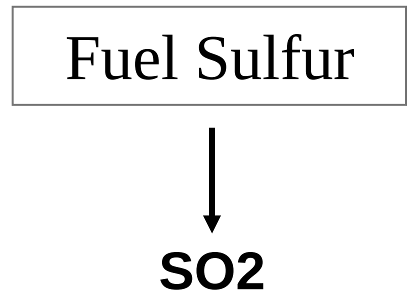
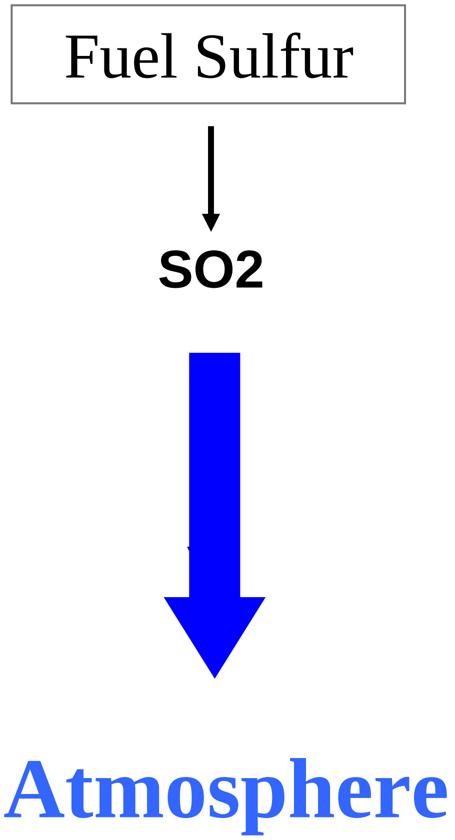
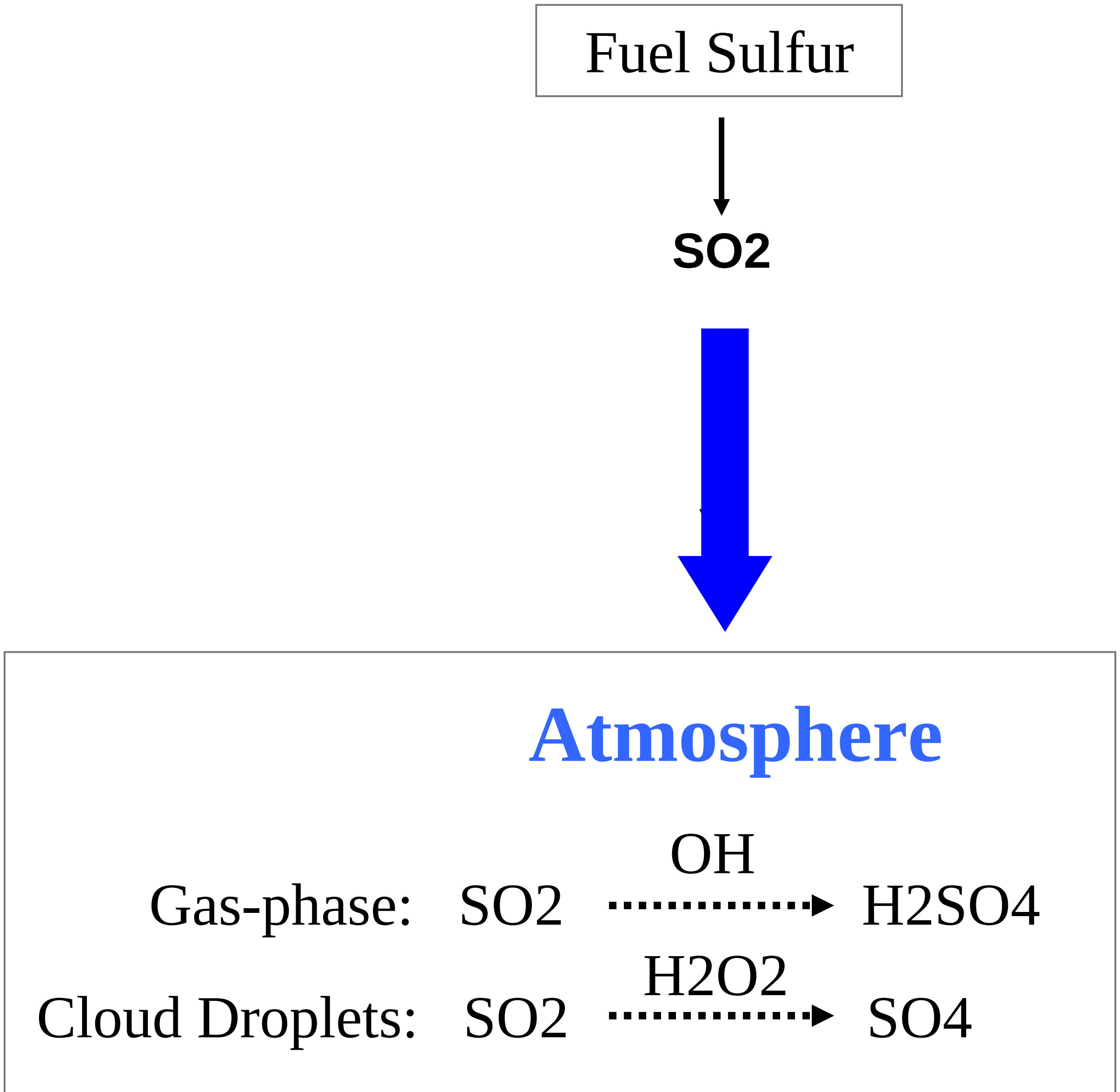
  (Atmosphere : **H_2O**)
  → Gas-Phase Hydrates **$H_2SO_4(H_2O)_n$**
  → **Nucleation** **$(H_2SO_4)_a(H_2O)_w$** cluster
- Atmosphere :
  Secondary H_2SO_4: formed in Atmosphere from **SO_2**
  Primary H_2SO_4 : released from combustion

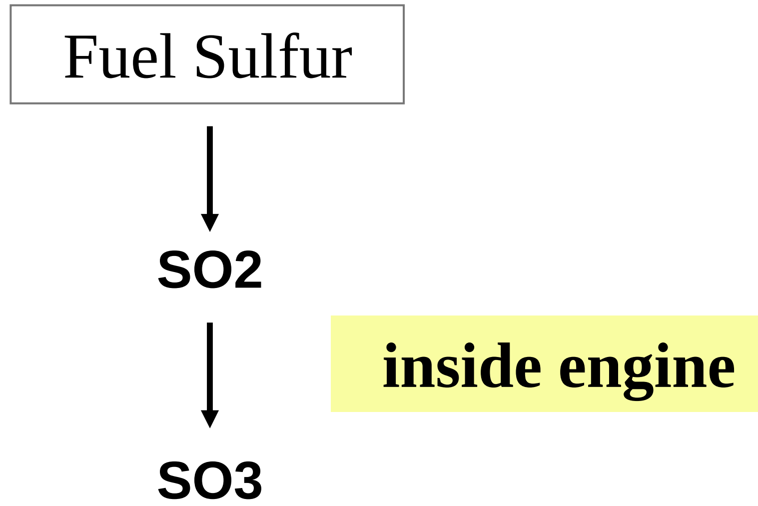
Example: mobile combustion sources (Aircraft, Ships, cars)

Simplified Scheme of Fuel Sulphur Conversion


Fuel Sulfur
SO_2


Fuel Sulfur
SO2
Atmosphere


Fuel Sulfur
SO2
Atmosphere
OH
Gas-phase: SO2 H2SO4
H2O2
Cloud Droplets: SO2 SO4


Fuel Sulfur
SO2
inside engine
SO3

Fuel Sulfur

↓

SO_2

↓

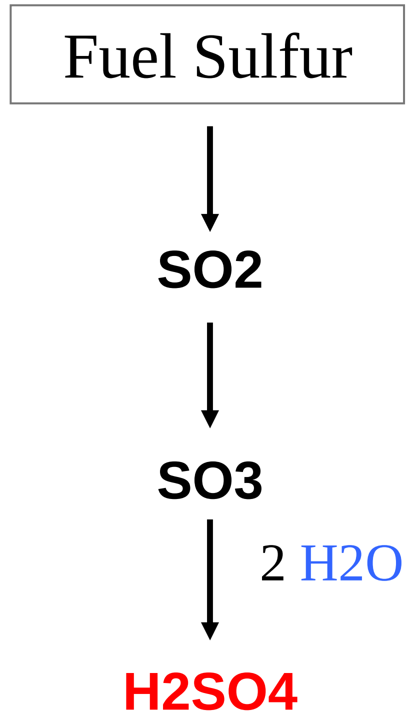
SO_3

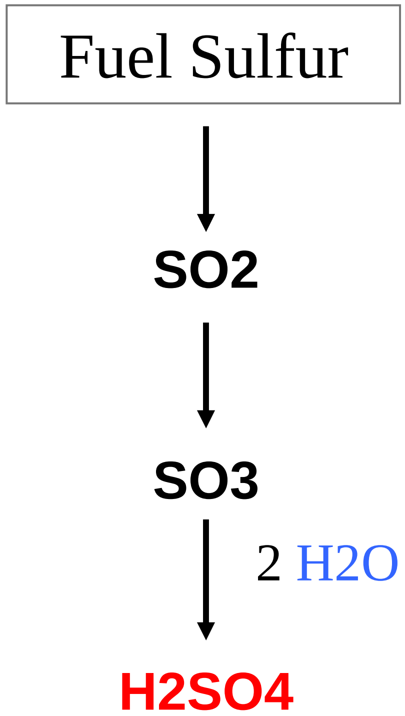
SO_2 to SO_3

conversion inside engine

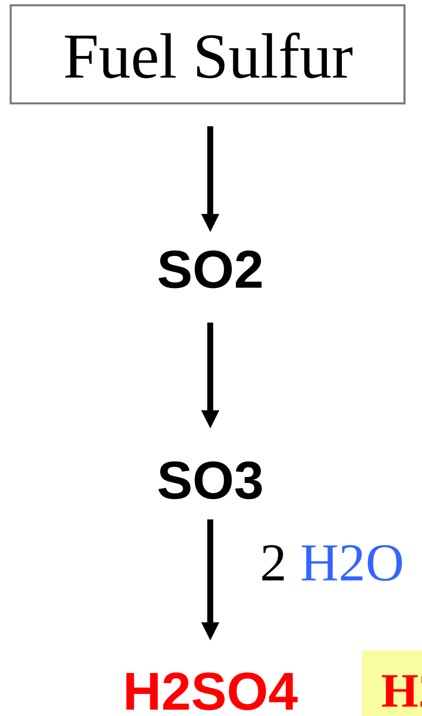
example:

aircraft gas turbine engine 2 %


Fuel Sulfur
SO2
SO3
2 H2O
H2SO4



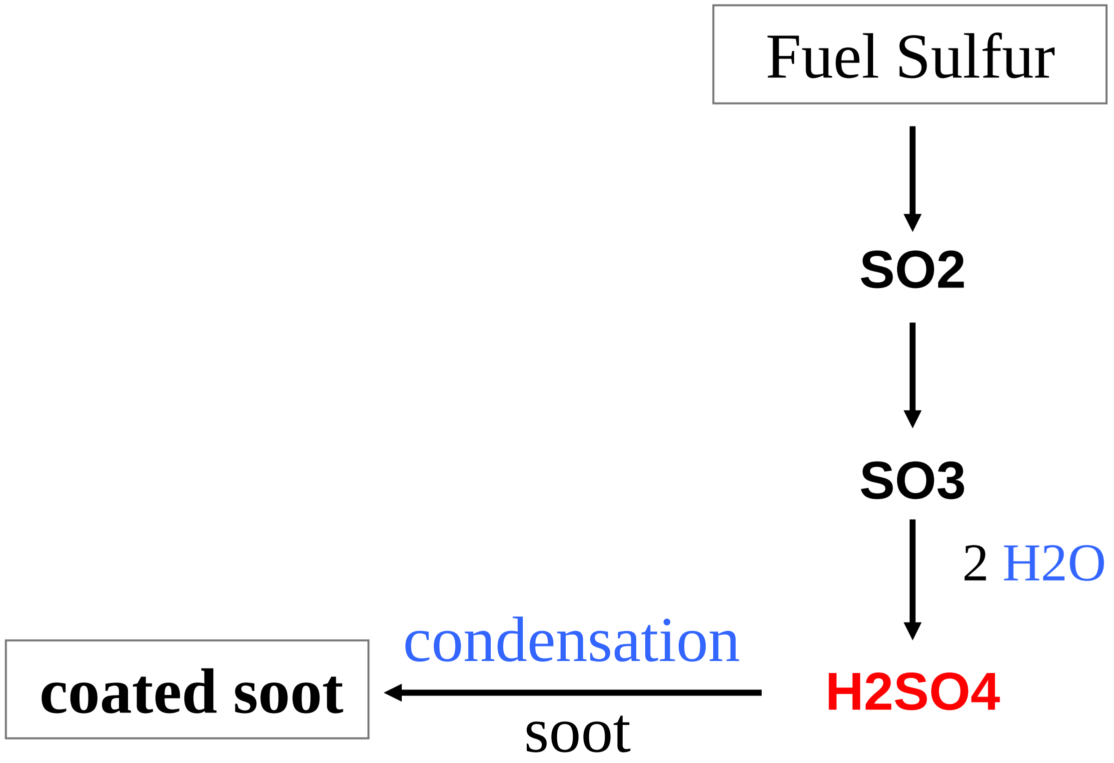
Process originally measured in the laboratory by MPIK-Heidelberg

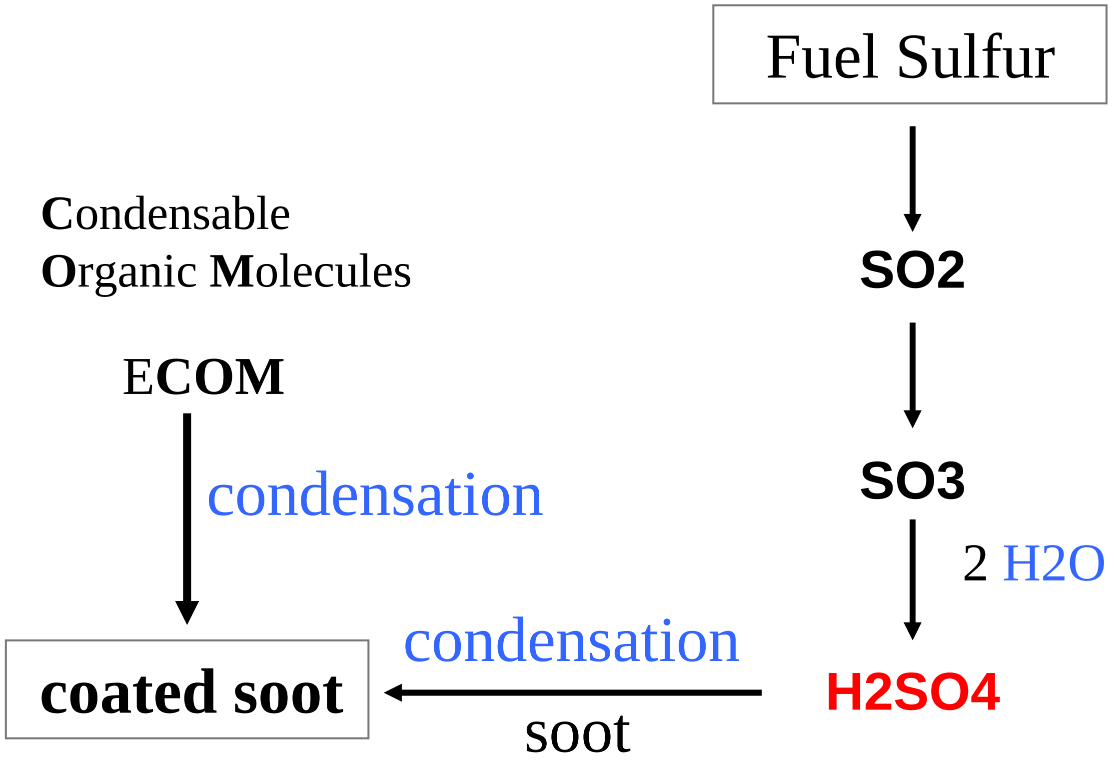


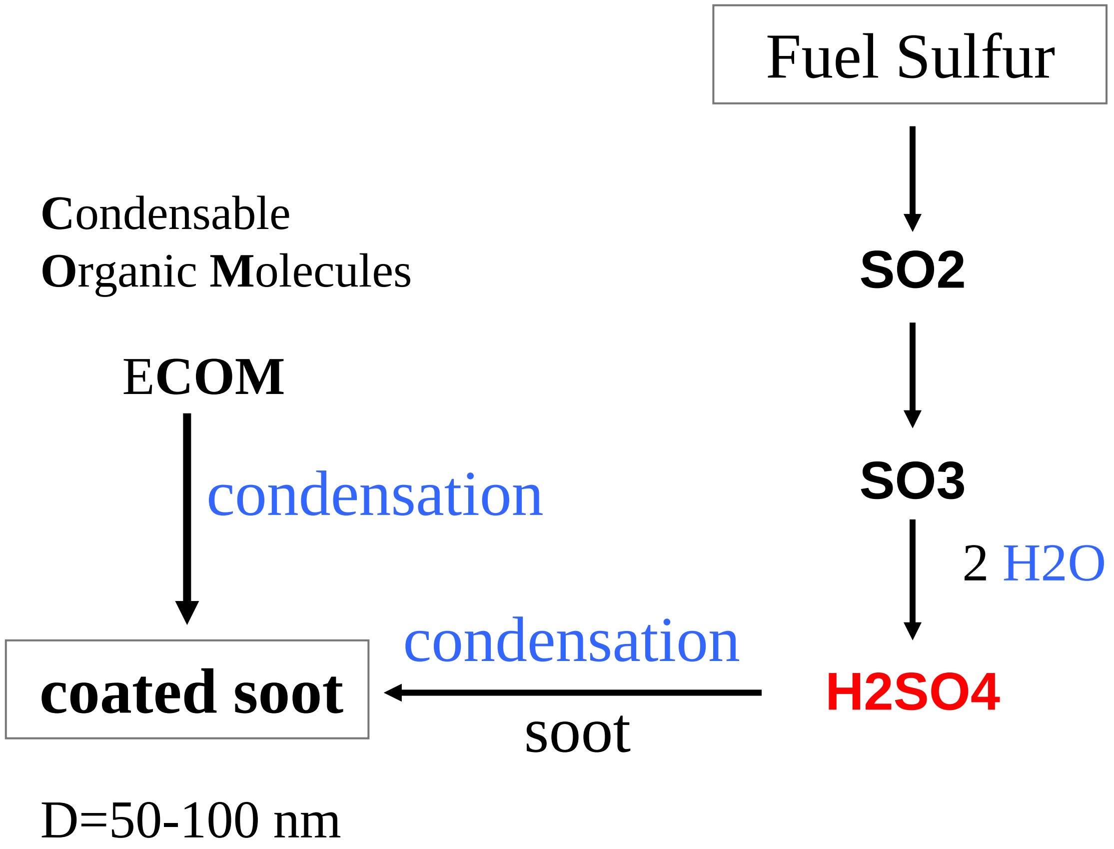
H2SO4 has very low vapour pressure

→ H2SO4 becomes supersaturated in cooling exhaust

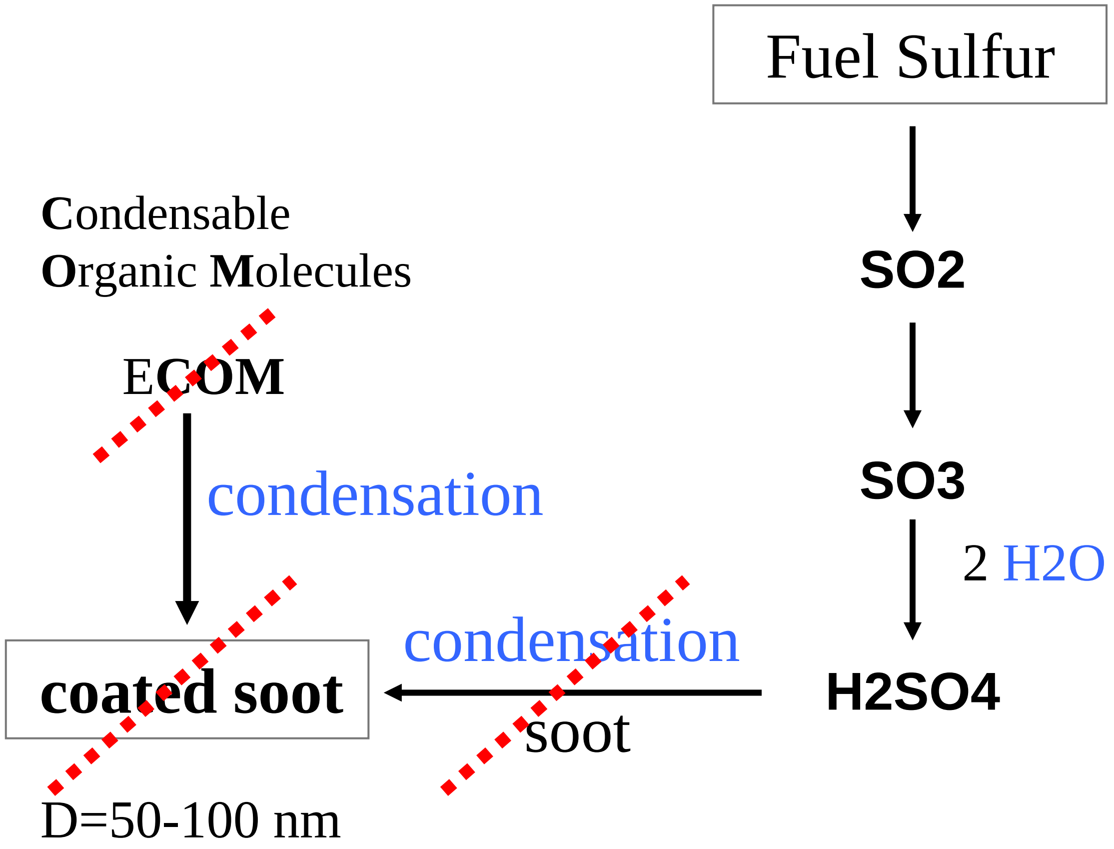
→ H2SO4 condensation

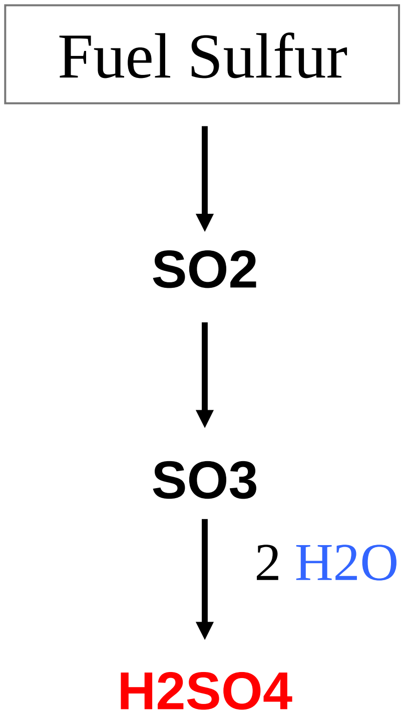

Fuel Sulfur
SO2
SO3
2 H2O
H2SO4
condensation
soot
coated soot


Fuel Sulfur
SO2
SO3
2 H2O
H2SO4
Condensable
Organic Molecules
ECOM
condensation
condensation
soot
coated soot

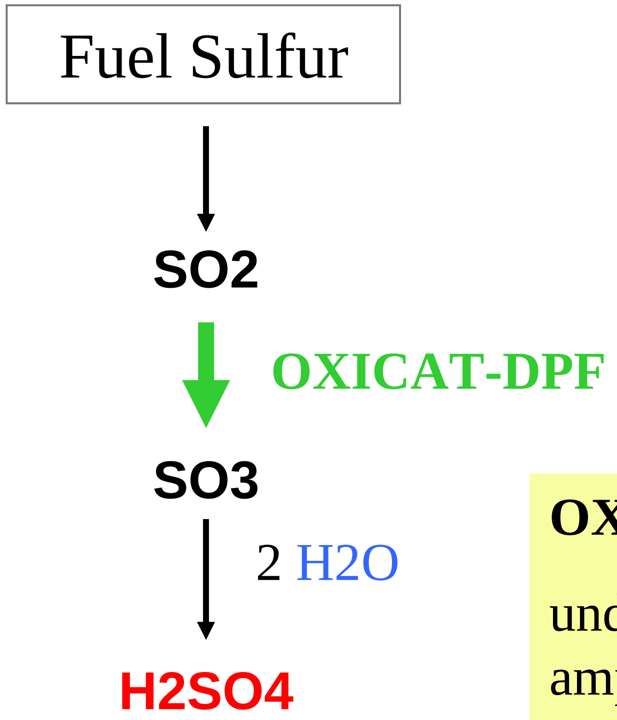

Fuel Sulfur
SO2
SO3
2 H2O
H2SO4
Condensable
Organic Molecules
ECOM
condensation
condensation
soot
coated soot
D=50-100 nm

Modern diesel car is equipped with OXICAT-DPF



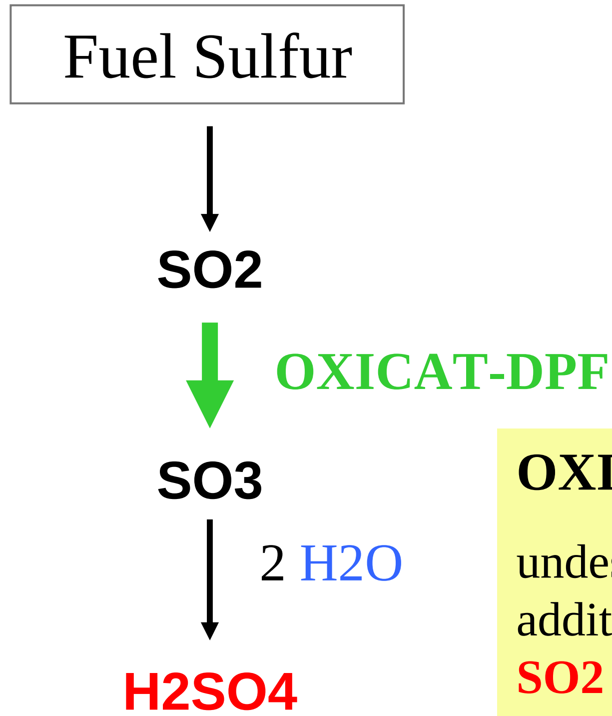


Modern diesel car is equipped with OXICAT-DPF



OXICAT

undesired side effect:
amplifies conversion
SO2 → SO3

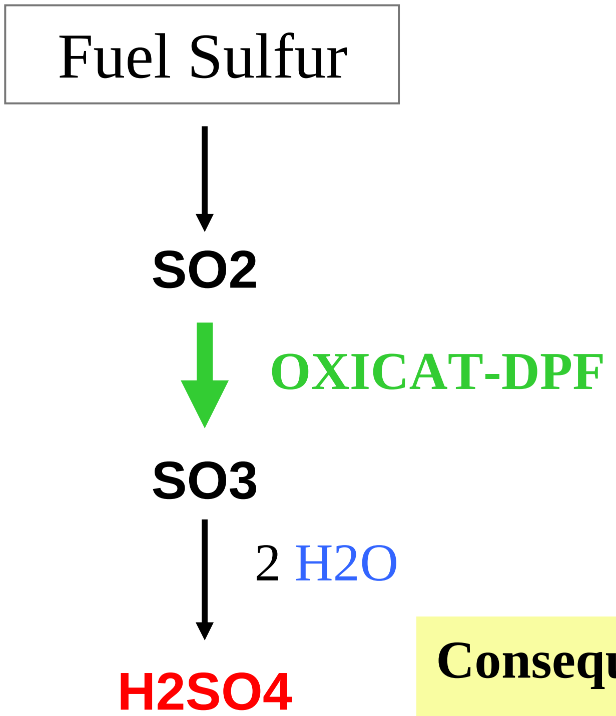


OXICAT

undesired side effect:
additional conversion
SO_2 → SO_3

→ increased

H_2SO_4 emission ?

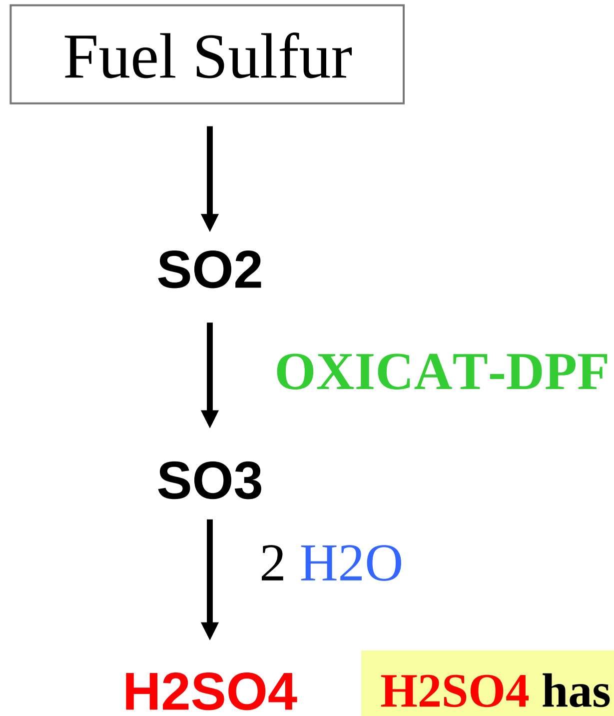


Consequence:

FSC regulation in EC

<50 ppmM (2005)

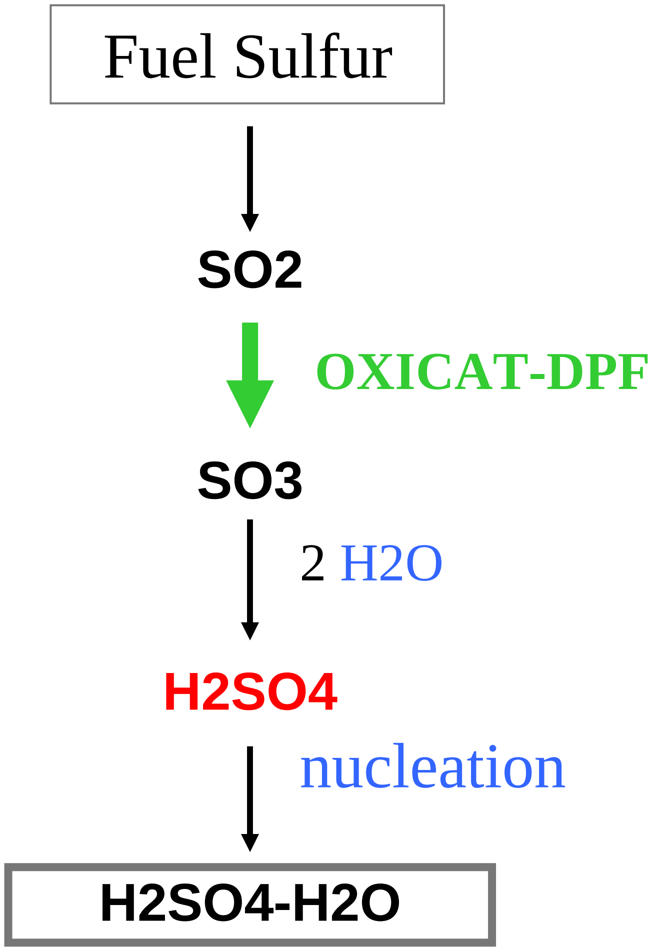
<10 ppmM (2009)



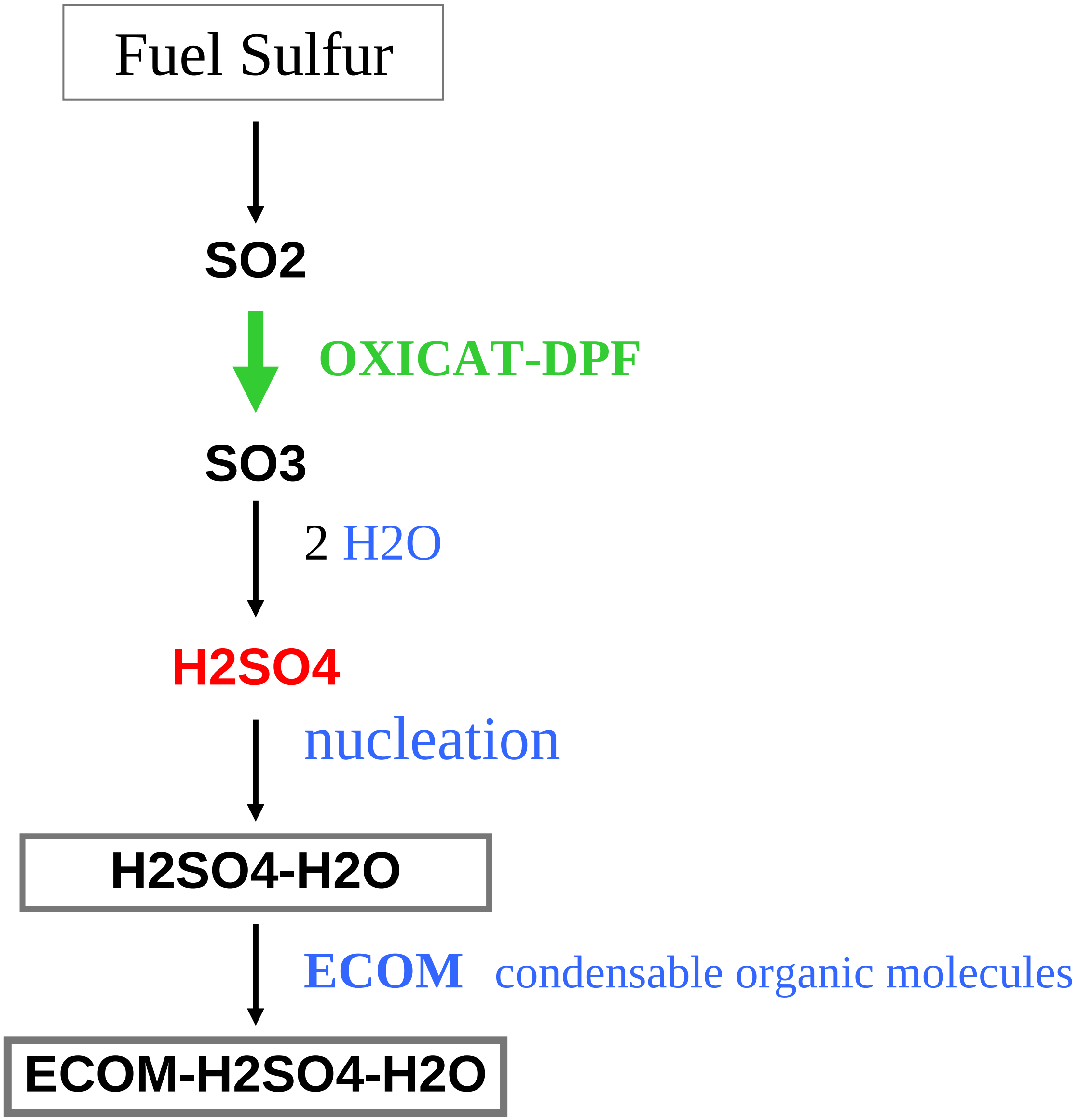
H_2SO_4 has very low vapour pressure

→ H_2SO_4 may become highly supersaturated in cooling exhaust

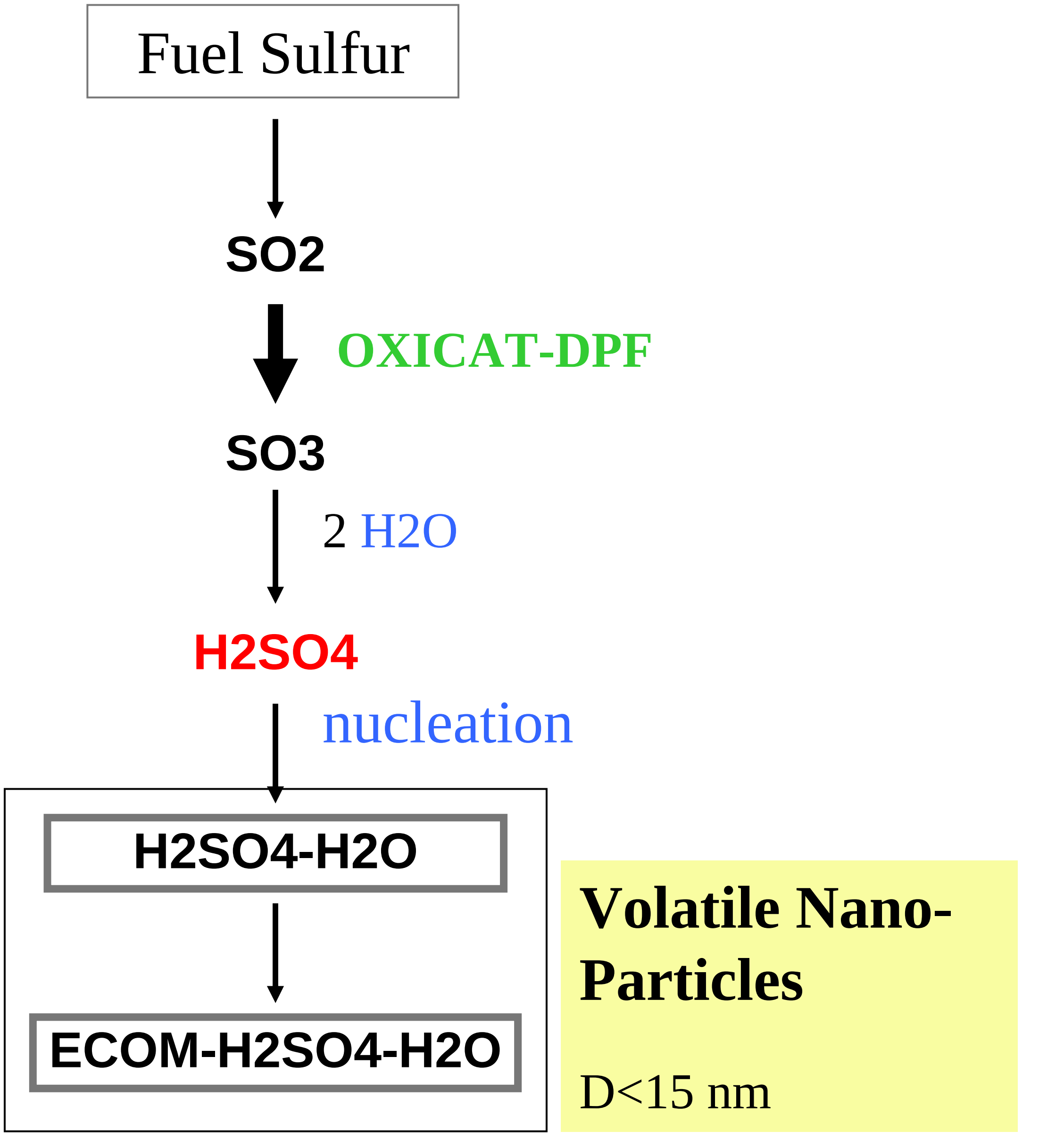
→ H_2SO_4/H_2O nucleation ?



Fuel Sulfur
SO2
OXICAT-DPF
SO3
2 H2O
H2SO4
nucleation
H2SO4-H2O



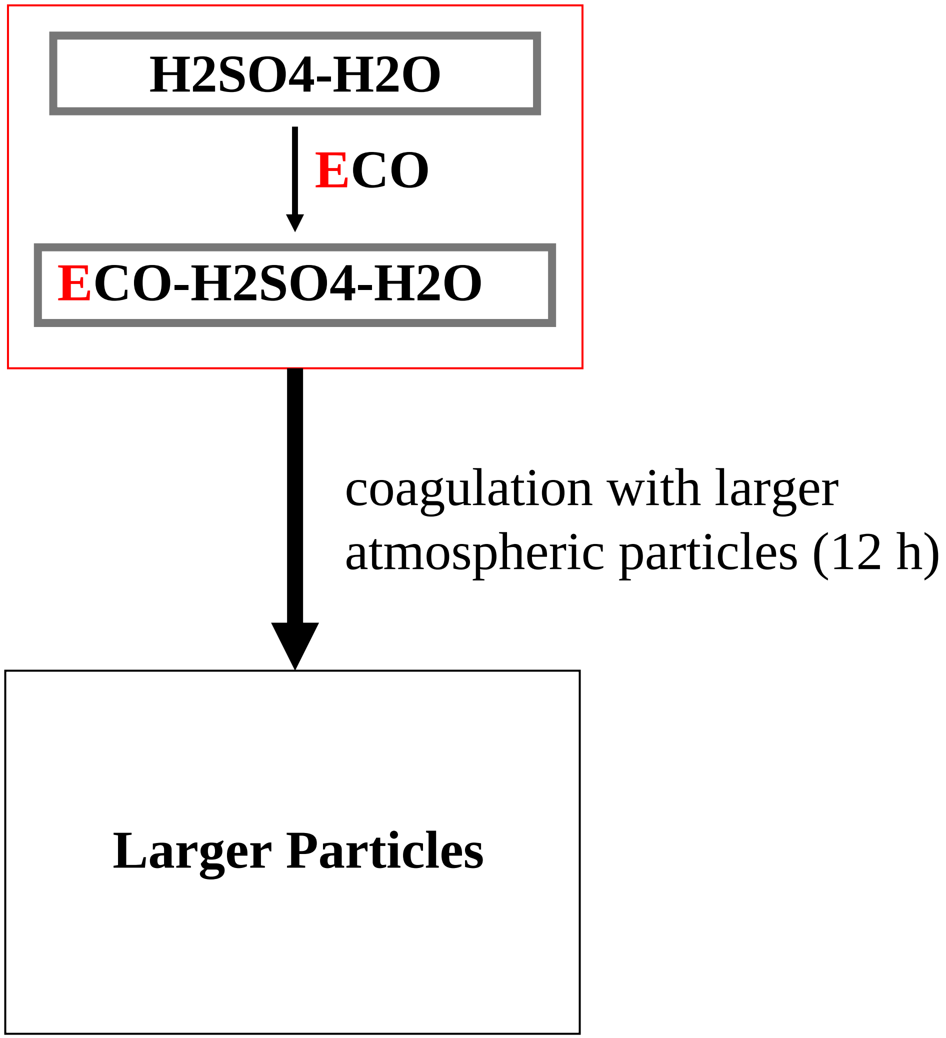
Fuel Sulfur
SO2
OXICAT-DPF
SO3
2 H2O
H2SO4
nucleation
H2SO4-H2O
ECOM
condensable organic molecules
ECOM-H2SO4-H2O

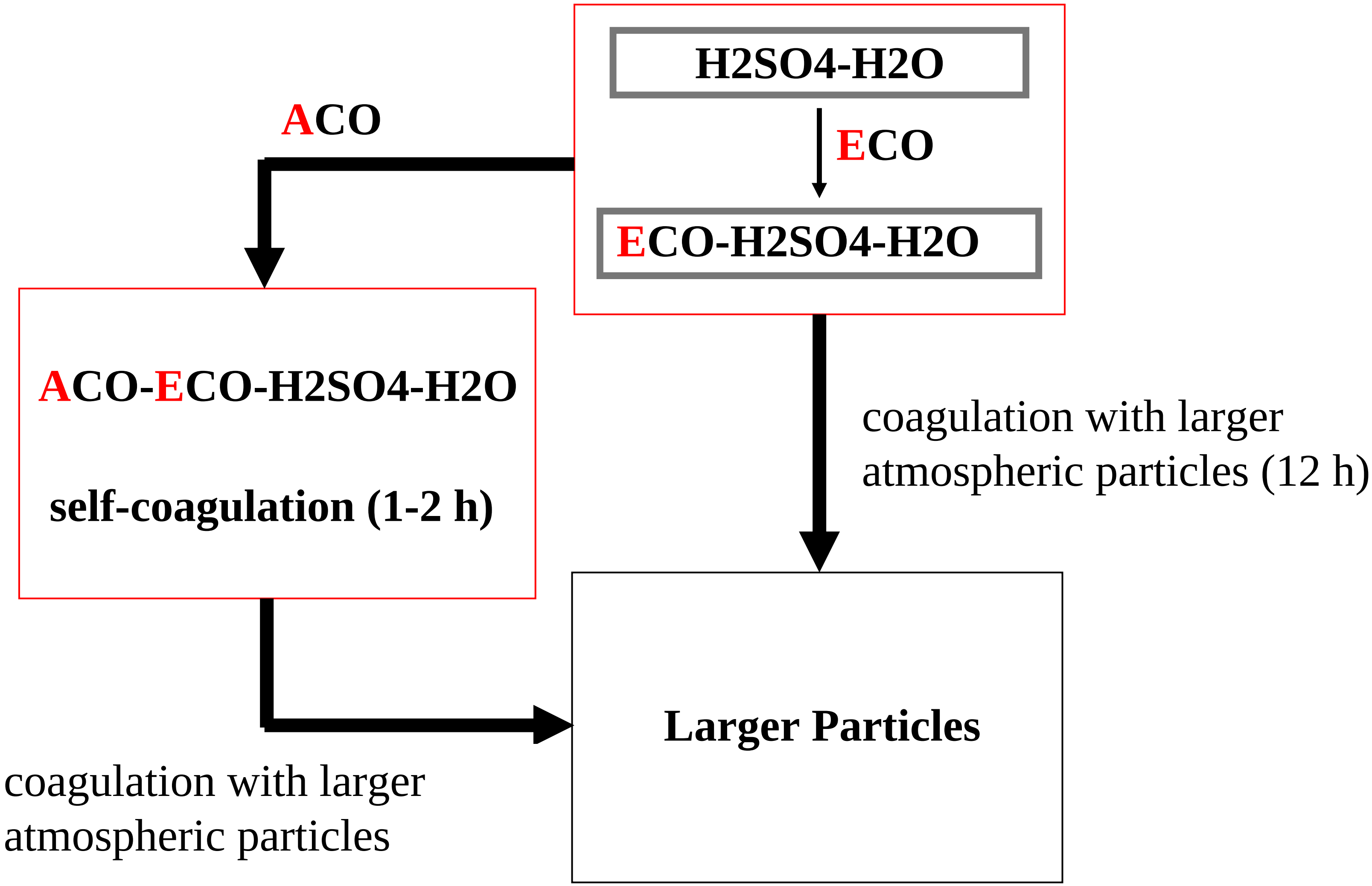


Fuel Sulfur
SO2
OXICAT-DPF
SO3
2 H2O
H2SO4
nucleation
H2SO4-H2O
ECOM-H2SO4-H2O
Volatile Nano-Particles
D<15 nm

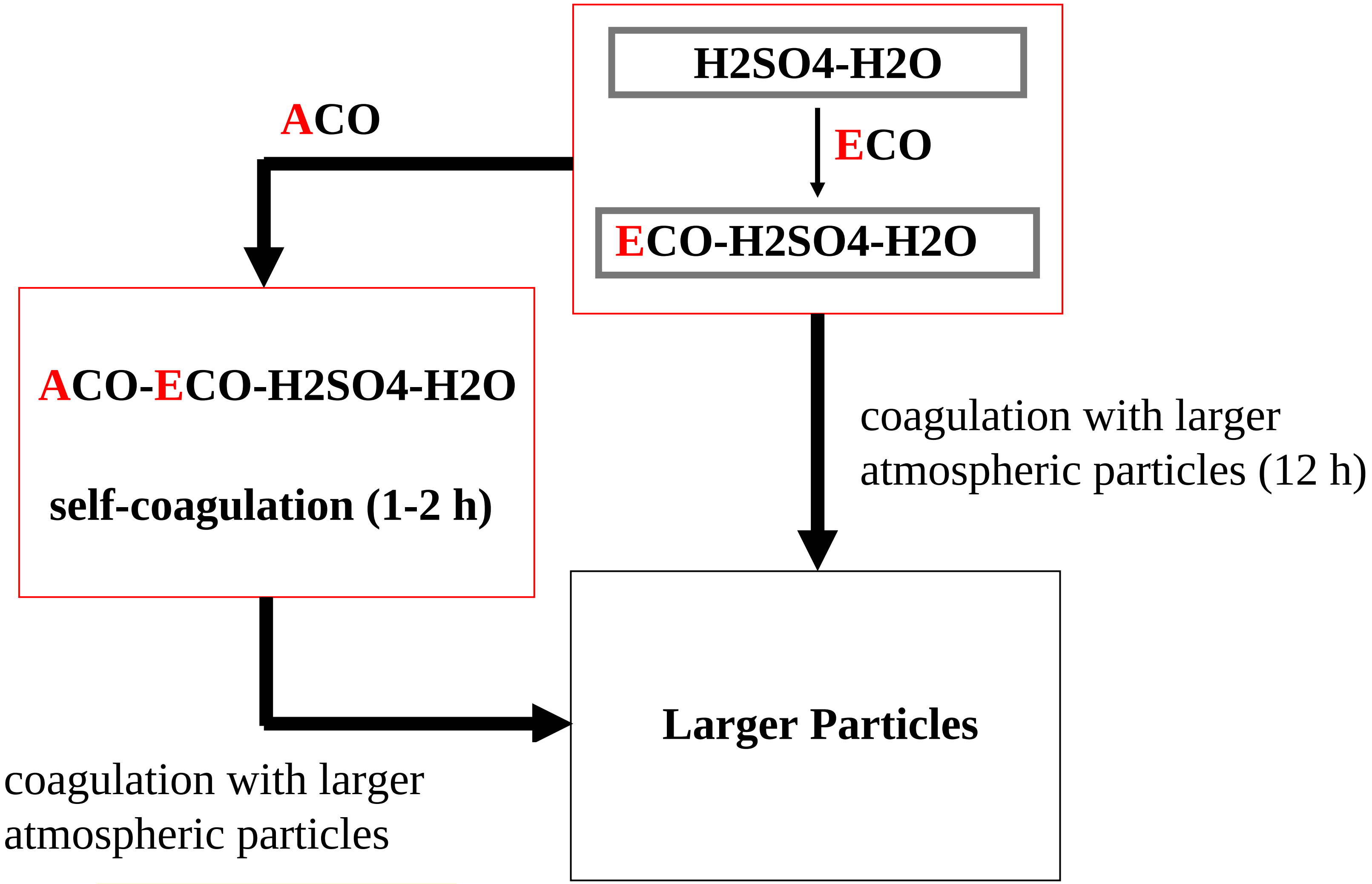
Fate of small particles in Atmosphere

Coagulation


H2SO4-H2O
ECO
ECO-H2SO4-H2O
coagulation with larger atmospheric particles (12 h)
Larger Particles



H2SO4-H2O
ACO
ECO
ECO-H2SO4-H2O
ACO-ECO-H2SO4-H2O
self-coagulation (1-2 h)
coagulation with larger atmospheric particles (12 h)
Larger Particles
coagulation with larger atmospheric particles



grown particles
live longer !

Open Questions

- Fraction F of fuel sulphur converted to gaseous H_2SO_4 emitted
- New particle formation by nucleation downstream of tail pipe
- New particle growth

Investigations of Nano-Particle Formation and Growth

- Stationary passenger car at Hyytiälä (Finland) (first test)
- Diesel engine test bed at MAN Nürnberg (Germany) (systematic measurements under well defined conditions)

Gaseous H_2SO_4 Measurements in Diesel Car Exhaust (First Test)

- Stationary experiment (low engine load EL)

Gaseous H_2SO_4 Measurements in Diesel Car Exhaust (First Test)

- Stationary experiment (low engine load EL)
- Engine frequency varied

Gaseous H_2SO_4 Measurements in Diesel Car Exhaust (First Test)

- Stationary experiment (low engine load EL)
- Engine frequency varied
- FSC=5 ppm

Gaseous H_2SO_4 Measurements in Diesel Car Exhaust (First Test)

- Stationary experiment (low engine load EL)
- Engine frequency varied
- FSC=5 ppm
- Passenger diesel car: Peugeot 607 (year 2004) equipped with OXICAT-DPF

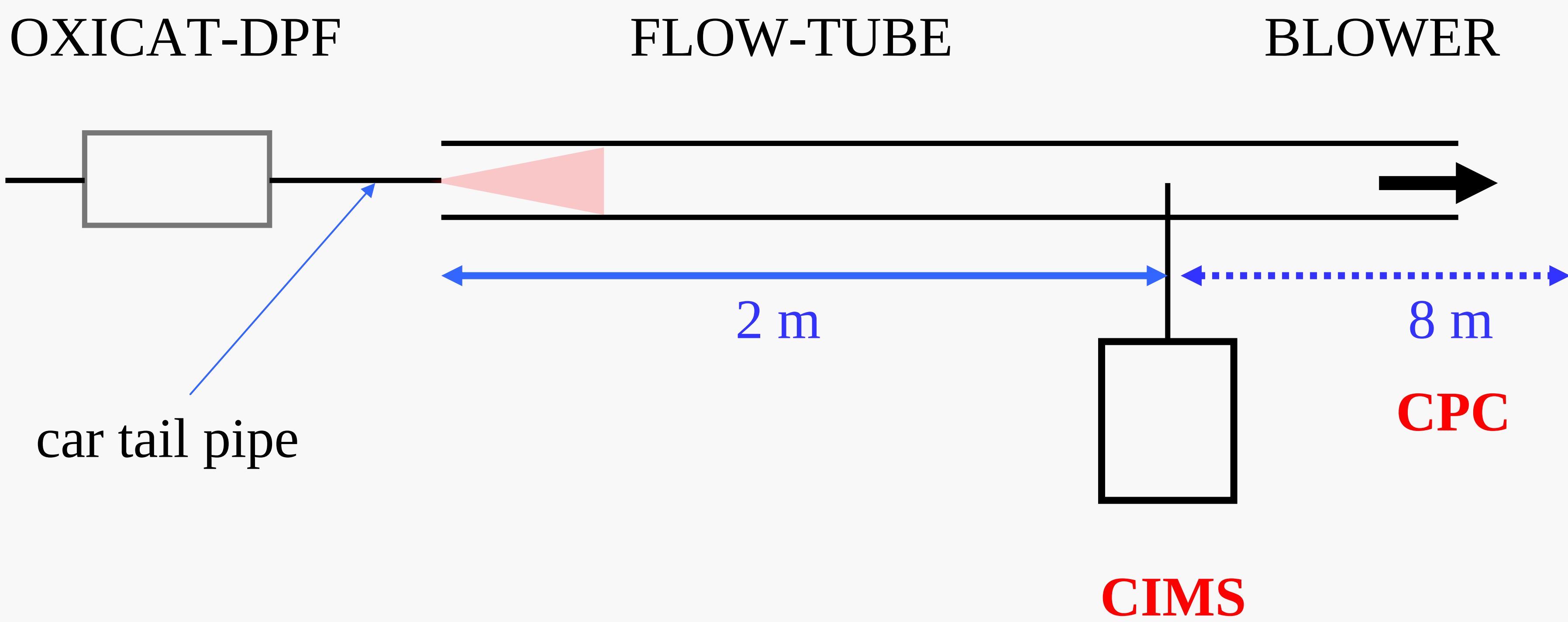
Gaseous H_2SO_4 Measurements in Diesel Car Exhaust (First Test)

- Stationary experiment (low engine load EL)
- Engine frequency varied
- FSC=5 ppm
- Passenger diesel car: Peugeot 607 (year 2004) equipped with OXICAT-DPF
- H_2SO_4 measurement 2 m downstream of exhaust pipe

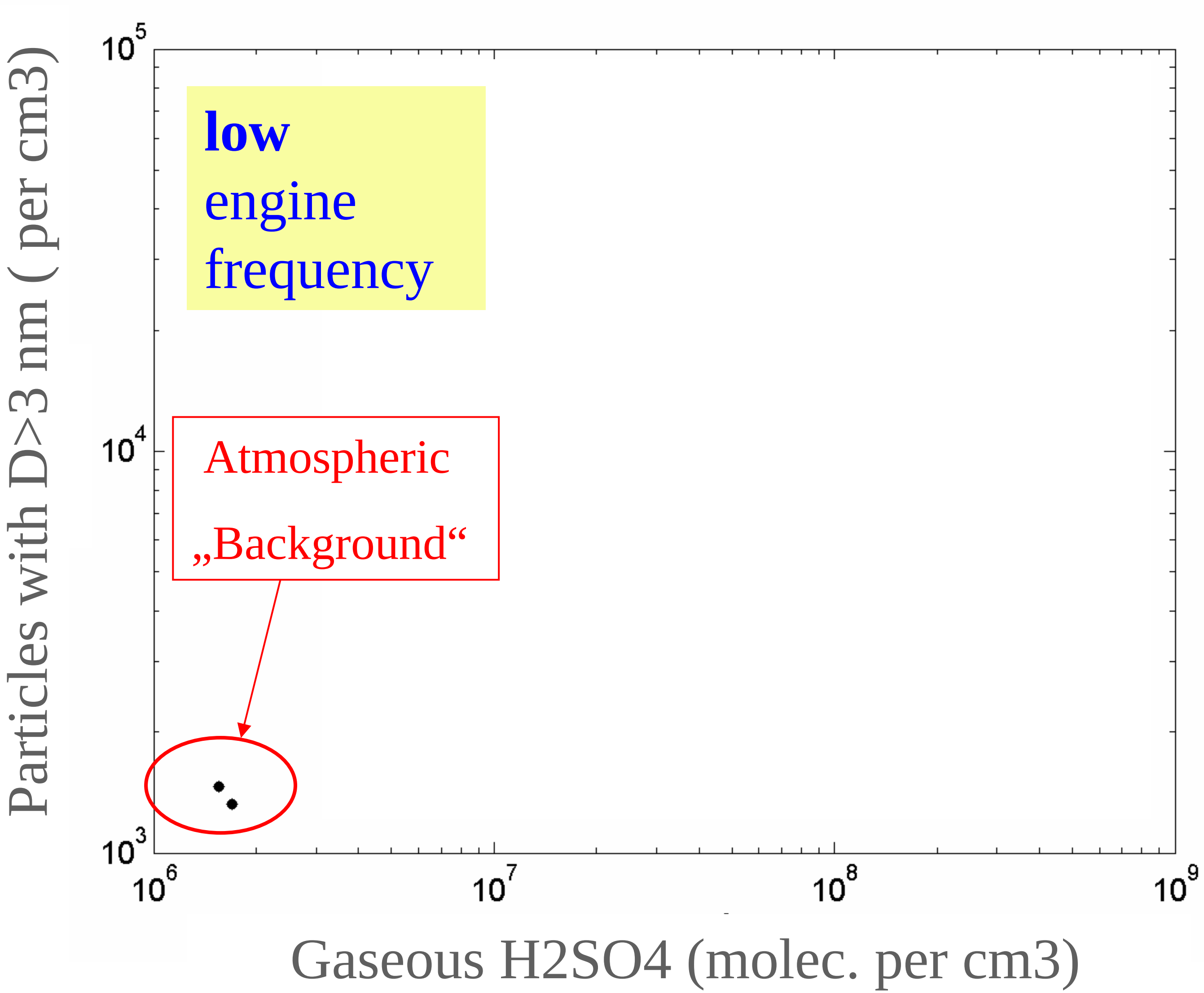
Gaseous H_2SO_4 Measurements in Diesel Car Exhaust (First Test)

- Stationary experiment (low engine load EL)
- Engine frequency varied
- FSC=5 ppm
- Passenger diesel car: Peugeot 607 (year 2004) equipped with OXICAT-DPF
- H_2SO_4 measurement 2 m downstream of exhaust pipe
- H_2SO_4 measurement by ITCIMS-method originally developed by MPIK- Heidelberg

Stationary Diesel Car Experiment



Gaseous **H2SO4** measured in Stationary Experiment with modern diesel passenger car (FSC=5 ppmM) ; as engine frequency is increased H2SO4 increases



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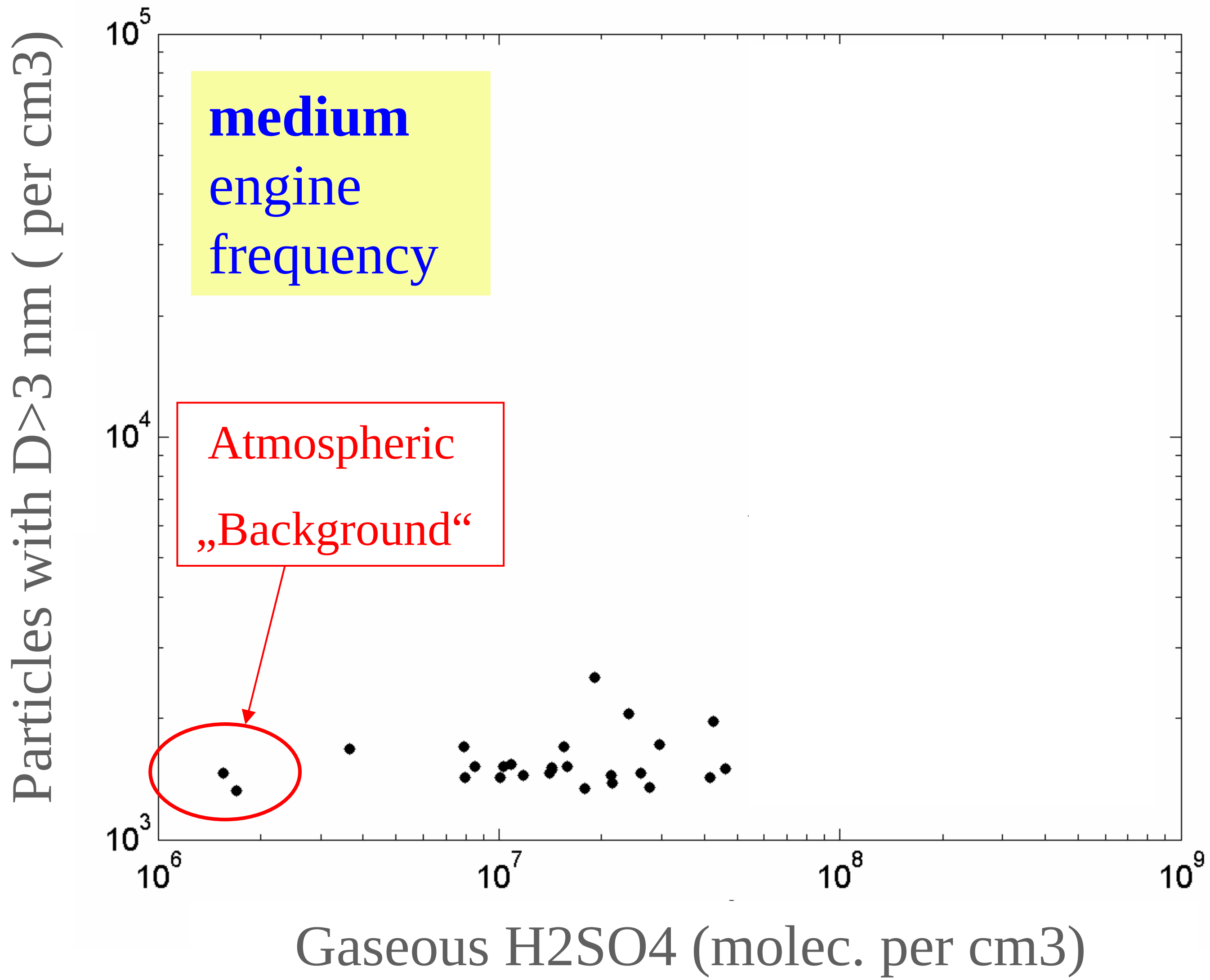

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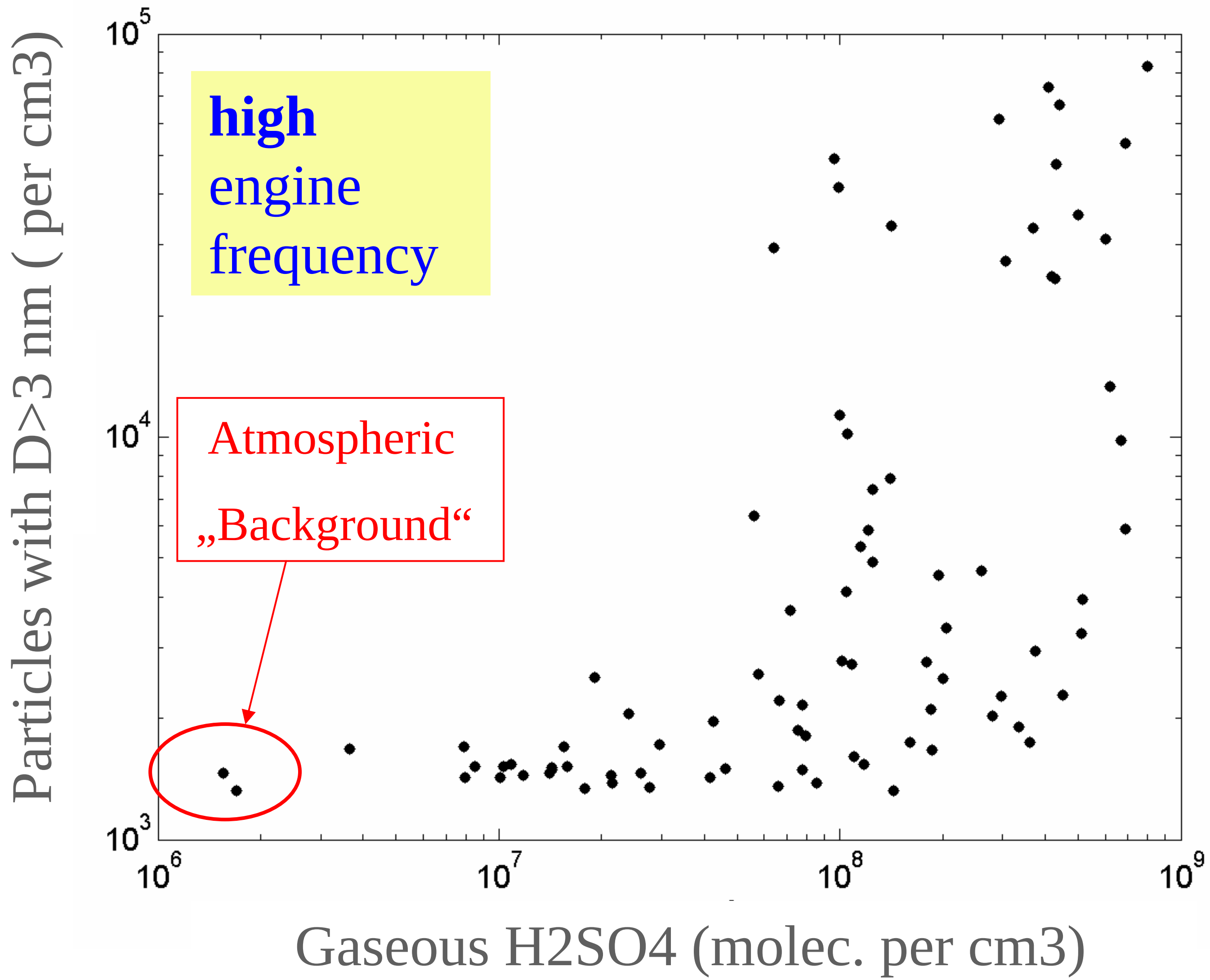

Diesel Engine exhaust Measurements at MAN Nutzfahrzeuge (Nürnberg, Germany)

- Heavy duty diesel vehicle engine

MAN heavy duty Diesel engine

- Type: MAN D 2066 LF 31
- Six cylinders (10.5 l)

  with common rail fuel injection
- Euro 4 norm
- Max power: 324 kW at 1900 rpm
- Max torque: 2100 Nm at 1000-1400 rpm

Diesel Engine exhaust Measurements at MAN Nutzfahrzeuge (Nürnberg, Germany)

- Heavy duty diesel vehicle engine
- Engine load: 25, 50, 75, 100 %
- FSC : 7 , 36 ppmM

Diesel Engine exhaust Measurements at MAN Nutzfahrzeuge (Nürnberg, Germany)

- Heavy duty diesel vehicle engine
- Engine load: 25, 50, 75, 100 %
- FSC : 7 , 36 ppmM
- exhaust aftertreatment scenarios

  - no aftertreatment

  - OXICAT (volume=5 l , 40 g Pt/ft3)

  - CDPF (sinter material coated with Pt (20gPt/m2)

Figures showing data of measurements at MAN

presently cannot be included since they are contained in a paper submitted to *NATURE* journal

Summary

- Gaseous H_2SO_4 in exhaust very low when catalyst not used
- Gaseous H_2SO_4 in exhaust is much higher when catalyst is used

  - OXICAT :

  - CDPF :
- Volatile nano particle formation by H_2SO_4/H_2O nucleation
- Volatile nano particle growth by condensation of H_2SO_4/H_2O
- Additional growth by ECOM condensation on H_2SO_4/H_2O particles

Conclusions

- A modern diesel car equipped with a catalyst combusting low FSC (50 ppmM) fuel produces much more H_2SO_4 than a diesel car without catalyst combusting high FSC (300 ppmM) fuel !
- Consequently a modern diesel car with catalyst produces more volatile nano particles
- Volatile nano particles are also formed via secondary H_2SO_4 which stems from combustion not related to car traffic

Acknowledgements

- Thanks to members of our MPIK Heidelberg research group
- Thanks to cooperation partners from Finland
- Thanks to MAN company
- Thanks to Dr. Jacob (MAN) for helping to plan the experiments at MAN

THANK YOU FOR YOUR INTEREST