Modern Diesel Vehicle generated Nucleation-Particles

Formation, Nature, Lung-Intrusion

F. Arnold (1,2, *) , L. Pirjola (3,4), T. Rönkkö (5), U. Reichl (1), H. Schlager (2),
T. Lähde (3,4), J. Heikkilä (5), and J. Keskinen (5)

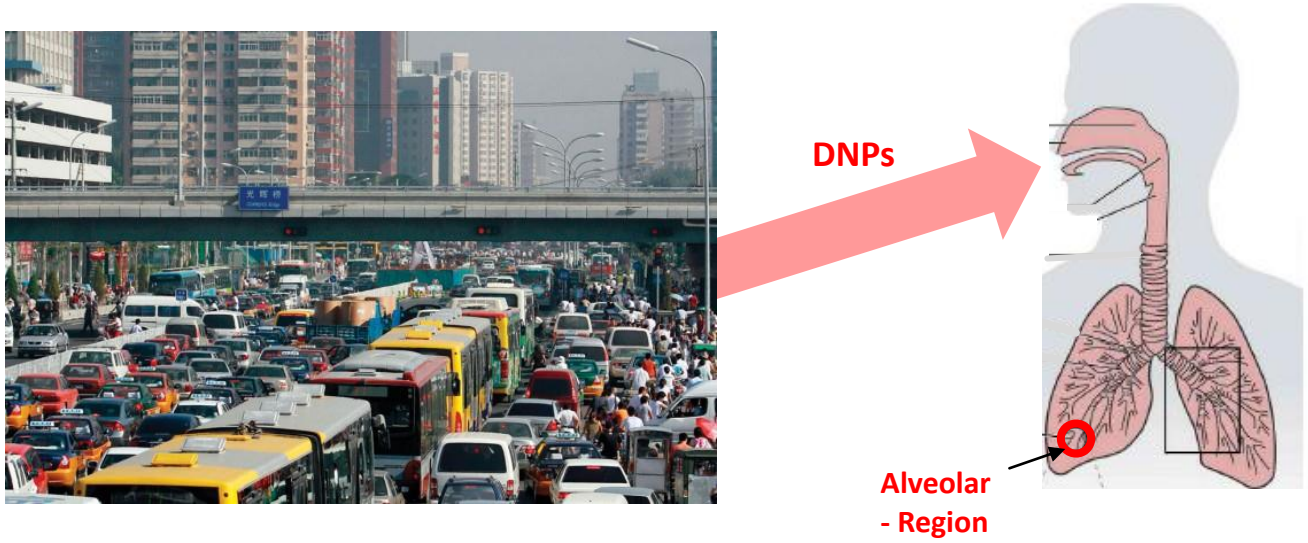
(1) Max Planck Institute for Nuclear Physics (MPIK), Heidelberg, Germany
(2) Deutsches Zentrum für Luft und Raumfahrt (DLR), Oberpfaffenhofen, Germany
(3) Department of Technology, Metropolia University of Applied Sciences, Helsinki, Finland
(4) Department of Physics, University of Helsinki, Helsinki, Finland
(5) Aerosol Physics Laboratory, Department of Physics, Tampere University of Technology, Finland

* Speaker

Oral presentation at ETH-Conference „Combustion generated nanoparticles“, Zuerich 13 June 2016

Modern Diesel Vehicle generated Nucleation-Particles (DNUPs)

- are of considerable current interest
- their potential adverse health effects are of increasing concern
- have just the ideal size to intrude with maximum efficiency the **alveolar region**
- alveolar region is particularly vulnerable



DNUP-Formation

- **DNUPs** form in cooling exhaust just downstream of the vehicles tailpipe
- There, certain exhaust gases reach sufficiently high supersaturations to undergo nucleation
  (Striking Example: homogeneous bi-molecular nucleation of H_2SO_4/H_2O)
- DNUPs grow by condensation and coagulation
- DNUP-characteristics (next slide)

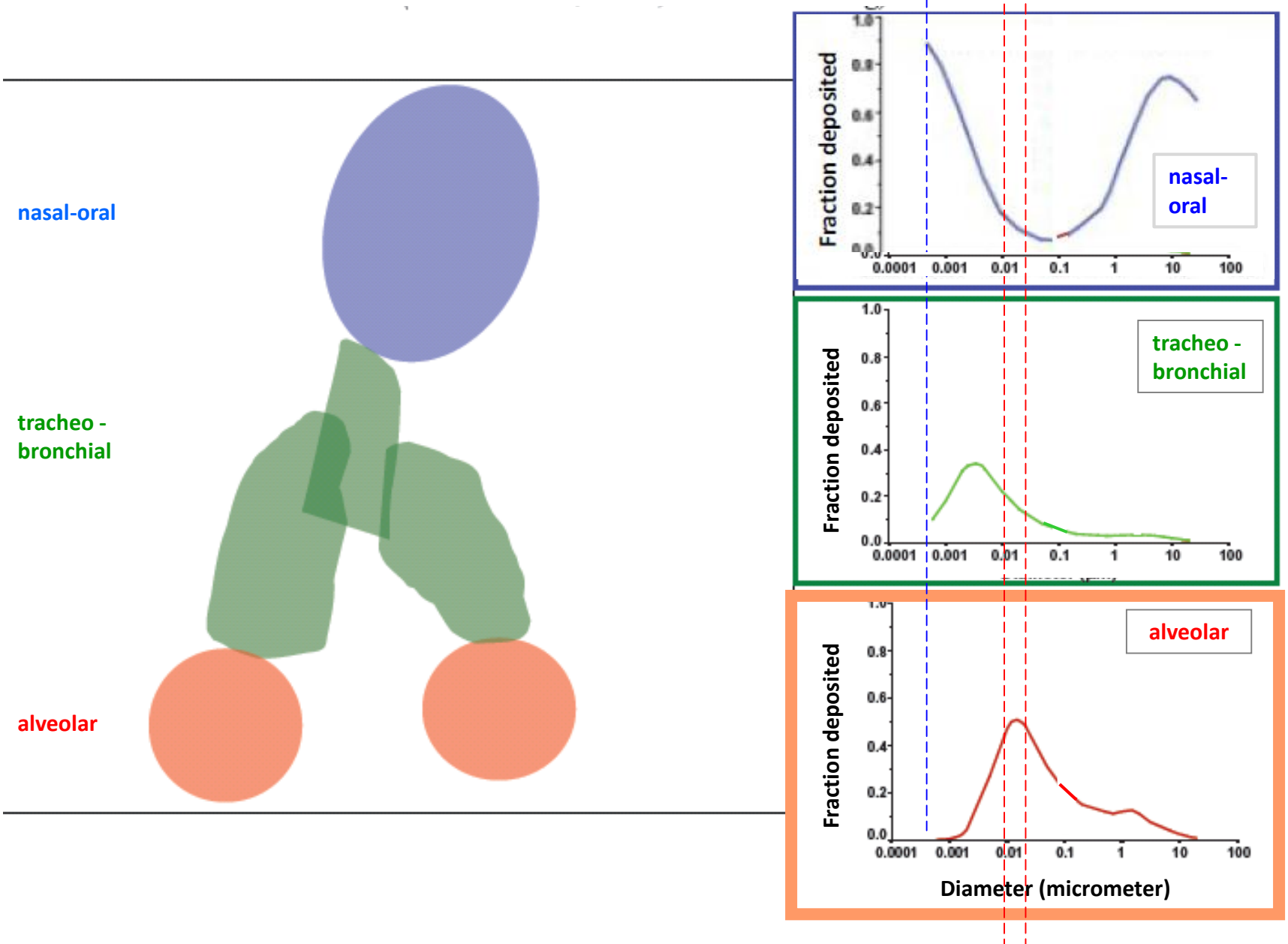
DNUP-Characteristics

- **Diameters:** very small (ca 5-20 nm)
- **Volatile**: at T > 250 C
- **Number-Concentrations:** large (up to about 1E(9) cm-3)
- **Total surface area concentration:** large
- **Total mass concentration:** small

DNUP-Characteristics

- **Diameters:** very small (ca 10-20 nm)

  → maximum efficiency for intrusion of alvaeolar region


Sticky gas-molecules
(e.g. H2SO4)
DNP
nasal-oral
tracheo -
bronchial
alveolar
Fraction deposited
nasal-
oral
tracheo -
bronchial
alveolar
0.0001
0.001
0.01
0.1
1
10
100
Diameter (micrometer)

DNP-Characteristics

- **Total surface area concentration:** large
  → DNUPs may take up significant numbers of sticky molecules
  → DNUPs will act as carriers for transport of attached molecules
  → thereby toxic molecules may reach the alvaeolar region

- **Total mass concentration:** small
  → DNUPs escape from legal regulations (mostly mass oriented)

Our DIESEL EXHAUST Investigations
(Measurements and Model-Simulations)

- ***Test-bed Engine-Exhaust Measurements***
  (Heavy Duty Diesel Vehicle Engine with and without ATS)
  - Exhaust-gases on-line
  - D-Particles after ageing chamber (t-res = 2.7 sec) on-line

  Conditions:
  - different Fuels
  - different Fuel-Sulfur-Content (FSC)
  - different engine loads (EL)
  - different exhaust aftertreatment systems (ATS: ODPC; CDPF)
- ***Model Simulations***
  - different nucleation mechanisms
  - different organics
  - different Fuel-Sulfur-Content (FSC

Further information on our Diesel-Exhaust work

- Two more recent publications (see next slide)

ENVIRONMENTAL Science & Technology

Article

pubs.acs.org/est

First Online Measurements of Sulfuric Acid Gas in Modern Heavy-Duty Diesel Engine Exhaust: Implications for Nanoparticle Formation

F. Arnold,*[,†,‡] L. Pirjola,[§,∥] T. Rönkkö,[⊥] U. Reichl,[†] H. Schlager,[‡] T. Lähde,[§,⊥] J. Heikkilä,[⊥] and J. Keskinen[⊥]

[†]Max Planck Institute for Nuclear Physics (MPIK), P.O. Box 103980, D-69029 Heidelberg, Germany

[‡]Deutsches Zentrum für Luft und Raumfahrt (DLR), Oberpfaffenhofen, Germany

[§]Department of Technology, Metropolia University of Applied Sciences, P.O. Box 4021, FIN-00180 Helsinki, Finland

[∥]Department of Physics, University of Helsinki, P.O. Box 64, FIN-00014 Helsinki, Finland

[⊥]Aerosol Physics Laboratory, Department of Physics, Tampere University of Technology, P.O. Box 692, FIN-33101 Tampere, Finland

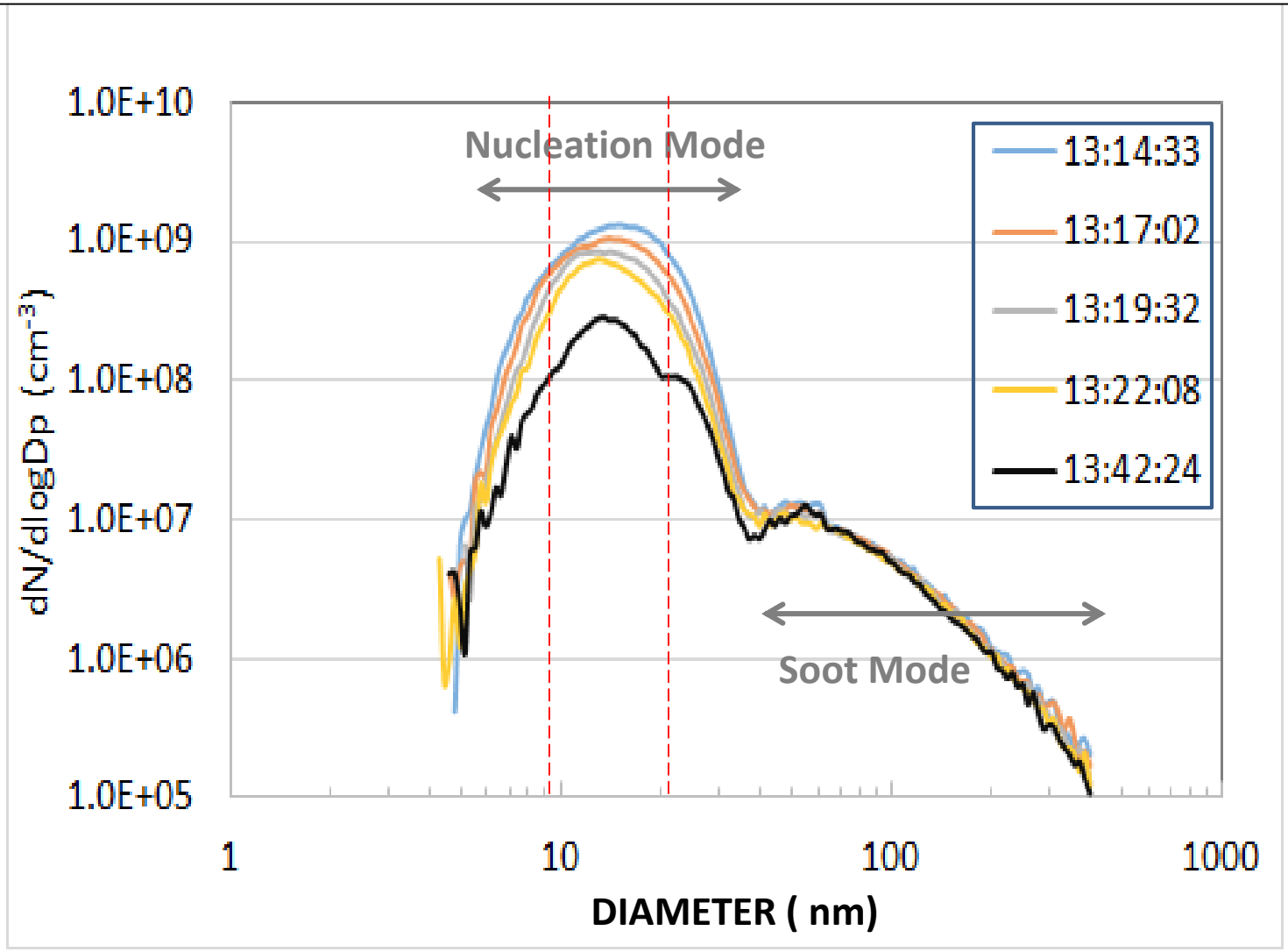
Model studies of volatile diesel exhaust particle formation: are organic vapours involved in nucleation and growth?

Atmospheric Chemistry and Physics Open Access

L. Pirjola[1,2], M. Karl[3], T. Rönkkö[4], and F. Arnold[5,6]

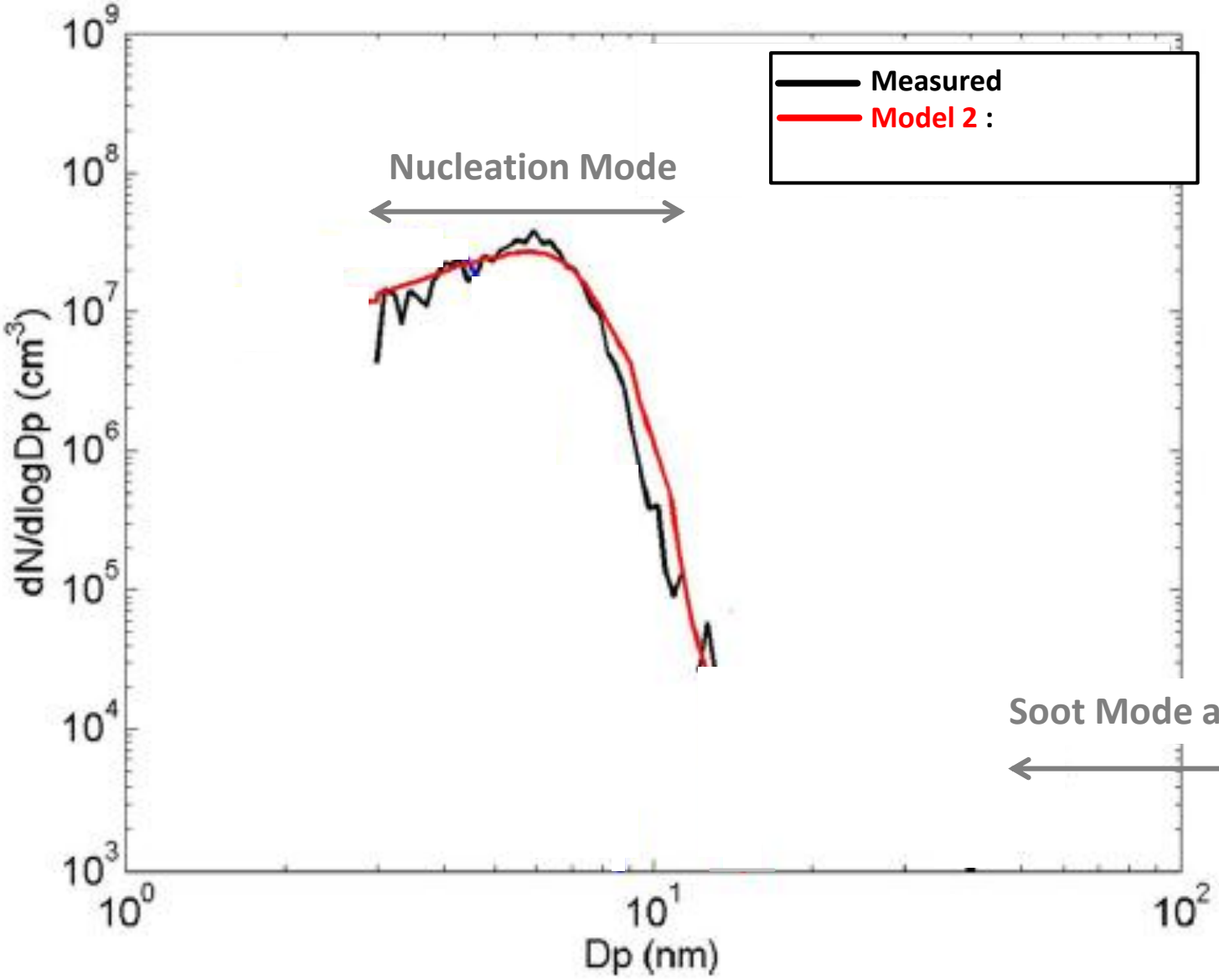
[1]Department of Technology, Metropolia University of Applied Sciences, P.O. Box 4021, 00180 Helsinki, Finland
[2]Department of Physics, University of Helsinki, P.O. Box 64, 00014 Helsinki, Finland
[3]Norwegian Institute for Air Research, P.O. Box 100, 2027 Kjeller, Norway
[4]Aerosol Physics Laboratory, Department of Physics, Tampere University of Technology, P.O. Box 692, 33101 Tampere, Finland
[5]Max-Planck-Institut für Kernphysik, Heidelberg, Germany
[6]Deutsches Zentrum für Luft and Raumfahrt (DLR), Obenpfaffenhofen, Germany

Diesel-Particle Number Size Distributions : FSC = 36 ppm ; EL = 100 % ; ATS (DOC + **ODPF**)

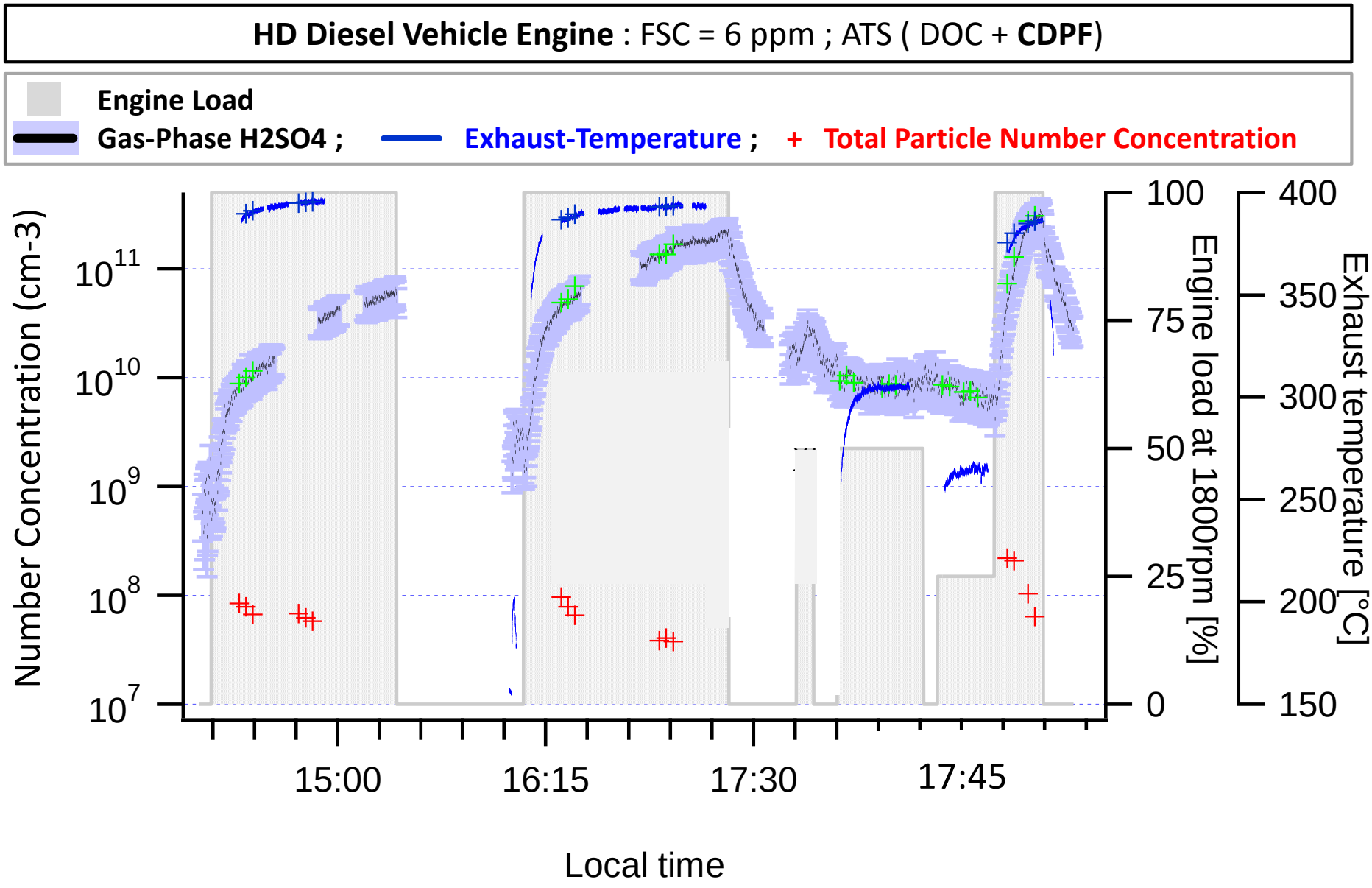


Pirjola, Karl, Rönkkö, Arnold (2015)

Diesel-Particle Number Size Distribution : FSC = 6 ppm ; EL = 100 % ; ATS (DOC + **CDPF**)



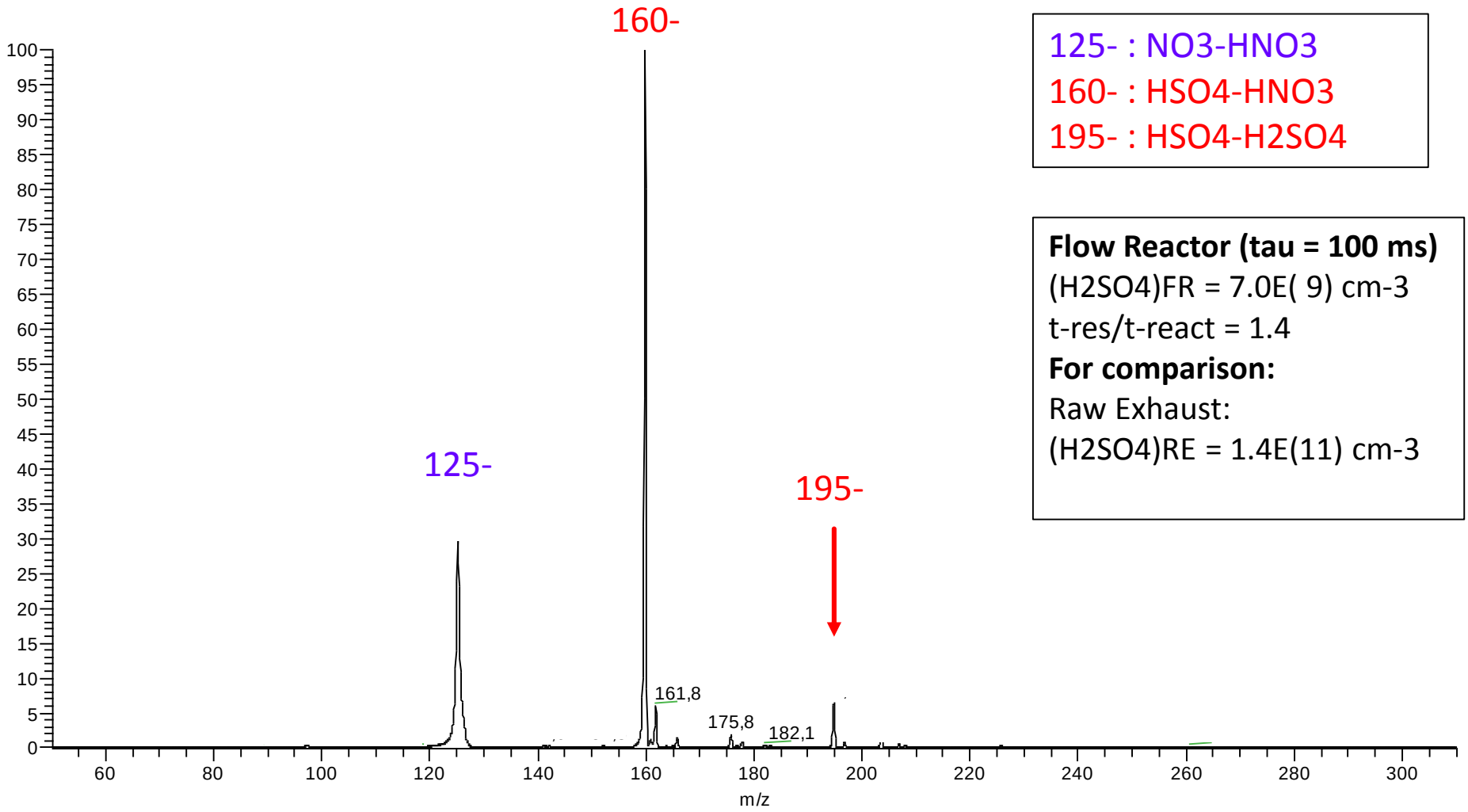
Arnold et al (2012)


HD Diesel Vehicle Engine : FSC = 6 ppm ; ATS (DOC + CDPF)
Engine Load
Gas-Phase H2SO4 ;
Exhaust-Temperature ;
+ Total Particle Number Concentration
Number Concentration (cm-3)
10^11
10^10
10^9
10^8
10^7
100
75
50
25
0
Engine load at 1800rpm [%]
400
350
300
250
200
150
Exhaust temperature [°C]
15:00
16:15
17:30
17:45
Local time

Ion and reagent neutral molecule identification by:
Mass selected Ion fragmentation

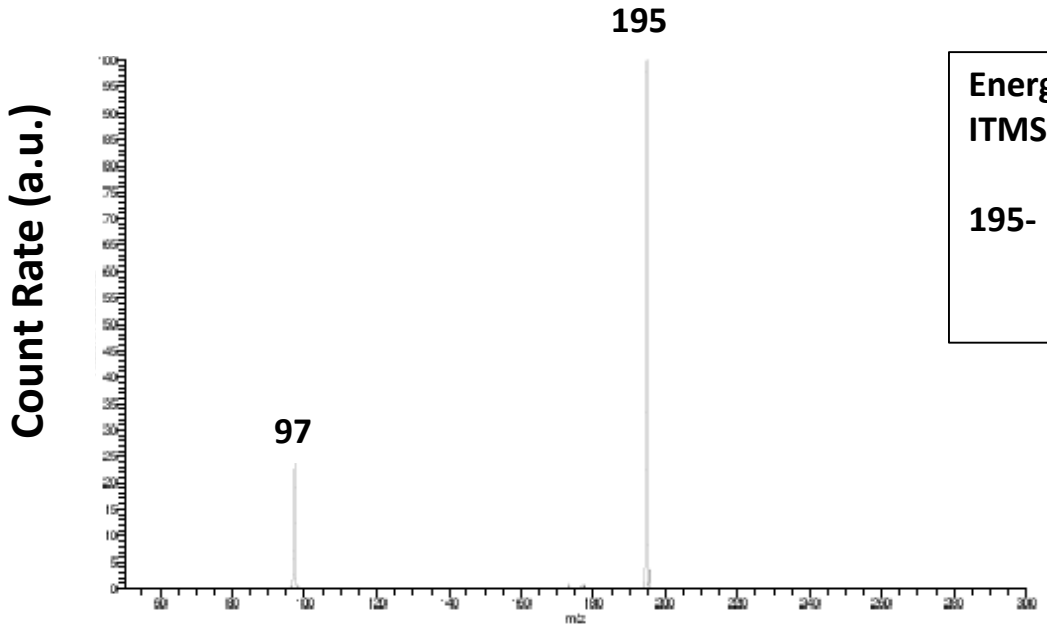
- Example: H_2SO_4 identification by
  - mass selected ion fragmentation
  - isotope analysis
- See following 2 slides

CI-ITMS Mass spectrum of negative ions :
Reagent ion: **NO3-HNO3** is introduced into flow reactor
there it reacts with gas-phase H2SO4 via : **NO3-HNO3** + H2SO4 → **HSO4-HNO3** + **HNO3**



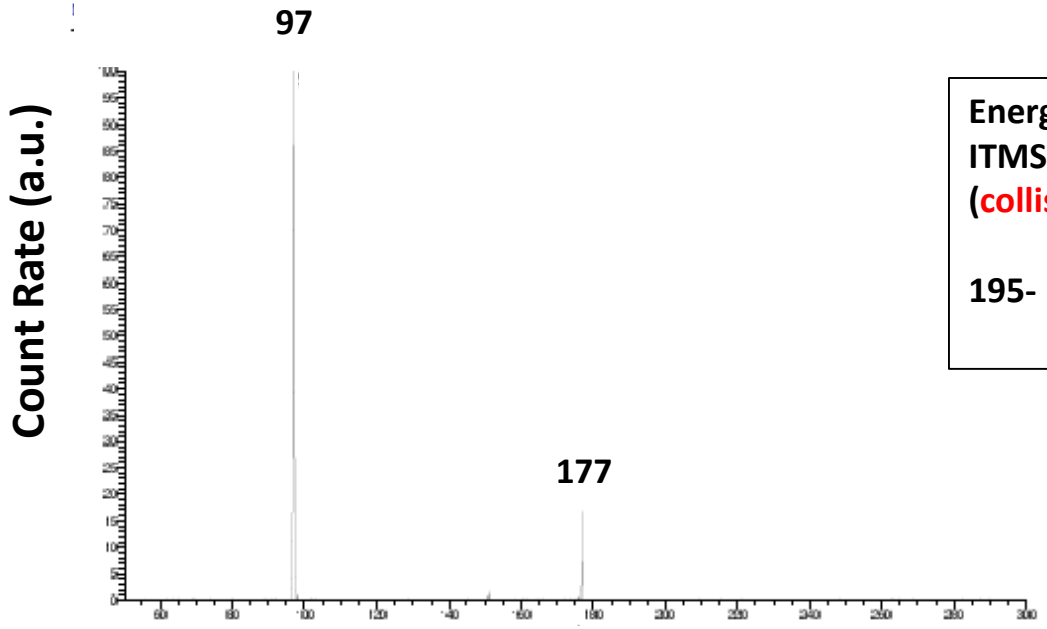
125- : NO3-HNO3
160- : HSO4-HNO3
195- : HSO4-H2SO4

Flow Reactor (tau = 100 ms)
(H2SO4)FR = 7.0E(9) cm-3
t-res/t-react = 1.4
For comparison:
Raw Exhaust:
(H2SO4)RE = 1.4E(11) cm-3



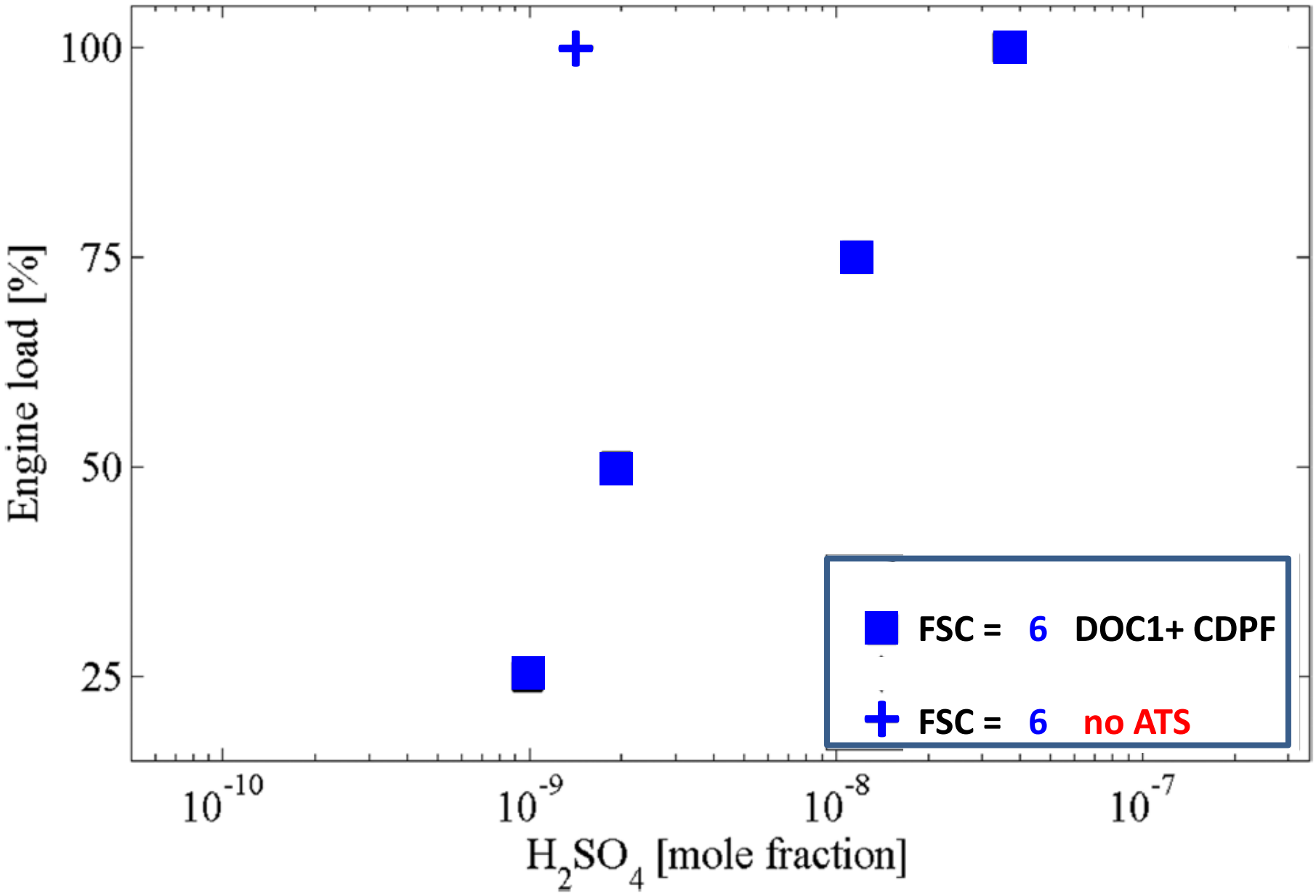
Energetic Ion-collisions with He atoms
ITMS-Mode MS-2

195- → 97- (HSO4-) + 98 (H2SO4)

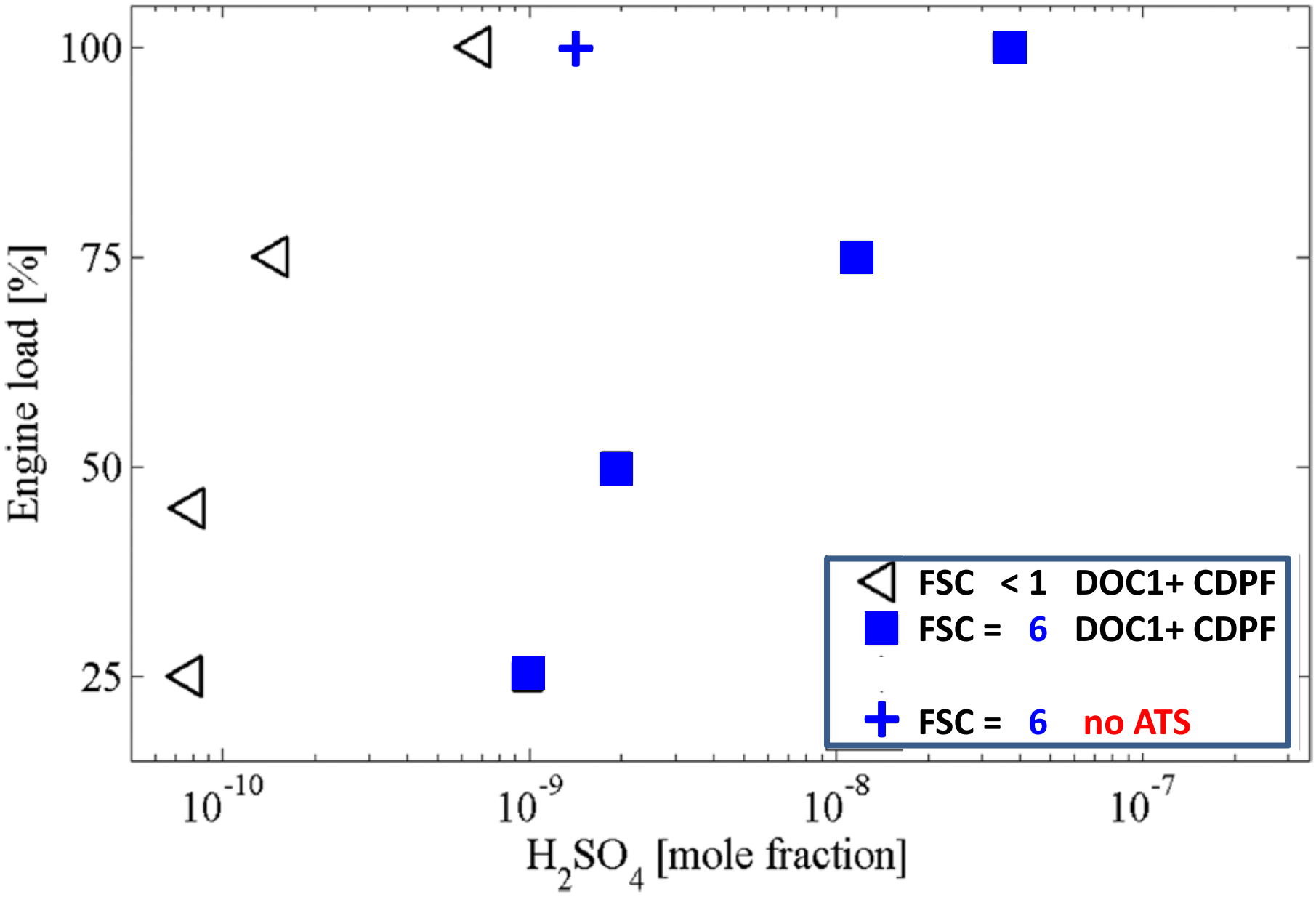


Energetic Ion-collisions with He atoms
ITMS-Mode MS-2
(collision energy increased)

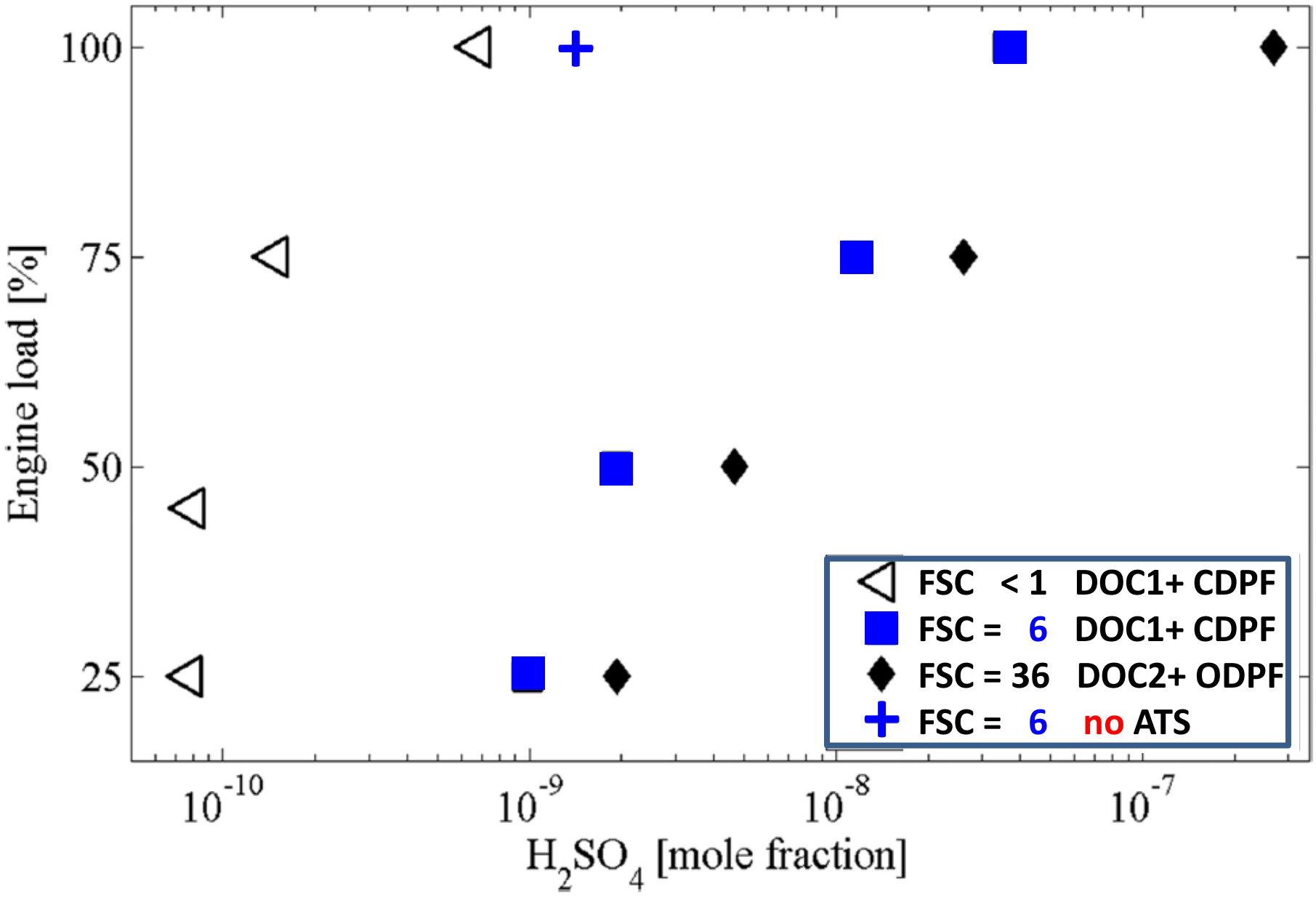
195- → 97- (HSO4-) + 98 (H2SO4)
→ 177- (HSO4-SO3) + 18 (H2O)



Arnold et al. (2012)



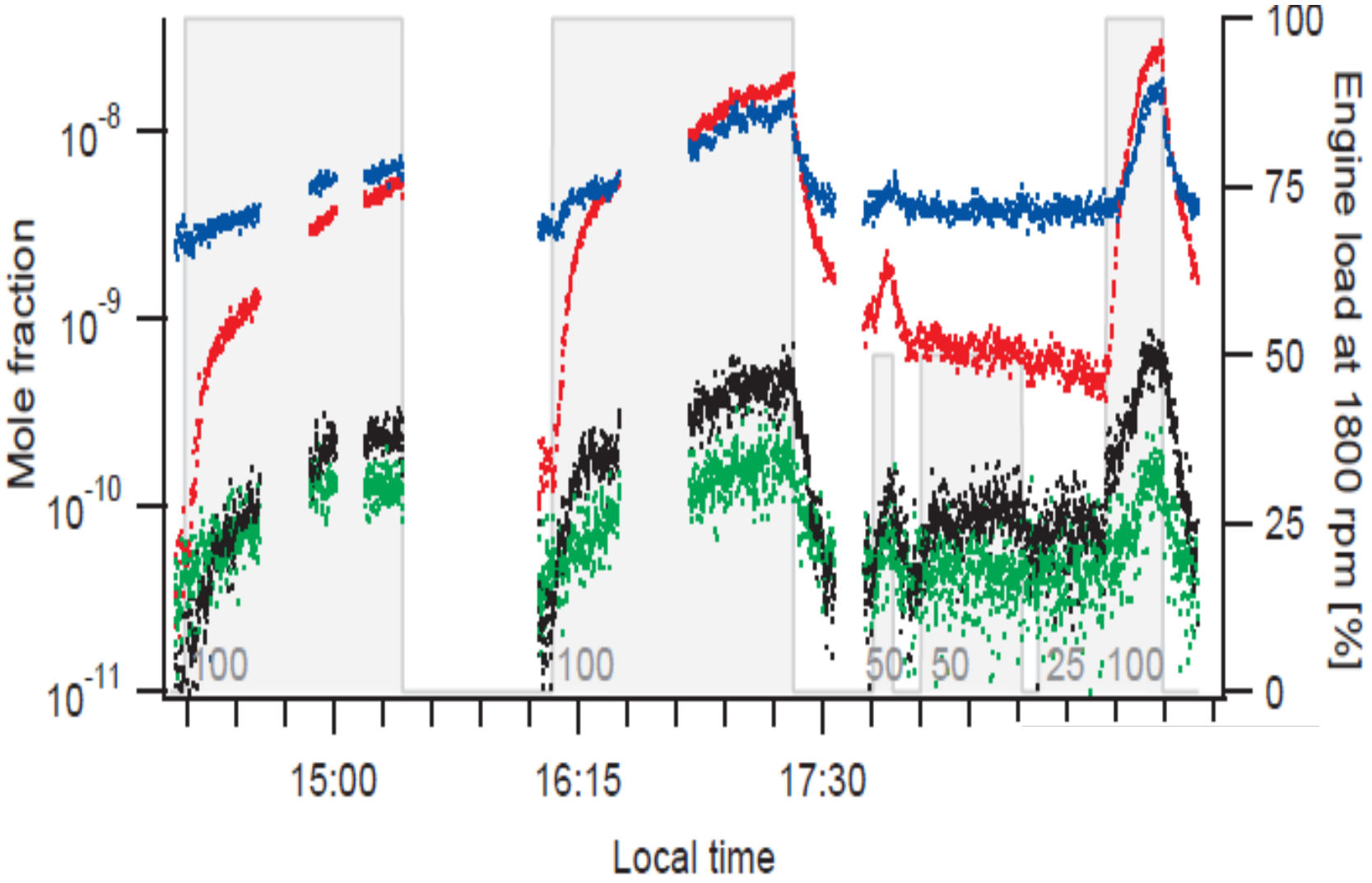
Arnold et al. (2012)



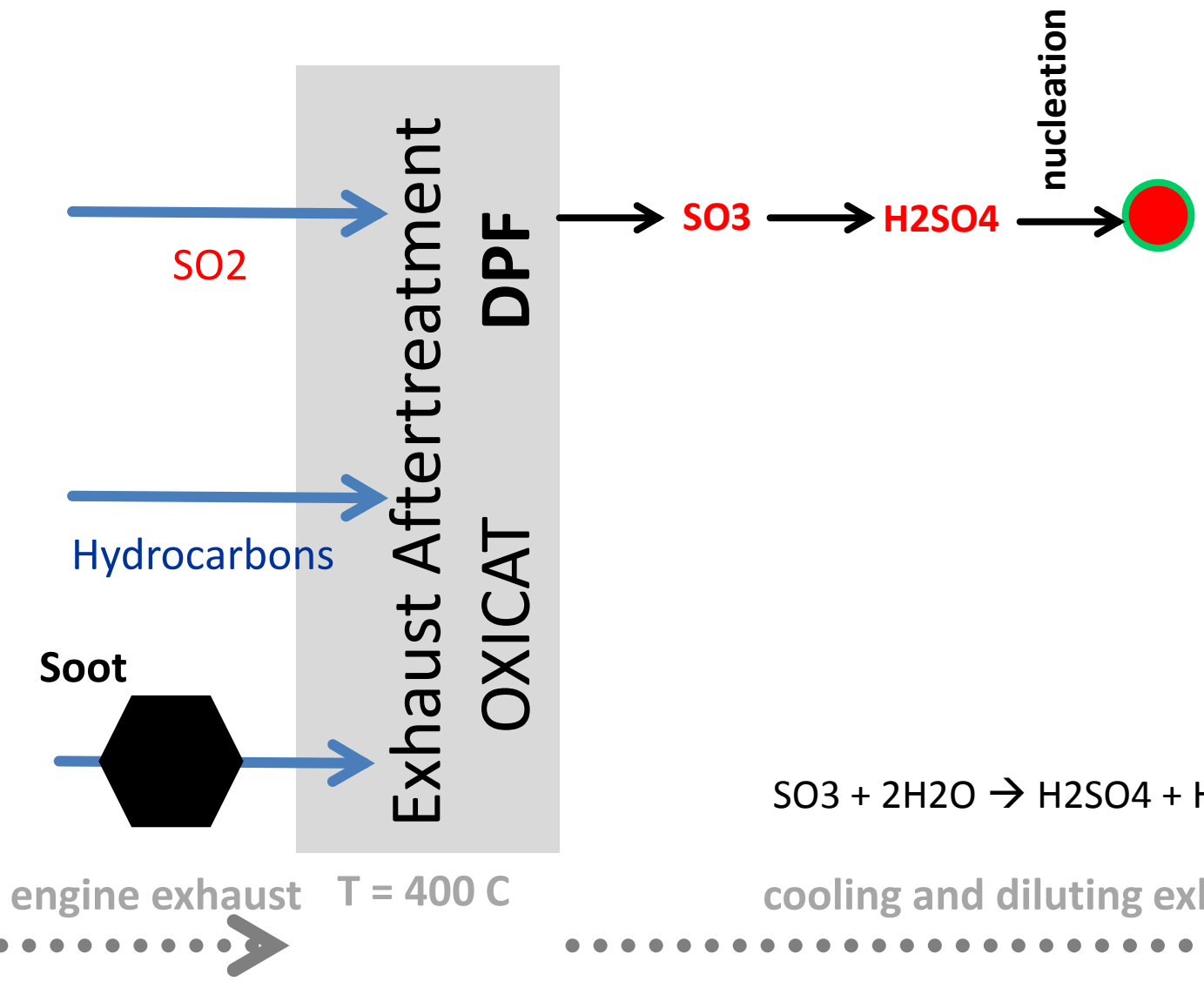
Arnold et al. (2012)

Time series of gas-phase acids (mole fraction of raw exhaust):
FSC = 6 ppm ; EL = 100 % ; ATS (DOC + **CDPF**)

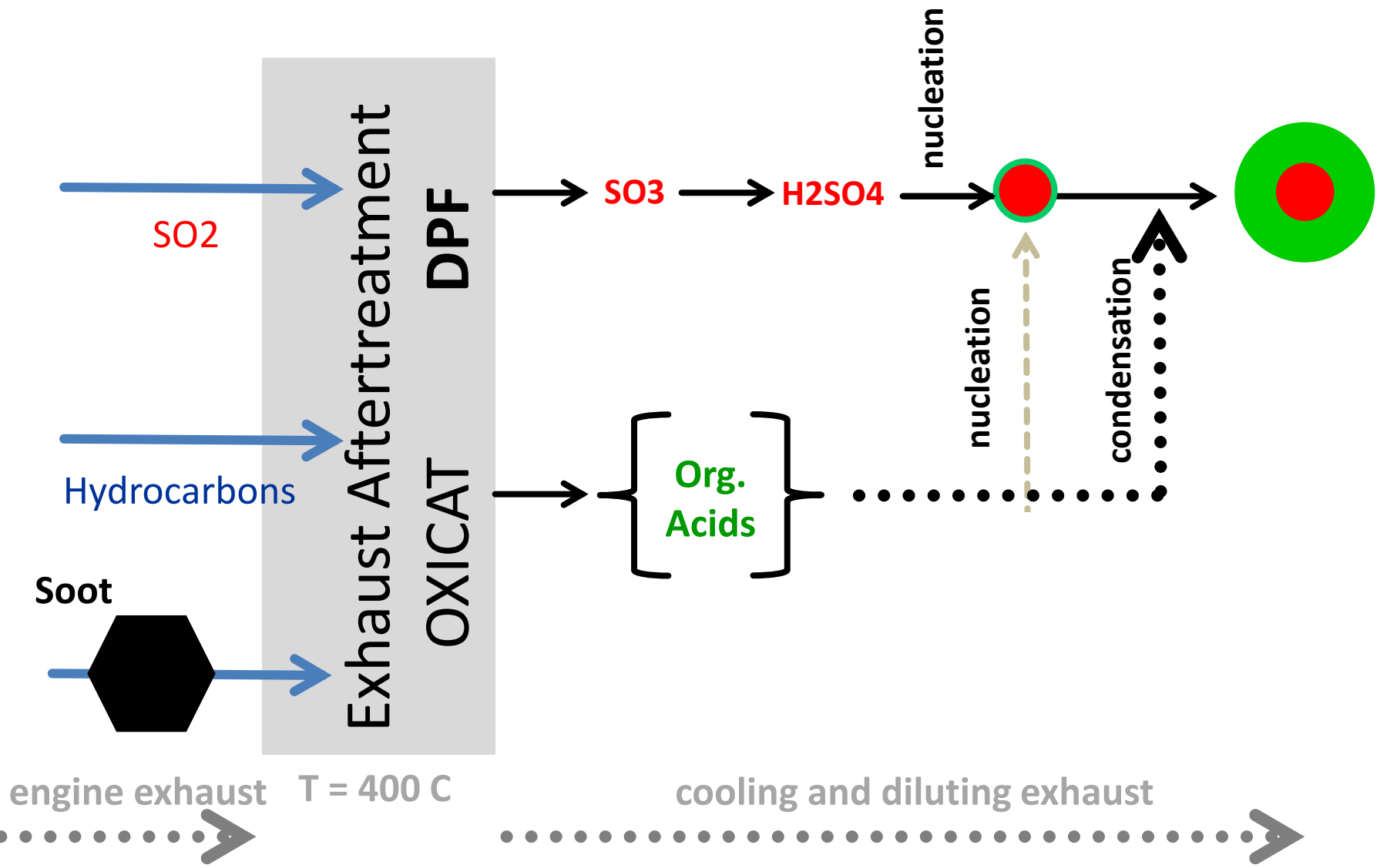
Engine Load ; H2SO4 ; sum of all acids except H2SO4 ; Acid in ion 204 ; Acid in ion 226



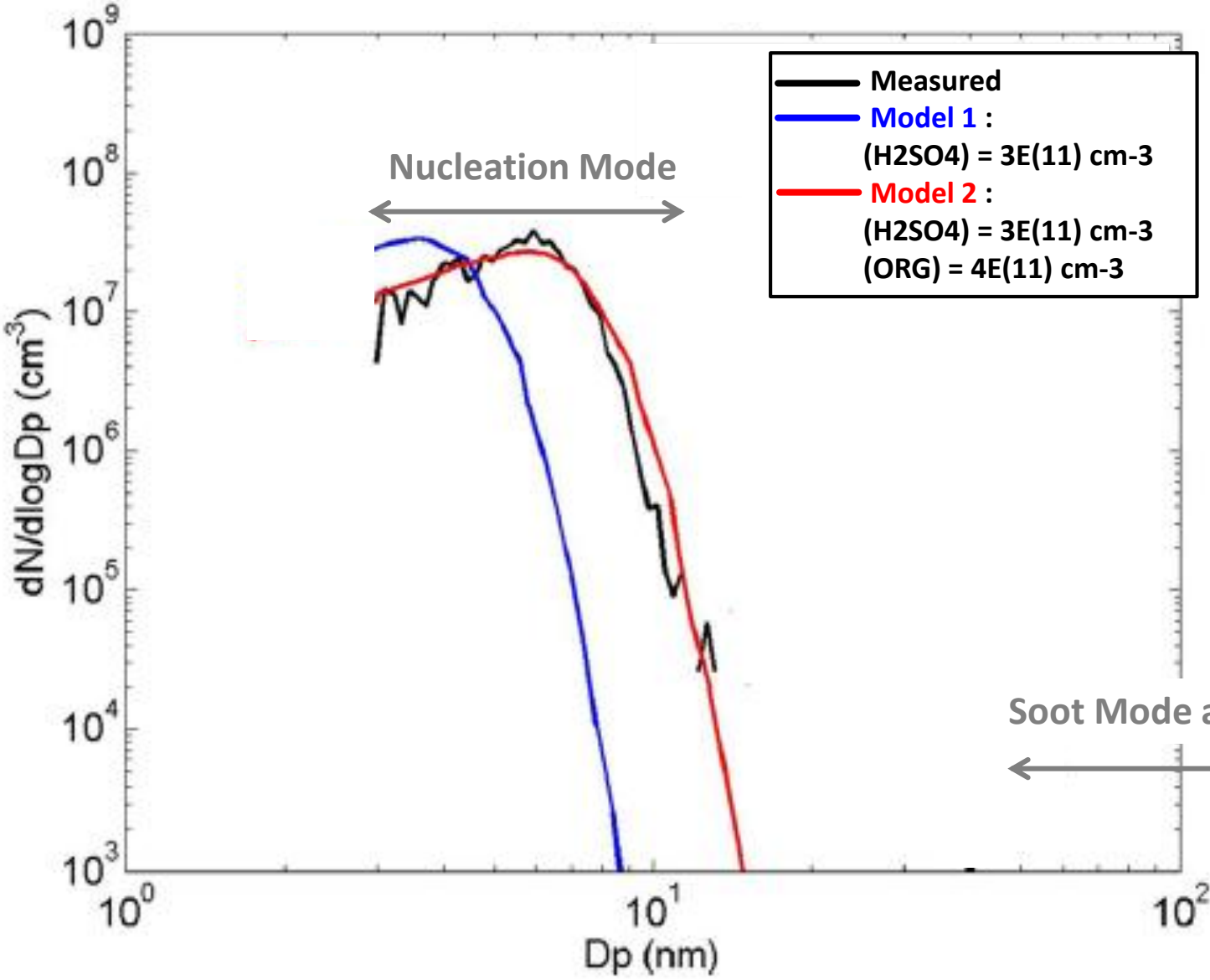
Nucleation Particle Formation in Diesel Vehicle Exhaust
MODEL 2 : simplified scheme <u>without</u> soot (DPF)



Nucleation Particle Formation in Diesel Vehicle Exhaust
MODEL 2 : simplified scheme without soot (DPF)



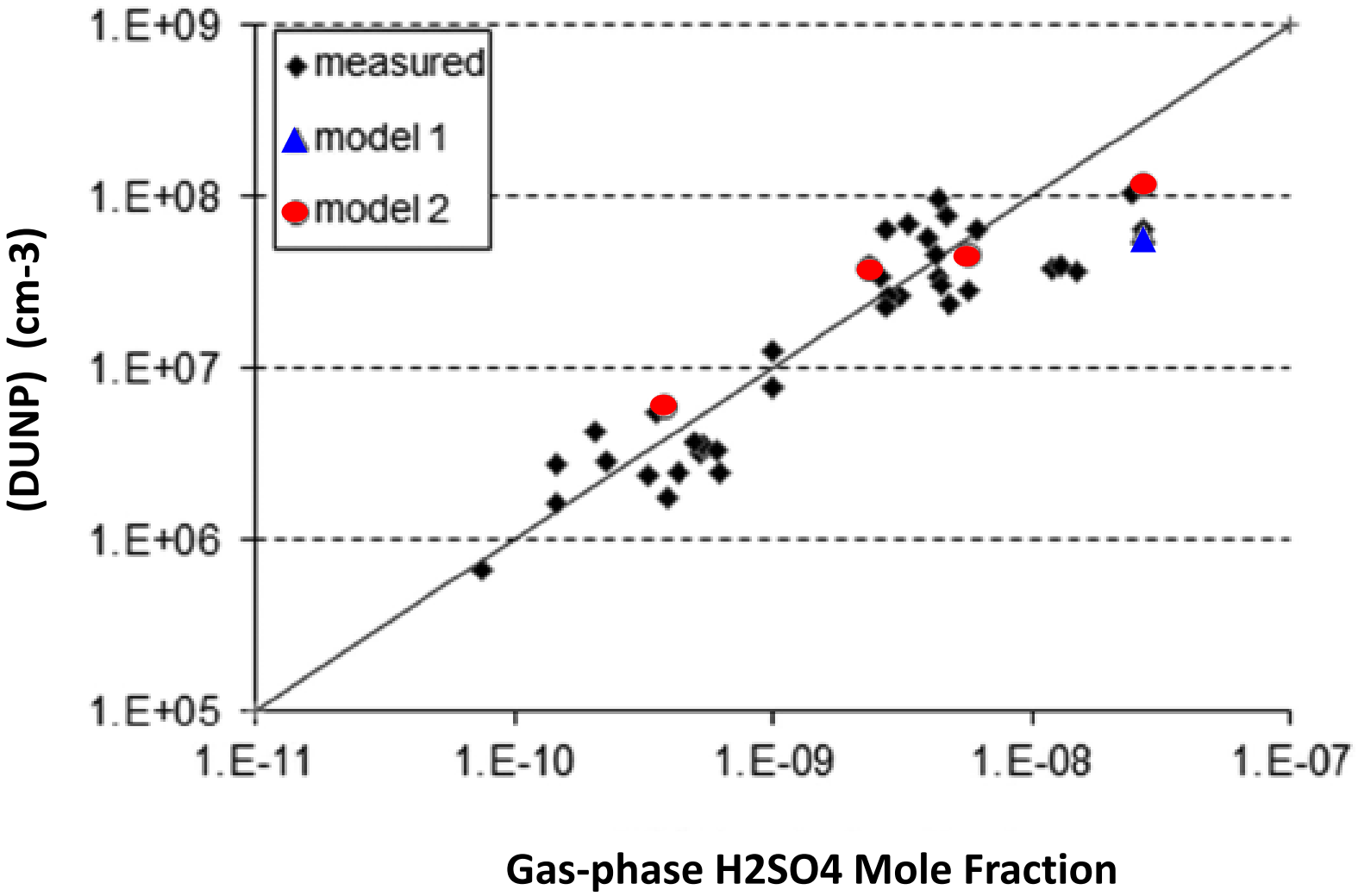
Particle Number Size Distribution : FSC = 6 ppm ; EL = 100 % ; ATS (DOC + **CDPF**)



Arnold et al (2012)

DNUP-number concentration (DNUP) versus gas-phase H2SO4 (GSA) mole fraction

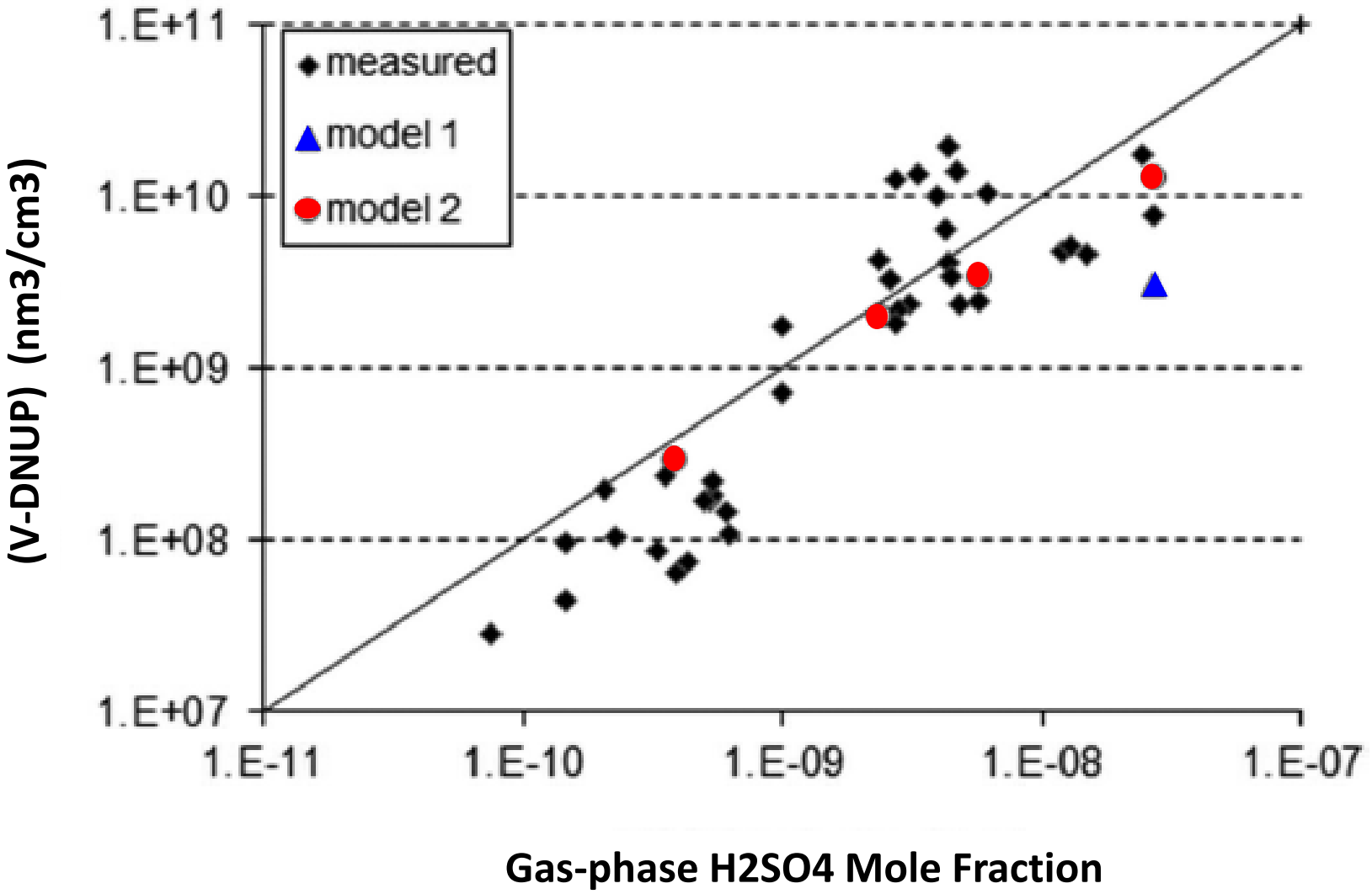
FSC = 6 ppm ; ATS (DOC + **CDPF**)



Arnold et al. (2012)

DNUP-Volume Concentration (V) versus gas-phase H2SO4 (GSA) mole fraction

FSC = 6 ppm ; ATS (DOC + **CDPF**)



Arnold et al. (2012)

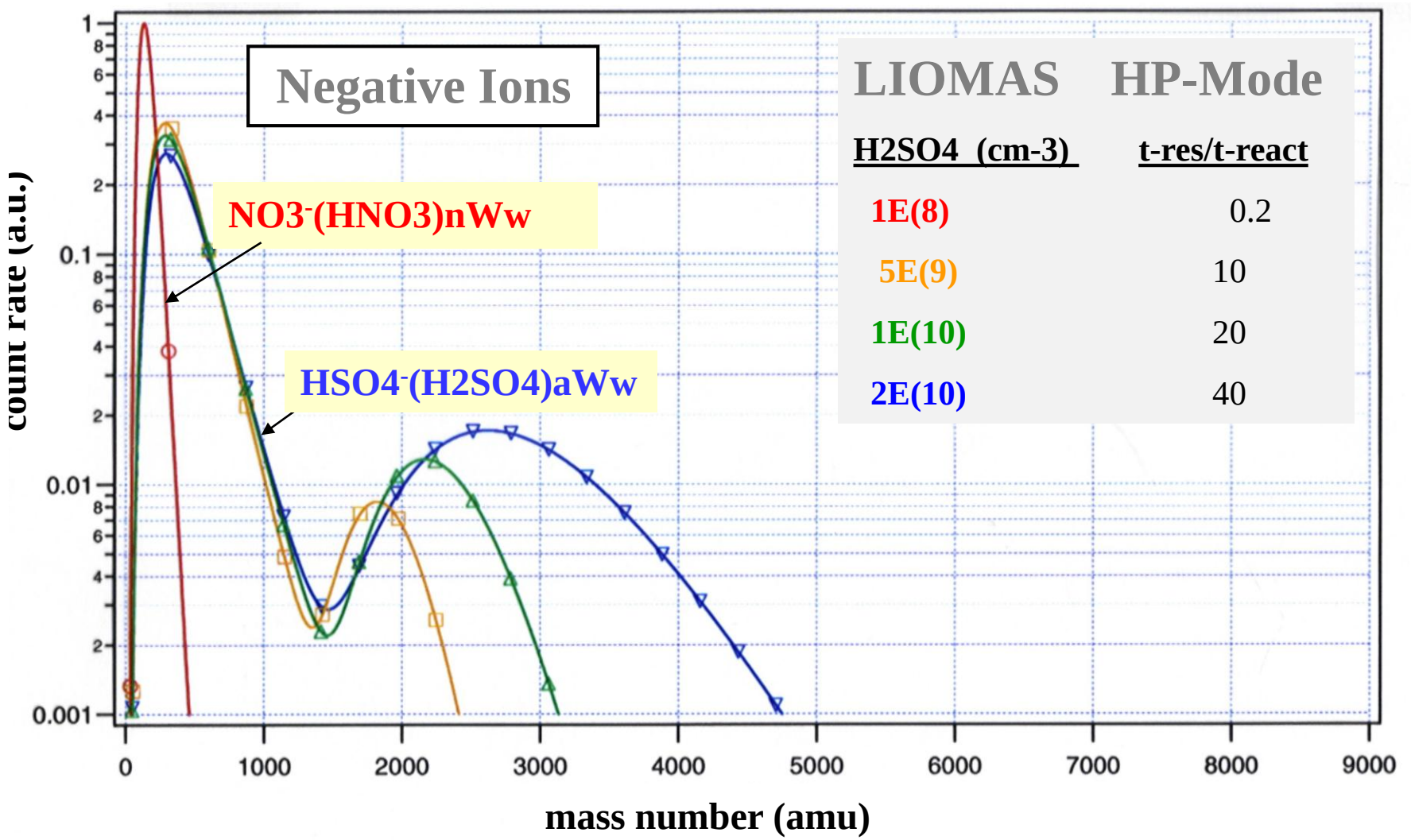
Ion-Nucleation in Diesel-Exhaust

interesting tool for improving understanding of DNPs

- Which molecular species, other than H2SO4 and H2O, are contained in nascent and evolved ionic DNUPs ?

- TEST-Experiment with H2SO4/H2O in synthetic air (without organics)

from review Arnold

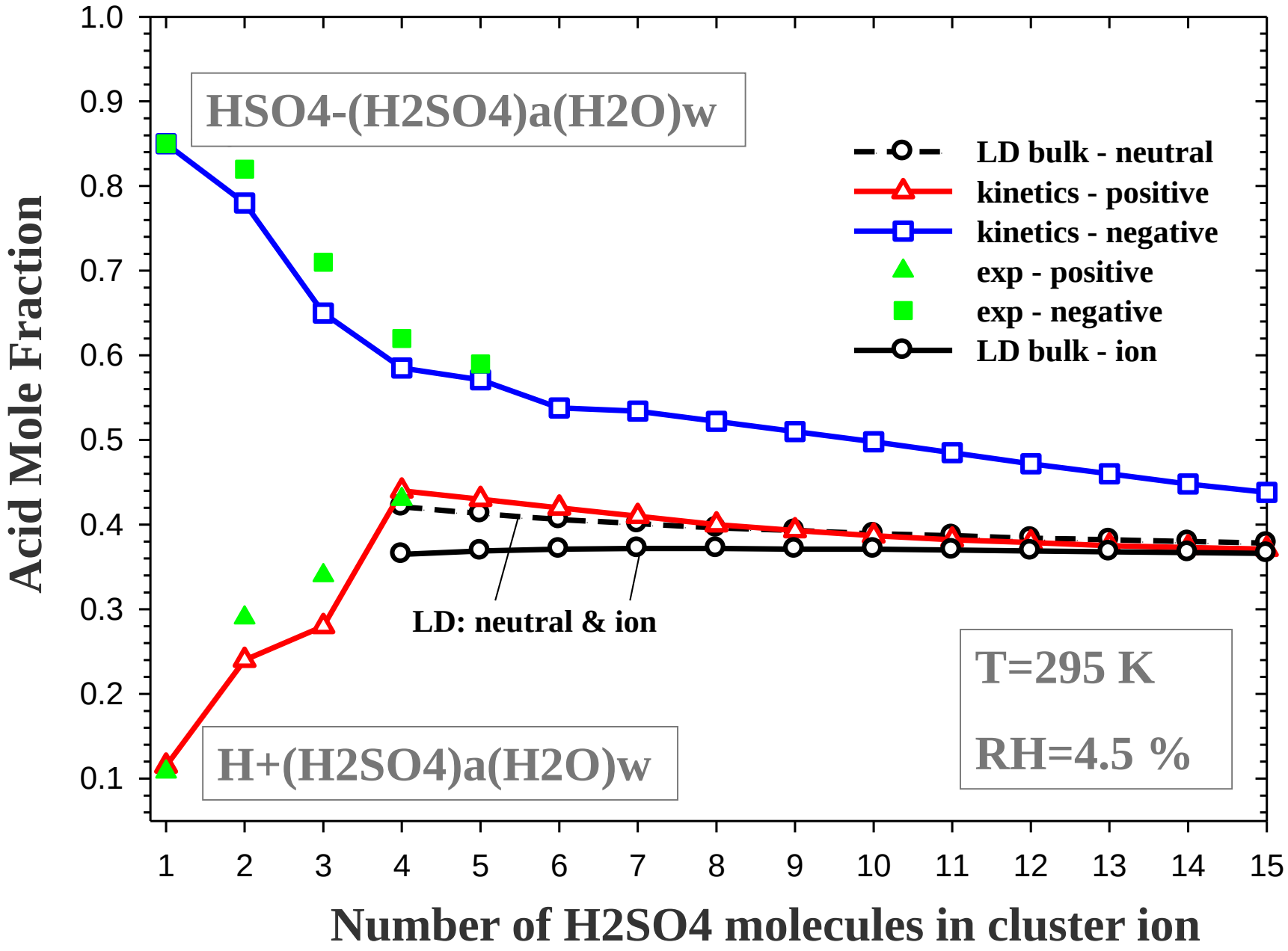


LIOMAS HP-Mode	
H2SO4 (cm-3)	**t-res/t-react**
1E(8)	0.2
5E(9)	10
1E(10)	20
2E(10)	40

FLOW REACTOR EXPERIMENT: Ion-Nucleation

T=295 K , RH= 4.7 % , RA< 2.0 % → no HONU ! , t-res = 1.0 s

from review Arnold



Conclusions

- Many modern D-ATS promote very efficient H_2SO_4 formation
- D-ATS : Strong store and release effects
- For FSC=6 ppmM D-ATS produce as much H_2SO_4 as previous vehicles with FSC = 300 ppmM (without ATS)
- H_2SO_4 is key nucleating gas
- Organics (possibly certain carboxylic acids like adipic acid) contribute to D-NUP growth
- Modern D-ATS do not completely remove organics
- Modern D-ATS may even promote formation of carboxylic acids
- D-NUPs intrude and may carry to alveolar region certain toxic and mutagenic molecular species
- DNUPs and their potential adverse health effects deserve increased future attention

Thank You
for your interest