Secondary nanoparticle formation in Diesel vehicle exhaust: New insights from first on-line and off-line measurements of key precursor gases and ions

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Diesel vehicle generated aerosol particles represent major health affecting air pollutants in cities, near motorways, and in many work places[1,2,3]. To mitigate this environmental problem, modern diesel vehicle exhaust after treatment systems (ATS) remove primary particles (soot and ash) and organics. However, ATS may lead to large concentrations of secondary nucleation particles (NUP), forming in the cooling exhaust by nucleation of low vapour pressure gases. NUP are much smaller (mean diameter: 10 nm) than soot particles (mean diameter: 50 nm), which allows NUP to intrude with maximum efficiency the deepest, least protected, and most vulnerable compartment of the human lung[3,4,5]. To explore the unknown NUP formation and nature, we have developed and deployed a highly selective, sensitive, and fast mass spectrometric method to make the first on-line diesel exhaust measurements of key NUP precursor gases and ions. In addition, we have also made off-line experiments involving exhaust sampling followed by thermo-desorption and mass spectrometric detection of desorbed molecules. Our on-line and off-line measurements, covering a wide range of diesel exhaust conditions, and our accompanying model simulations indicate that strong acids act as key NUP precursors. These include sulphuric acid, di-carboxylic acids, and probably also highly toxic superacids. Our findings support the view that diesel generated NUP and their potential adverse health effects deserve increased future attention.

Secondary volatile nanoparticle formation in modern diesel vehicle exhaust: First precursor gas measurements

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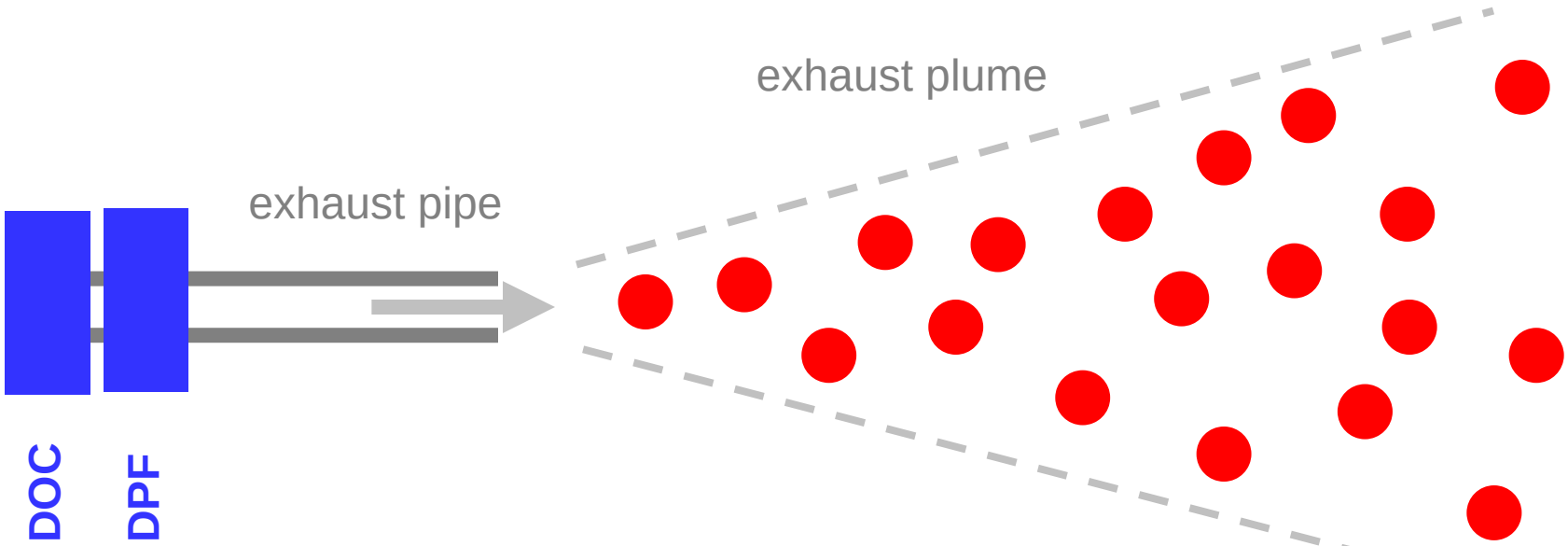
Modern diesel vehicles

- Equipped with catalytic soot filter systems are a major source of air polluting nanoparticles
- Ironically, modern filtered exhaust contains more numerous particles than unfiltered exhaust
- Modern exhaust particles are nucleation particles (NUP)

Particles contained in modern Diesel vehicle exhaust

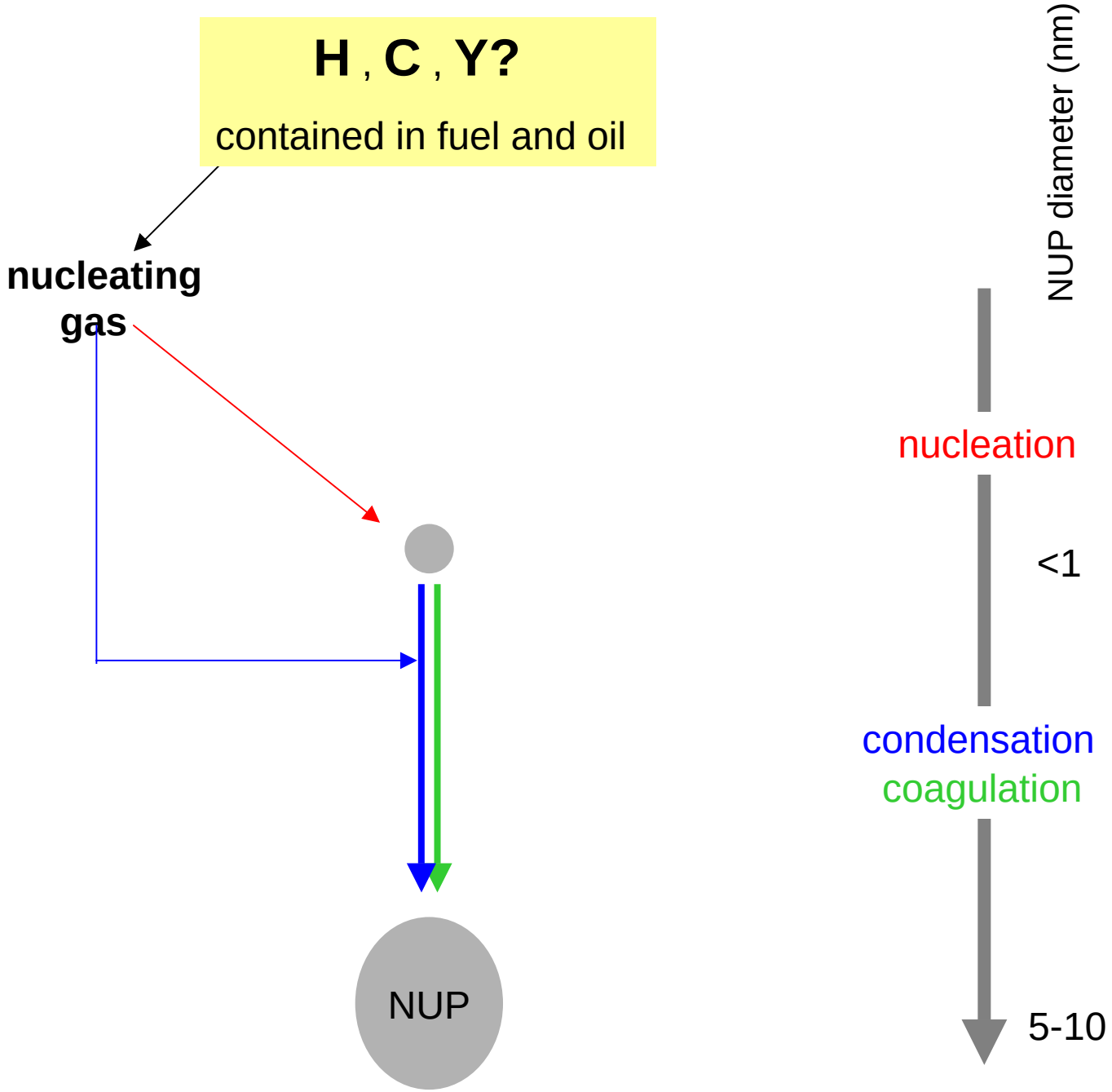
are formed downstream of the filter by nucleation of low-volatility exhaust gases

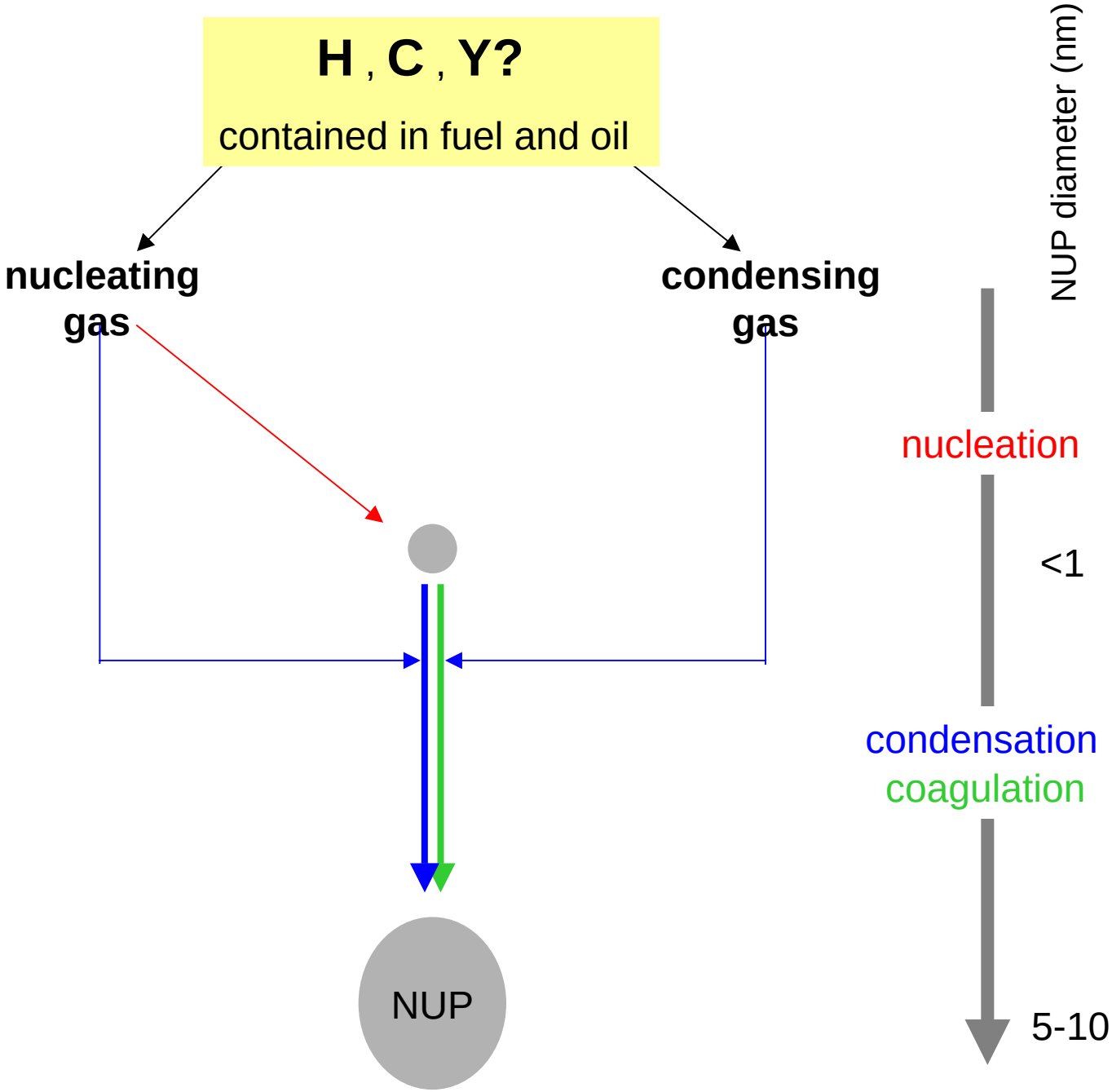


DOC = Diesel Oxidation Catalyst

DPF = Diesel particle filter

nucleation particles (NUP)


H , C , Y?
contained in fuel and oil
nucleating gas
NUP
NUP diameter (nm)
nucleation
<1
condensation
coagulation
5-10


H , C , Y?
contained in fuel and oil
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NUP diameter (nm)
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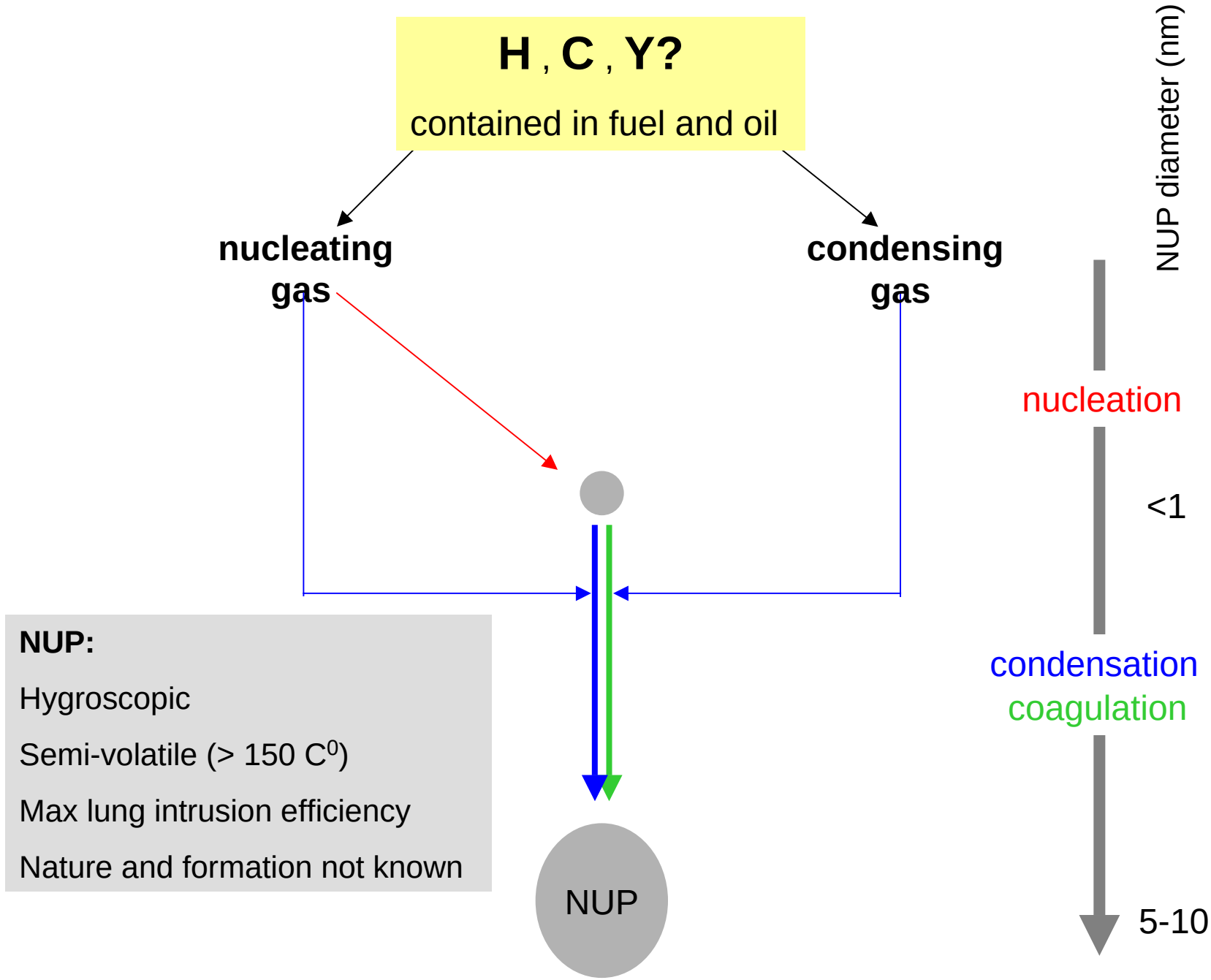
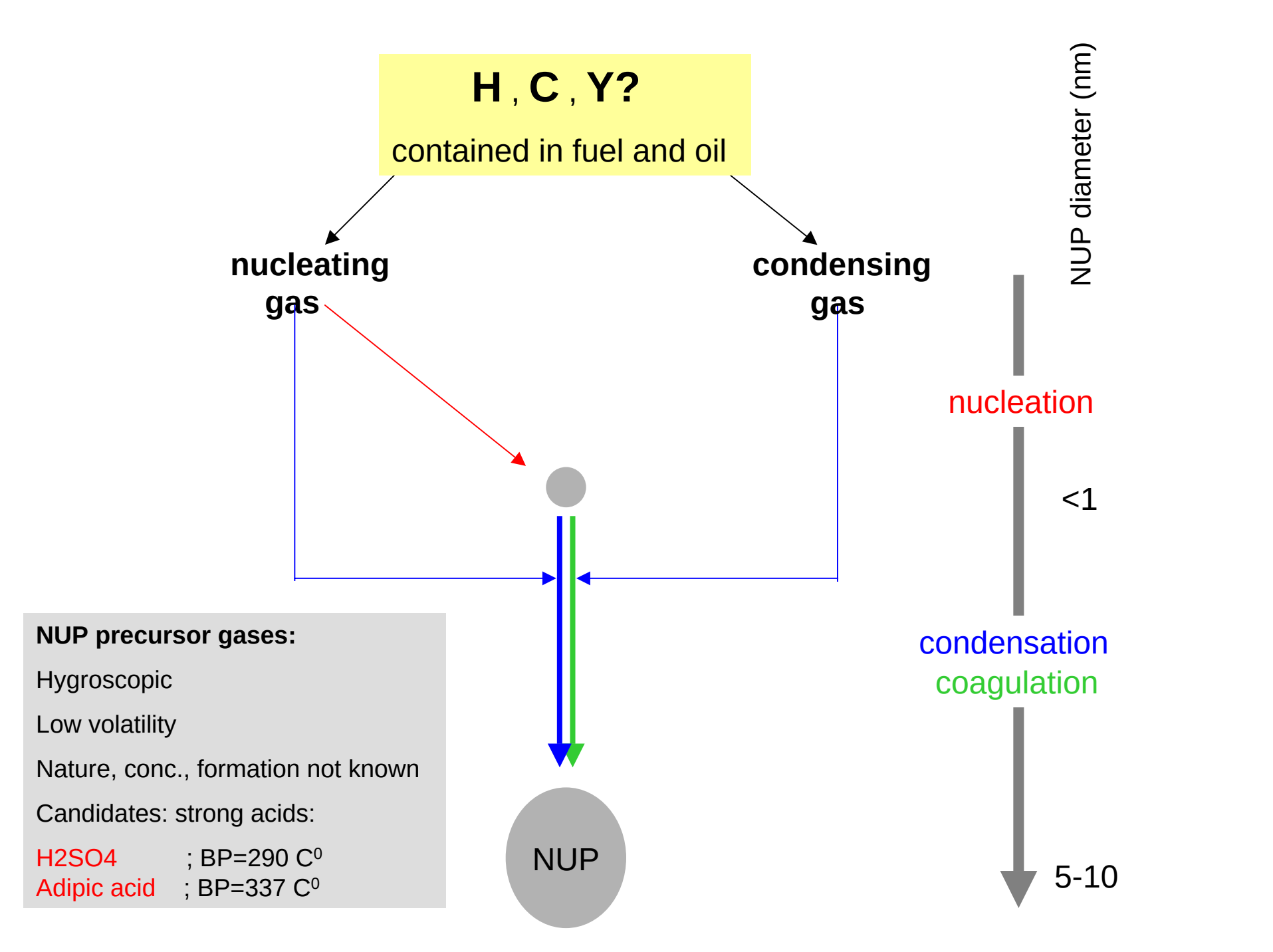
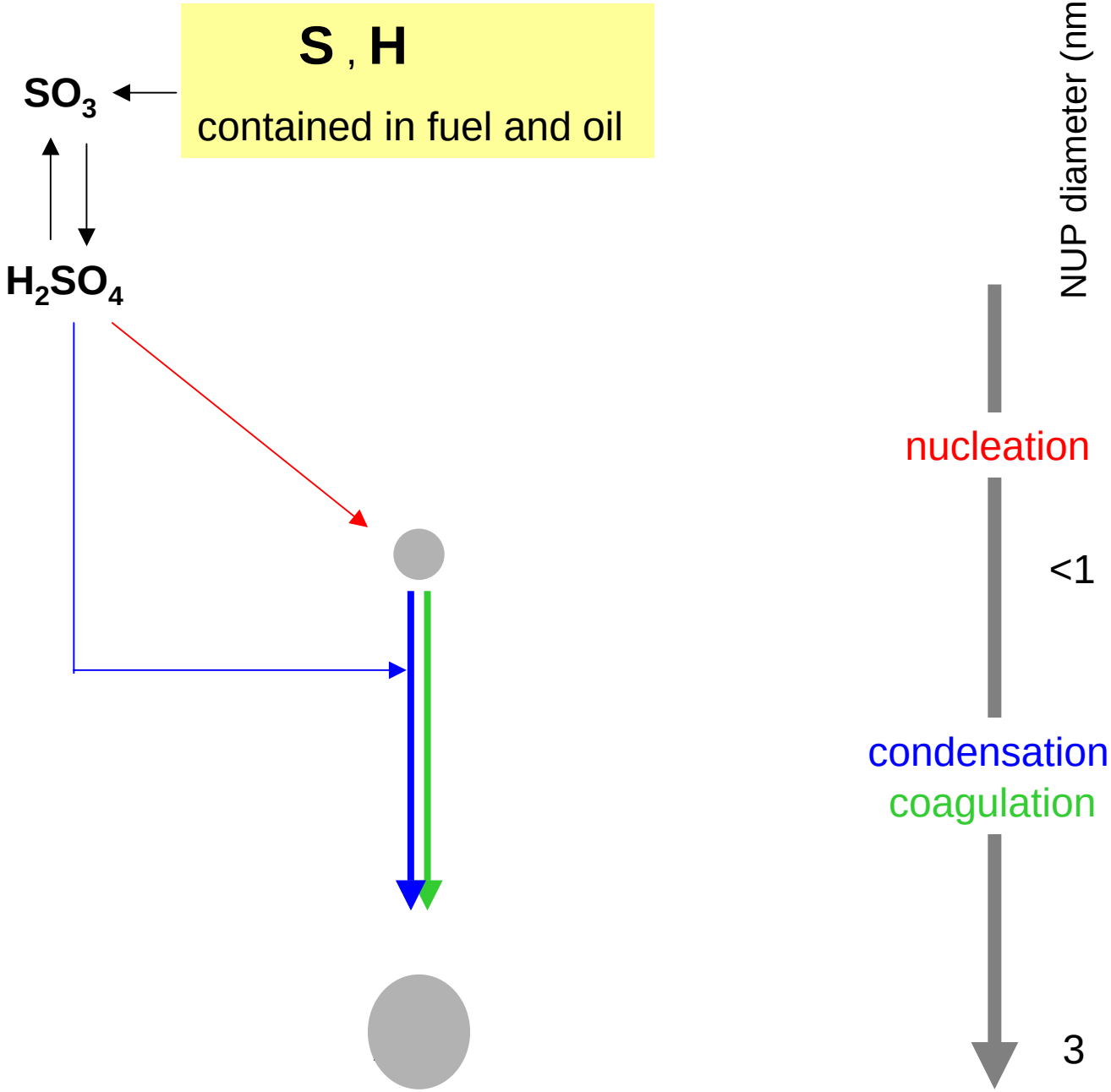
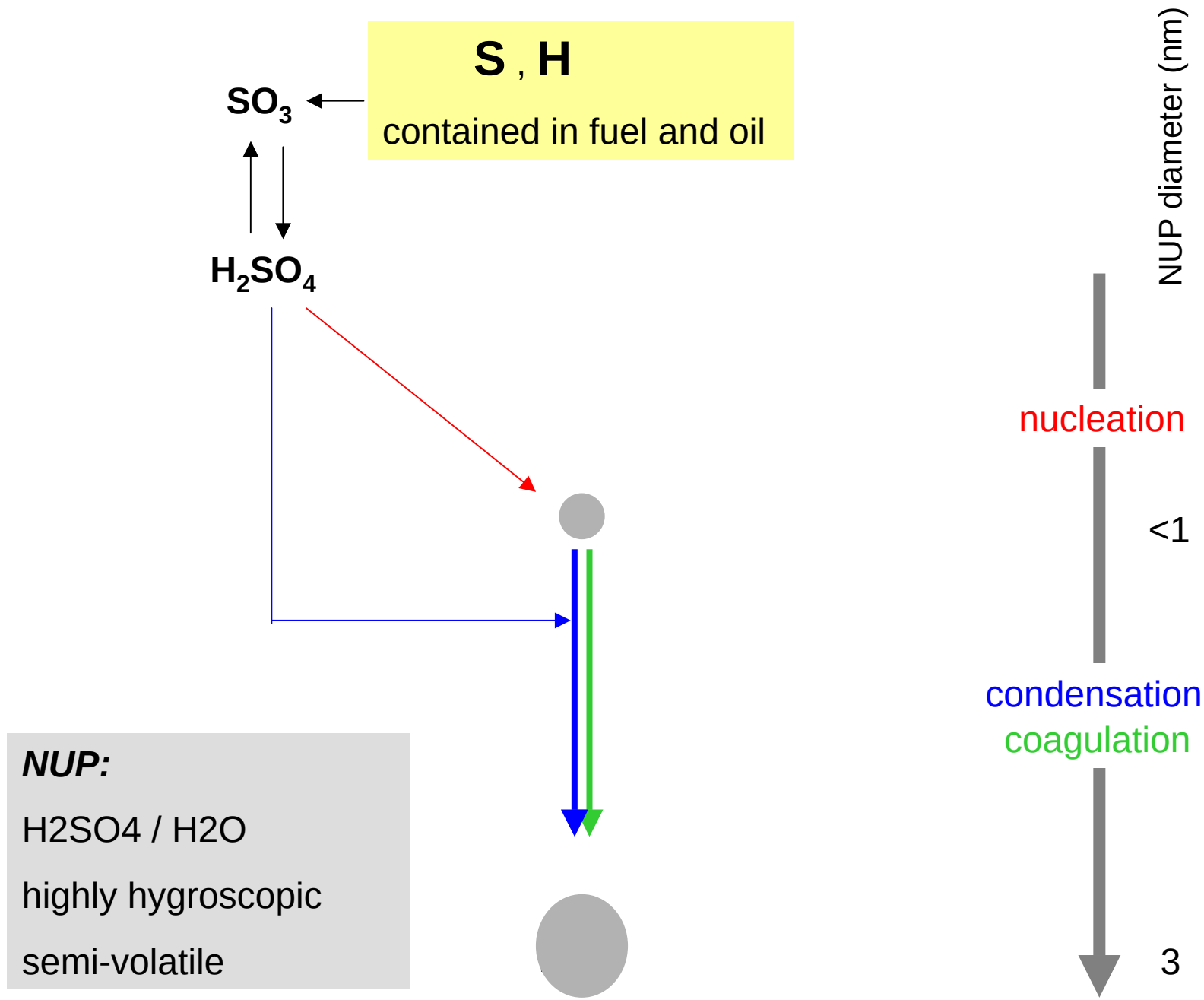
<1
condensation
coagulation
5-10


H , C , Y?
contained in fuel and oil
nucleating gas
condensing gas
NUP diameter (nm)
nucleation
<1
condensation
coagulation
5-10
NUP:
Hygroscopic
Semi-volatile (> 150 C0)
Max lung intrusion efficiency
Nature and formation not known
NUP


H , C , Y?
contained in fuel and oil
nucleating gas
condensing gas
NUP
NUP precursor gases:
Hygroscopic
Low volatility
Nature, conc., formation not known
Candidates: strong acids:
H2SO4 ; BP=290 C0
Adipic acid ; BP=337 C0
NUP diameter (nm)
nucleation
<1
condensation
coagulation
5-10


S , H
contained in fuel and oil
SO3
H2SO4
NUP diameter (nm)
nucleation
<1
condensation
coagulation
3


S , H
contained in fuel and oil
SO3
H2SO4
NUP diameter (nm)
nucleation
<1
condensation
coagulation
3
NUP:
H2SO4 / H2O
highly hygroscopic
semi-volatile

Exploration of the unknown nature of NUP and NUP precursors

- is a major experimental challenge
- should be a high priority objective of modern diesel particle reearch

Measurements in exhaust of EURO 4 heavy duty diesel vehicle on test bench (MAN-lab)

- First NUP precursor gases (hot exhaust)

  (using powerful CI-MS-MS technique developed by MPIK-Heidelberg)

- NUP size distribution and volatility (cooled exhaust)

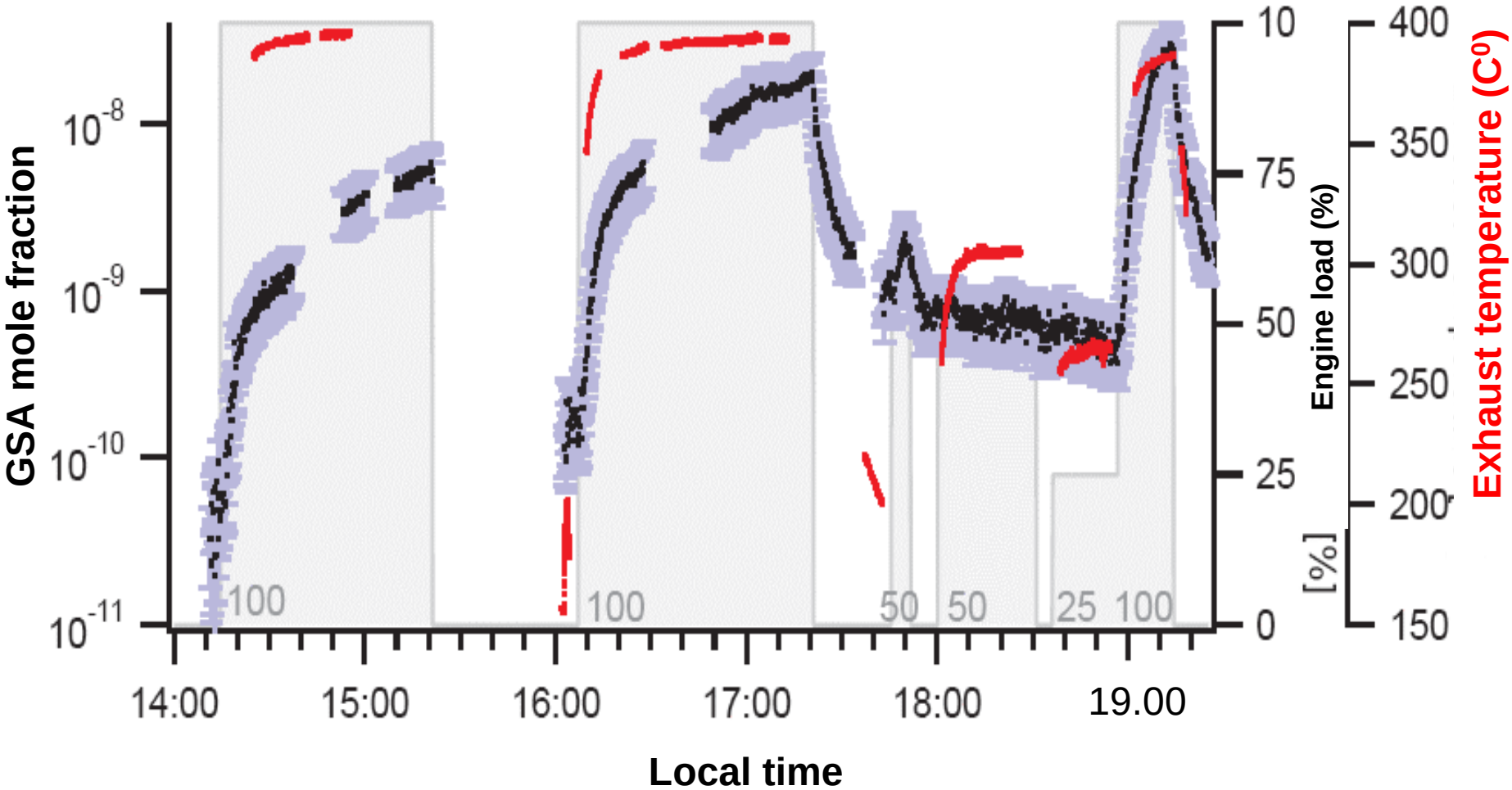
- Acompanying NUP model simulations

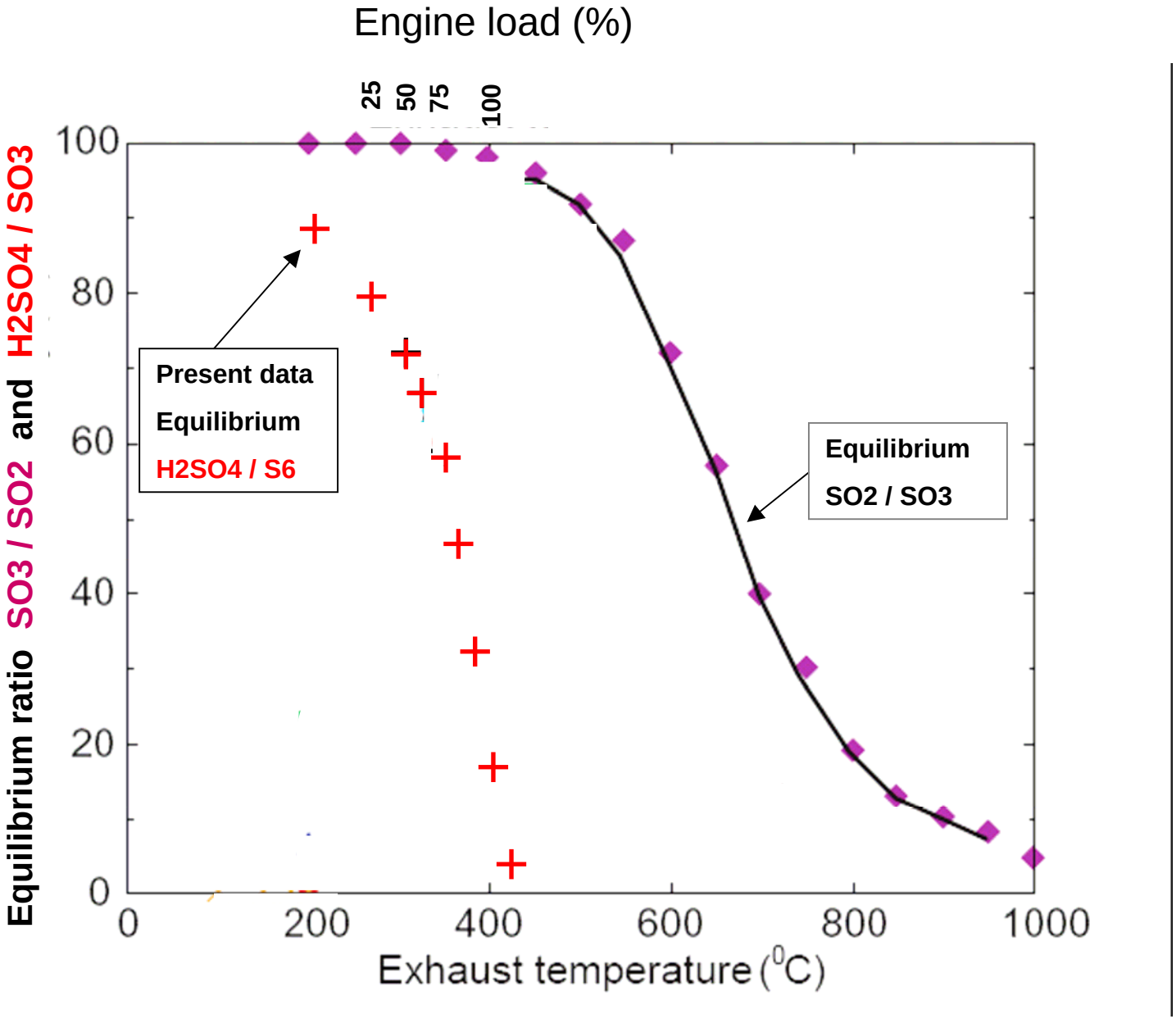
Following Figure:
Example of a gas-phase H2SO4 measurement

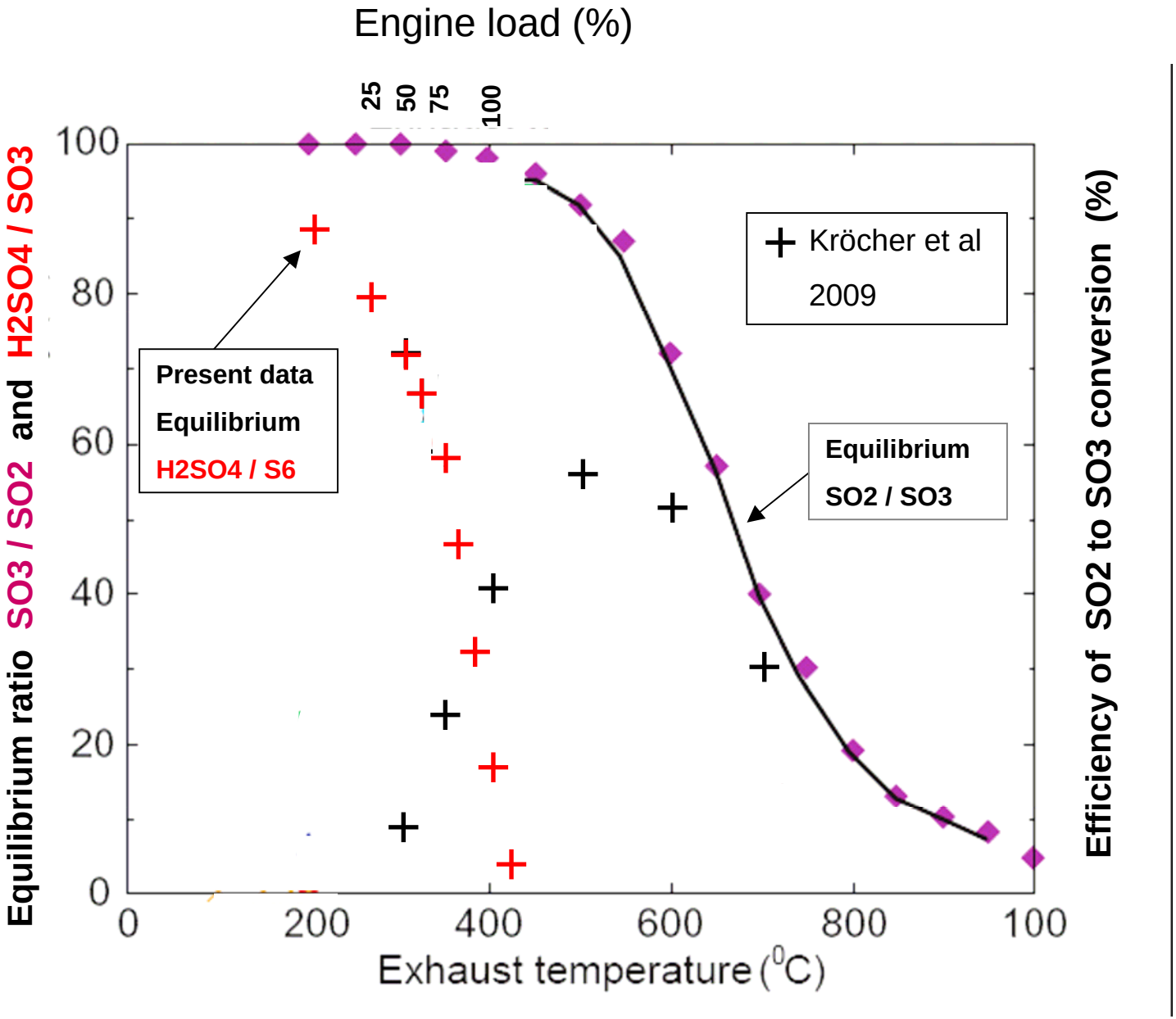
- GSA raw exhaust mole fraction

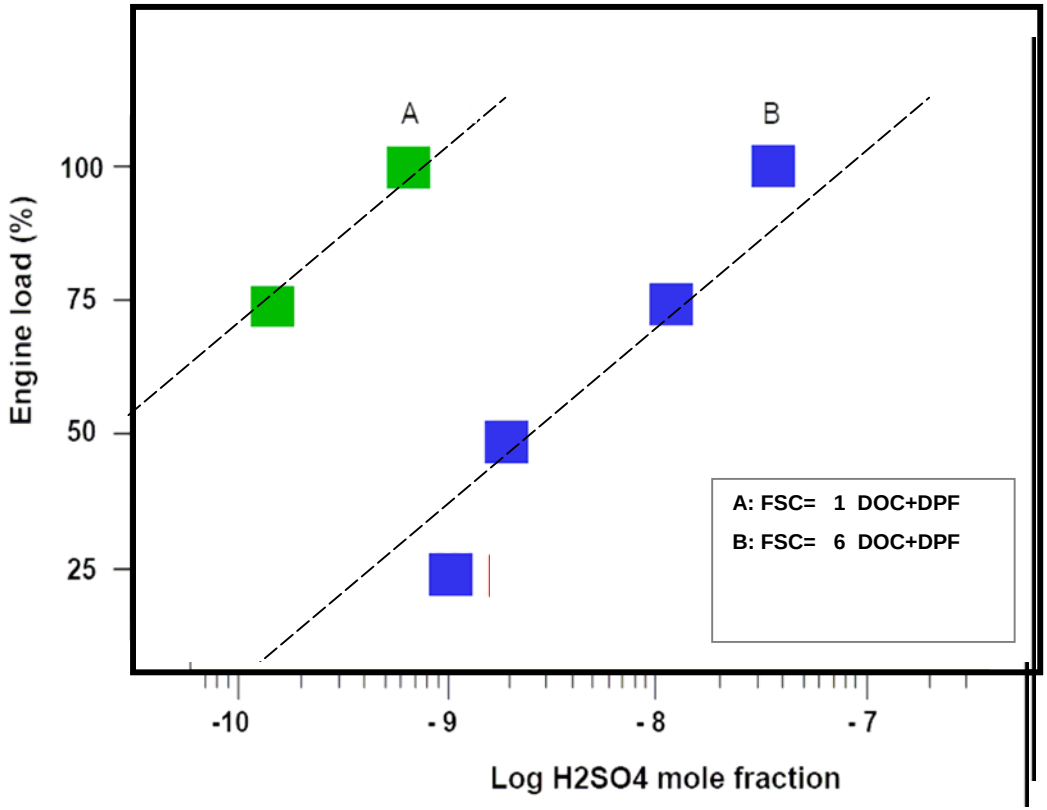
- test cycle:
  - FSC=6 ppmm
  - DOC+DPF
  - EL varied

FSC = 6 ppmm ; ATS: DOC+DPF



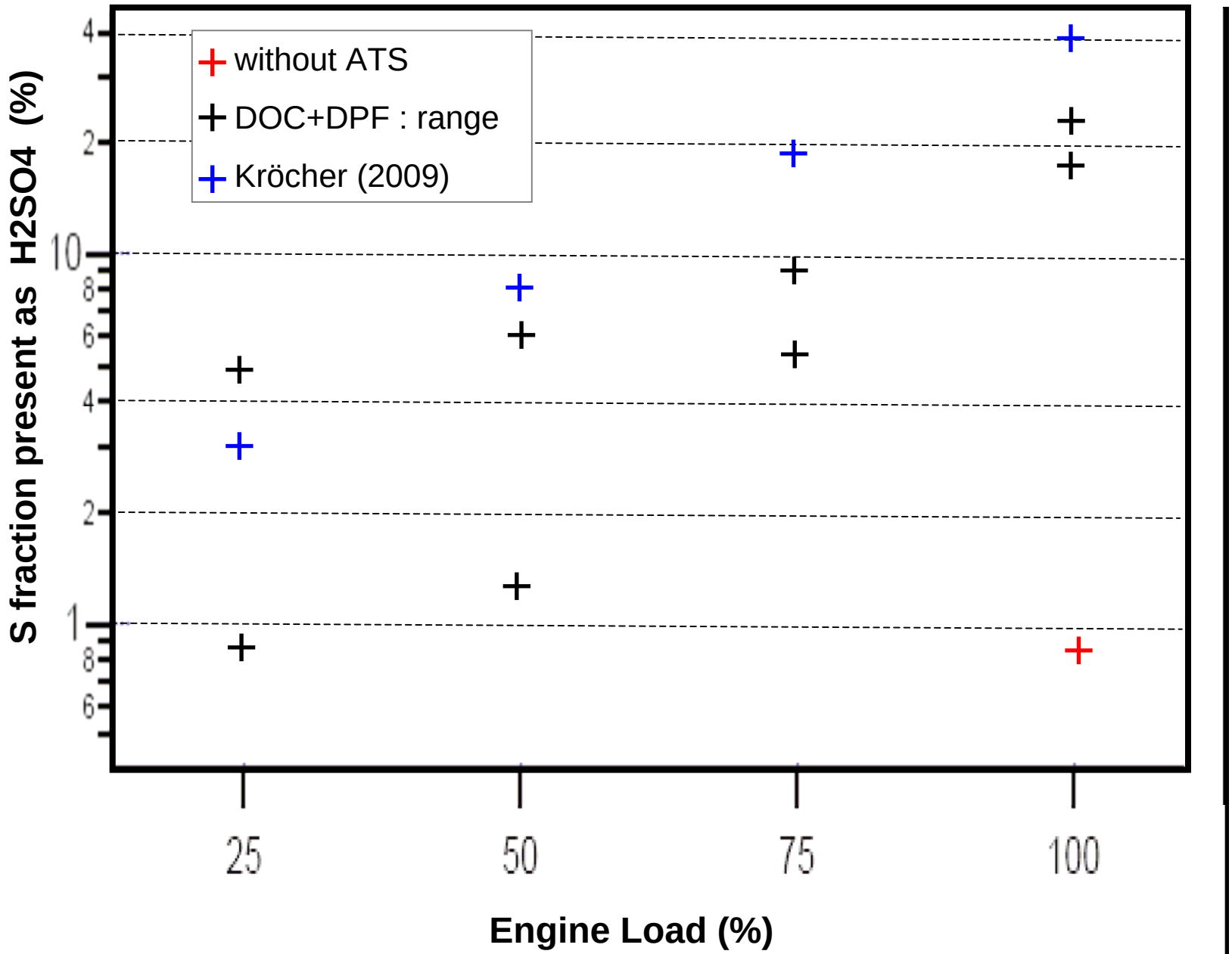

Engine load (%)
25
50
75
100
Equilibrium ratio SO3 / SO2 and H2SO4 / SO3
100
80
60
40
20
0
0
200
400
600
800
1000
Exhaust temperature (0C)
Present data
Equilibrium
H2SO4 / S6
Equilibrium
SO2 / SO3

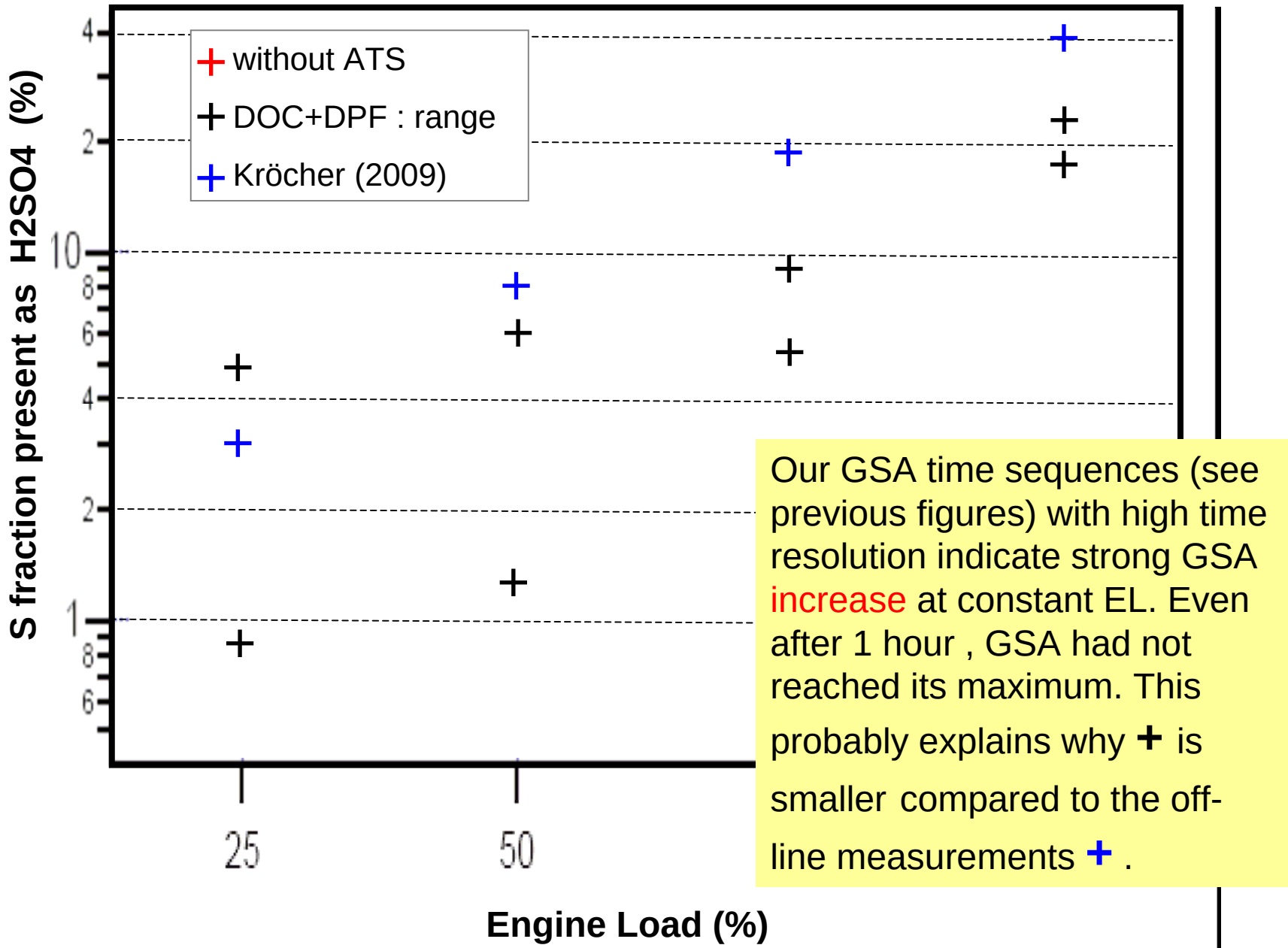

Engine load (%)
25
50
75
100
Equilibrium ratio SO3 / SO2 and H2SO4 / SO3
Efficiency of SO2 to SO3 conversion (%)
Exhaust temperature (0C)
0
20
40
60
80
100
0
200
400
600
800
100
Kröcher et al 2009
Present data
Equilibrium
H2SO4 / S6
Equilibrium
SO2 / SO3



A: FSC < 1 ppmm ; DOC+DPF

B: FSC= 6 ppmm ; DOC+DPF

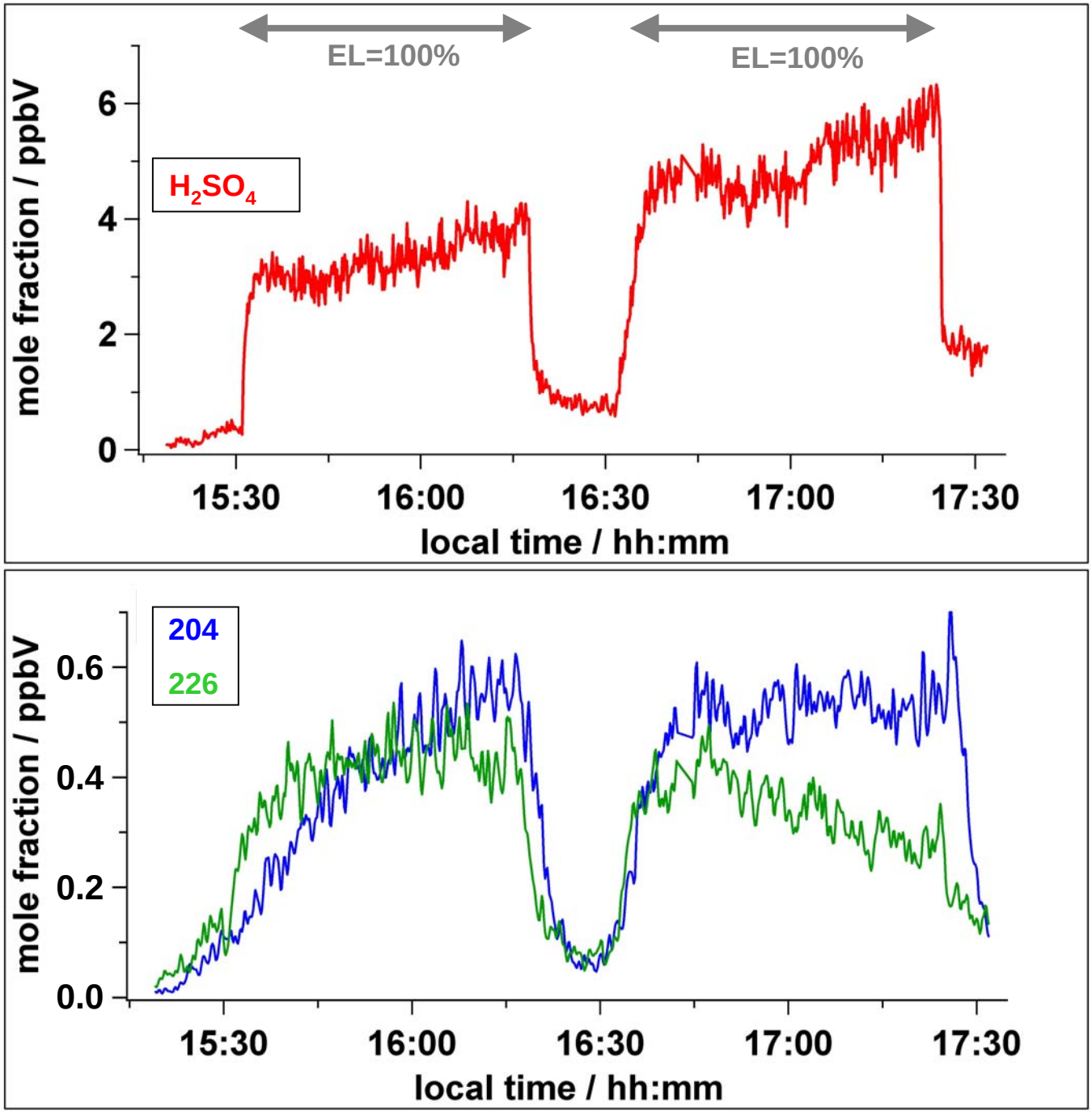

without ATS
DOC+DPF : range
Kröcher (2009)
S fraction present as H2SO4 (%)
4
2
10
8
6
4
2
1
8
6
25
50
75
100
Engine Load (%)

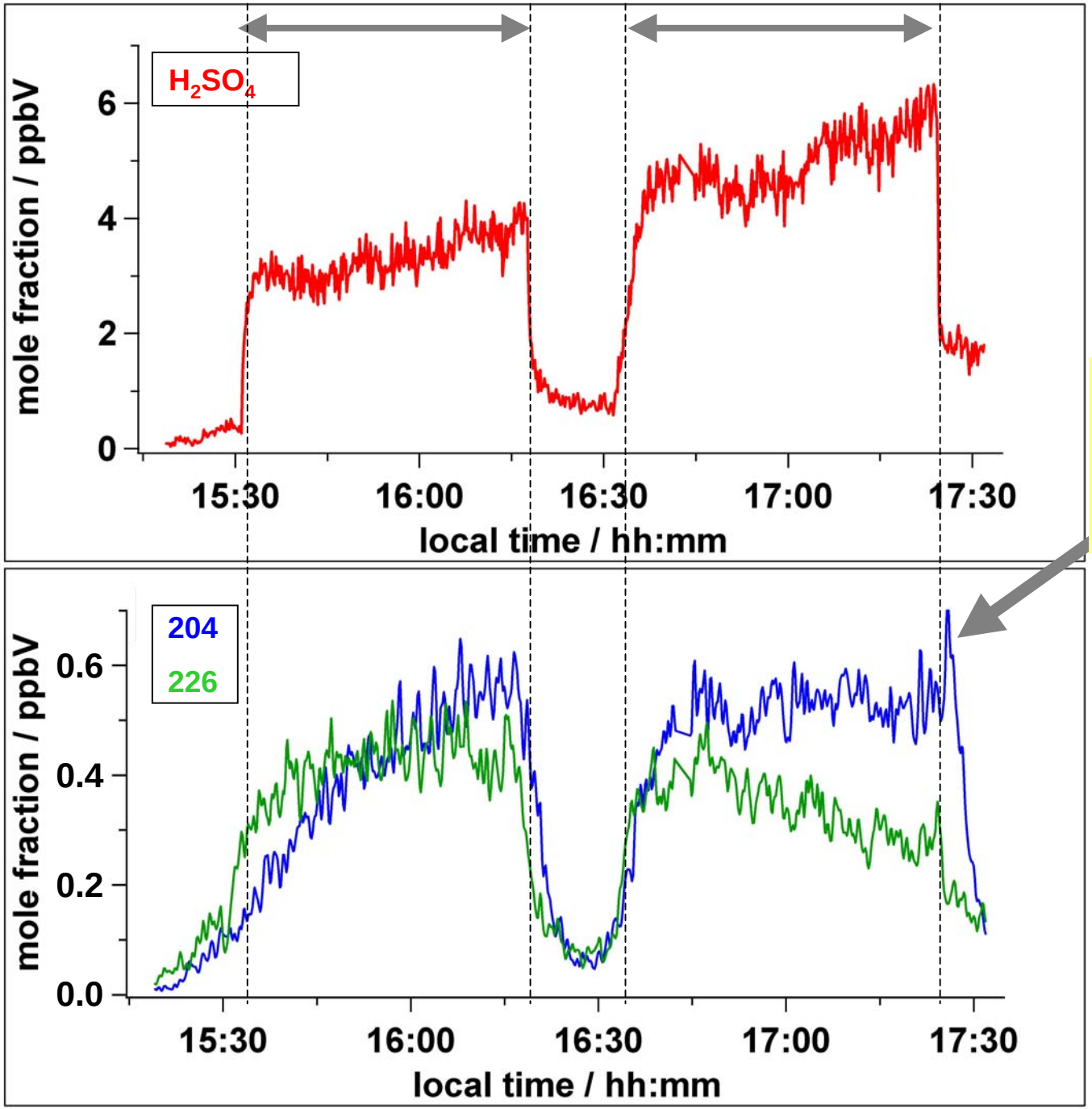


Our GSA time sequences (see previous figures) with high time resolution indicate strong GSA increase at constant EL. Even after 1 hour , GSA had not reached its maximum. This probably explains why + is smaller compared to the off-line measurements + .

HX

- Two examples

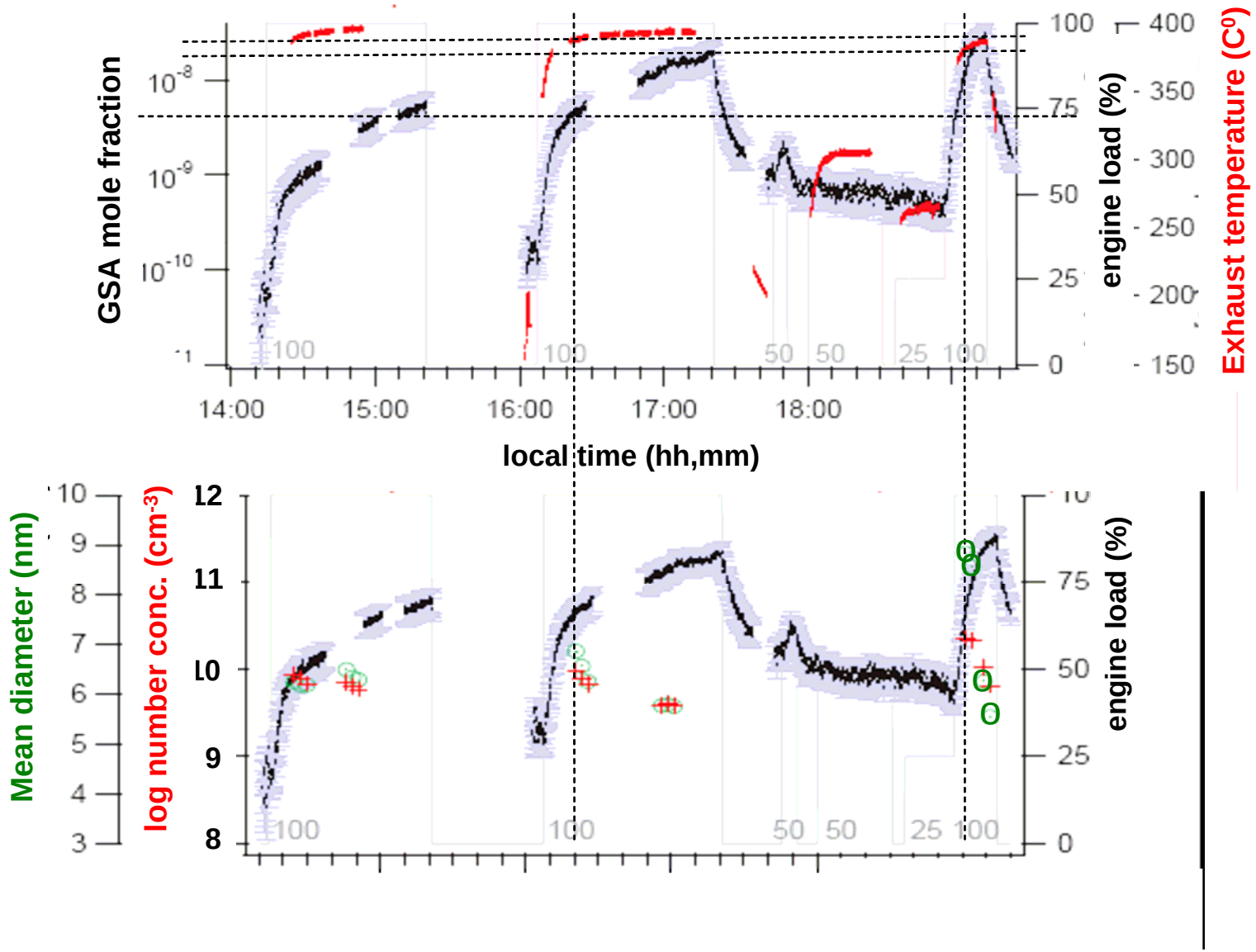

EL=100%
EL=100%
H_2SO_4
mole fraction / ppbV
0
2
4
6
15:30
16:00
16:30
17:00
17:30
local time / hh:mm
204
226
mole fraction / ppbV
0.0
0.2
0.4
0.6
15:30
16:00
16:30
17:00
17:30
local time / hh:mm



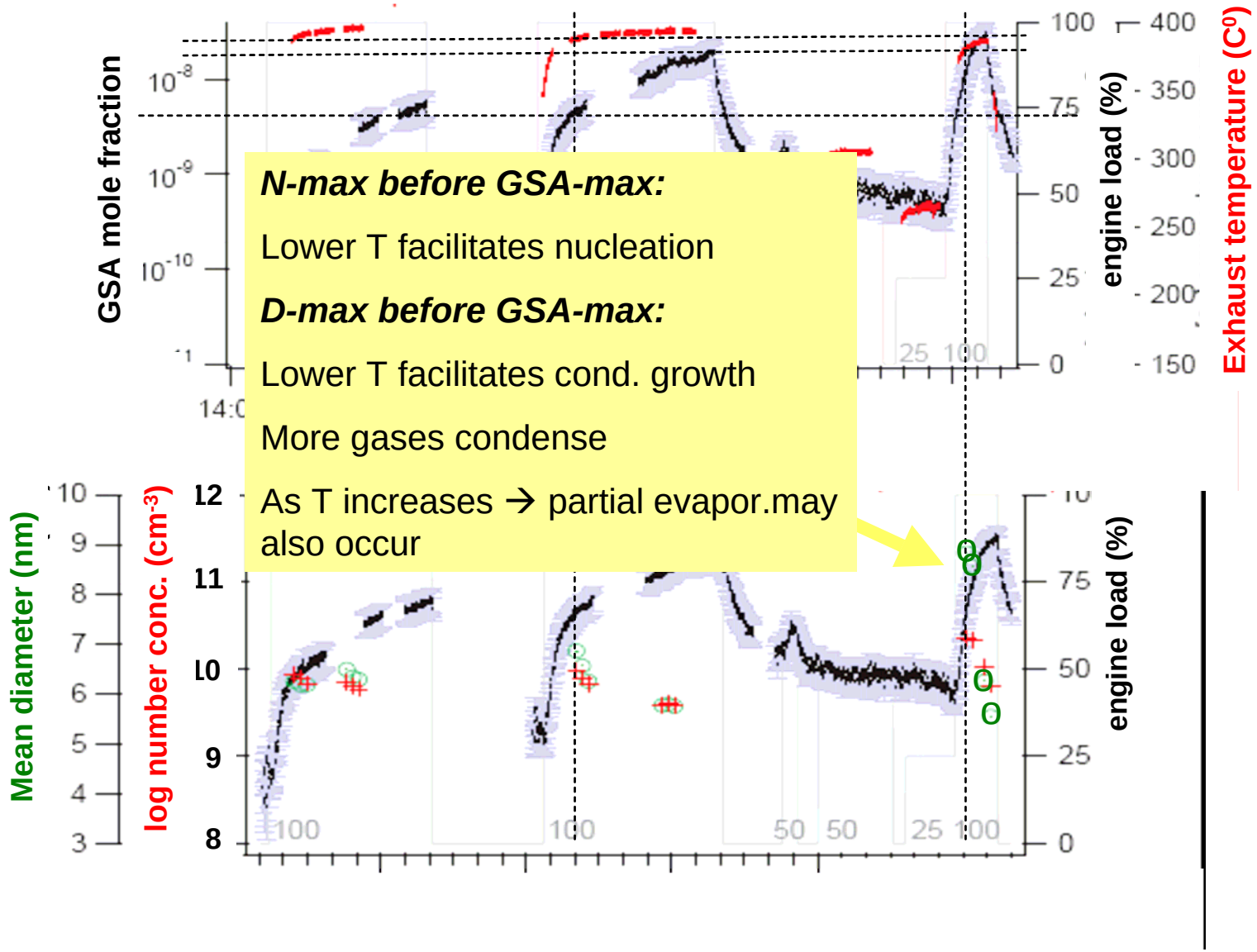
Maximum after H2SO4 release from DOC !

NUP

FSC=6 ppmm ; DOC+DPF



FSC=6 ppmm ; DOC+DPF



N-max before GSA-max:

Lower T facilitates nucleation

D-max before GSA-max:

Lower T facilitates cond. growth

More gases condense

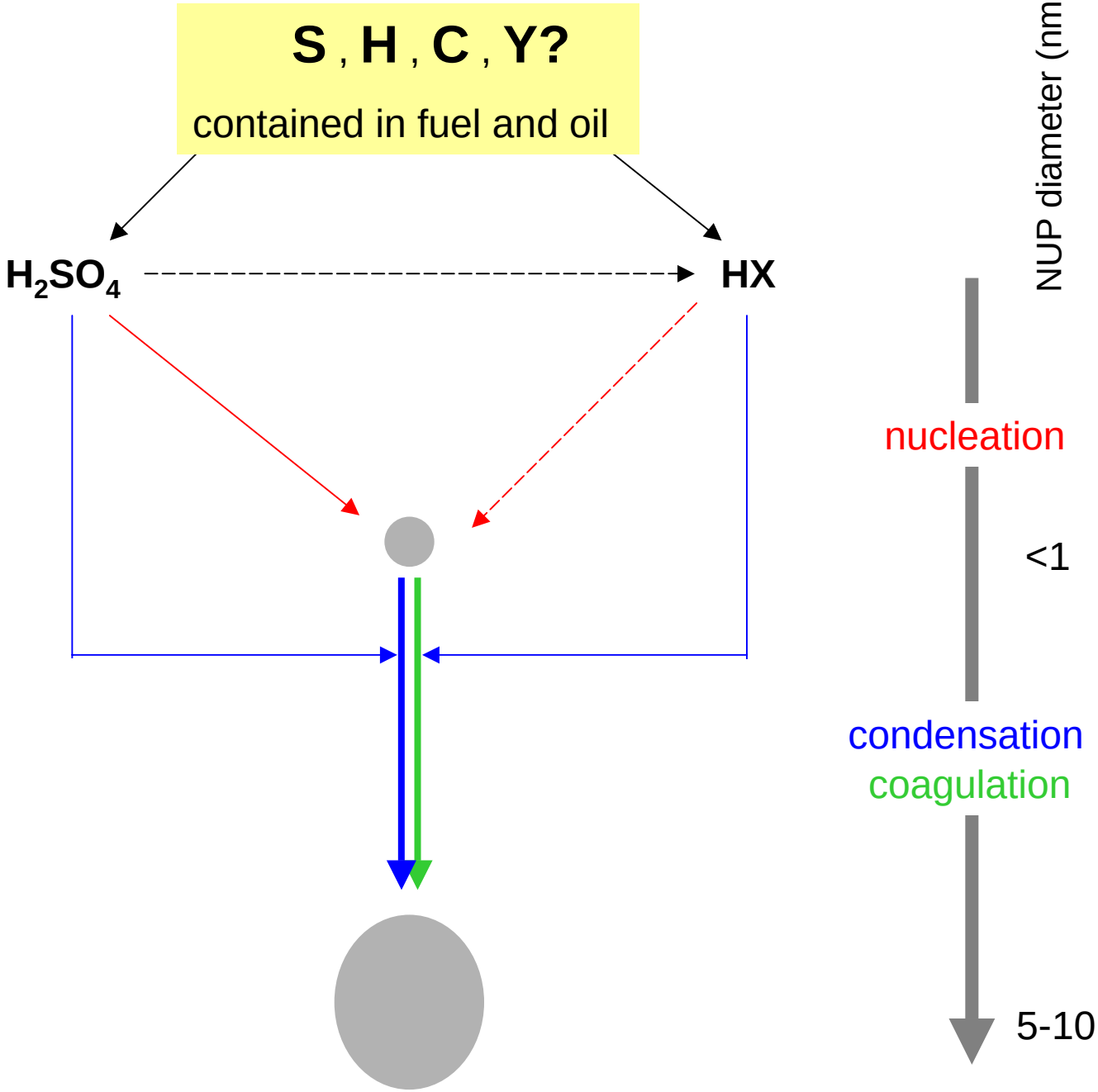
As T increases → partial evapor.may also occur

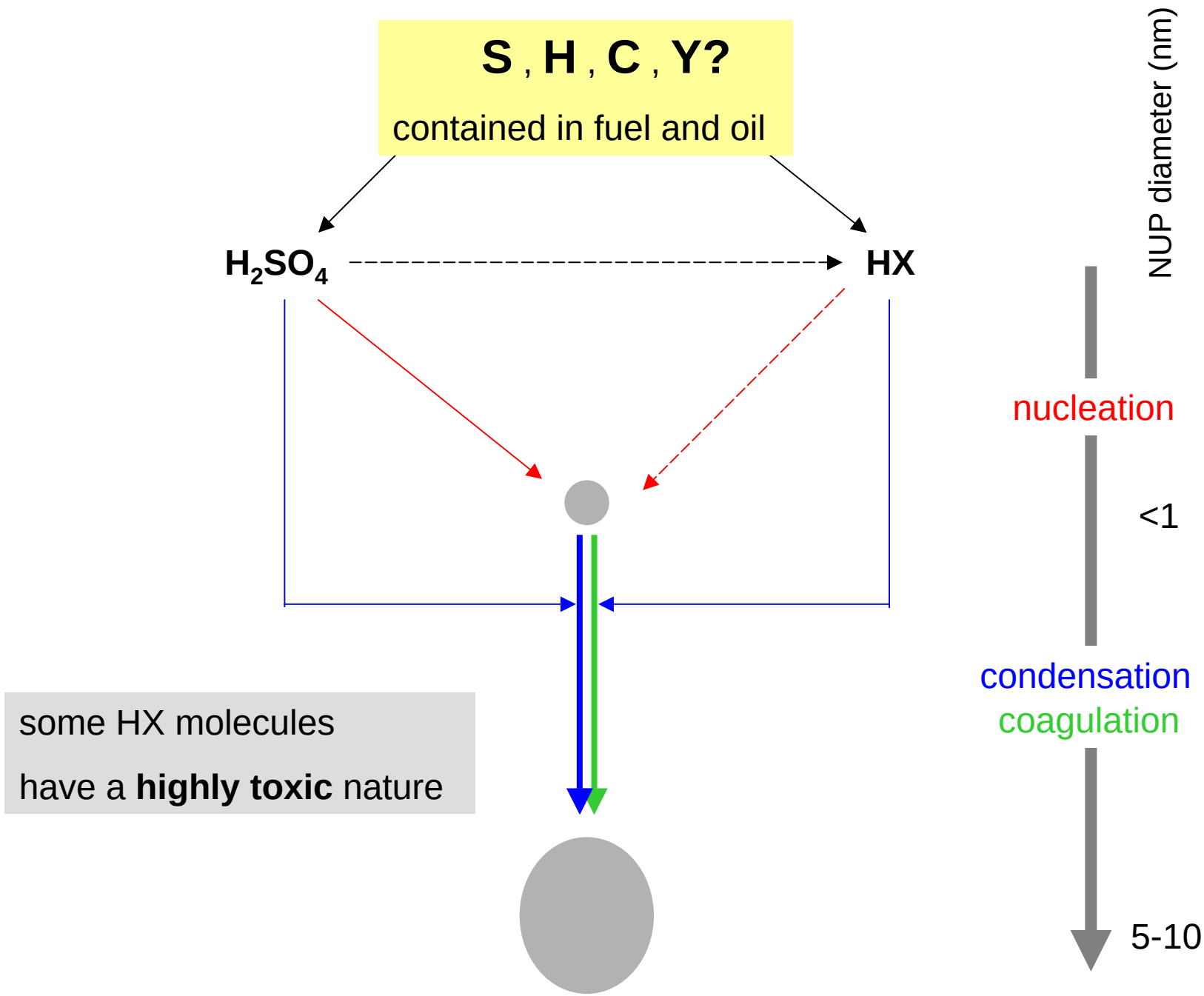
Our NUP model simulations indicate:

- ***Nucleation:***

  measured GSA is sufficient

- ***Condensation growth:***
  - measured GSA is not sufficient
  - measured GSA+HX is sufficient
  - HX strongly influence NUP nature


S , H , C , Y?
contained in fuel and oil
H2SO4
HX
NUP diameter (nm)
nucleation
<1
condensation
coagulation
5-10


S , H , C , Y?
contained in fuel and oil
H2SO4
HX
NUP diameter (nm)
nucleation
<1
condensation
coagulation
5-10
some HX molecules
have a highly toxic nature

Conclusions

- Exhaust GSA and HX show very strong storage in and release from the DOC
- Exhaust GSA increases strongly at constant EL. This has to be considered in NUP formation models
- Numerous HX species were detected. Some are highly toxic
- NUP formation by nucleation is driven mostly by GSA
- NUP growth is strongly influenced by HX
- NUP number concentration and mean diameter often showed pronounced transient behaviour. They were often observed to be maximum at the beginning of EL=100% phases.

Thank you for your attention