Contribution by Prof. Frank Arnold:

Combustion Generated Aerosol Precursors

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Combustion processes produce trace gases and gaseous ions which have a potential to act as aerosol-precursors. Here emphasis will be placed upon aerosol-precursors formed by aircraft preferably at altitudes around 8-12 km. A particularly important aerosol-precursor is gaseous sulfuric acid (GSA) which is formed from aircraft-fuel sulfur. Due to its large hygroscopicity GSA undergoes binary-nucleation with water vapour which leads to the formation of H2SO4/H2O aerosol particles. Ternary-nucleation involving also ammonia which is important in the lower atmospheric layers seems to be less important around 8-12 km due to very low ammonia abundances. Binary H2SO4/H2O nucleation may proceed via a homogeneous mechanism (HONU) or an ion-induced mechanism (INU). It seems that gaseous ions produced by chemi-ionization in aircraft gas turbine engines have a potentially important role in mediating H2SO4/H2O nucleation. The efficiency of ion-induced aerosol formation in aircraft engine exhaust depends critically on the GSA-concentration and on the nature and concentration of chemiions. Around 8-12 km further growth of freshly formed and still very small aerosols is to a large part controlled by condensation of atmospheric condensable trace gases probably mostly H2SO4. The latter mostly does not stem from aircraft but rather stems from photochemical conversion of SO2 emited by ground-level combustion sources.

The present talk reports on mass spectrometric measurements of gaseous and ionic aerosol-precursors in the free troposphere, in the wakes of aircraft, and in the exhaust of aircraft gast turbine engines at ground-level. Furthermore the talk reports on laboratory investigations of ion-induced nucleation of H2SO4/H2O.

More information on our work on combustion-generated atmospheric aerosols can be found in the following reference list.

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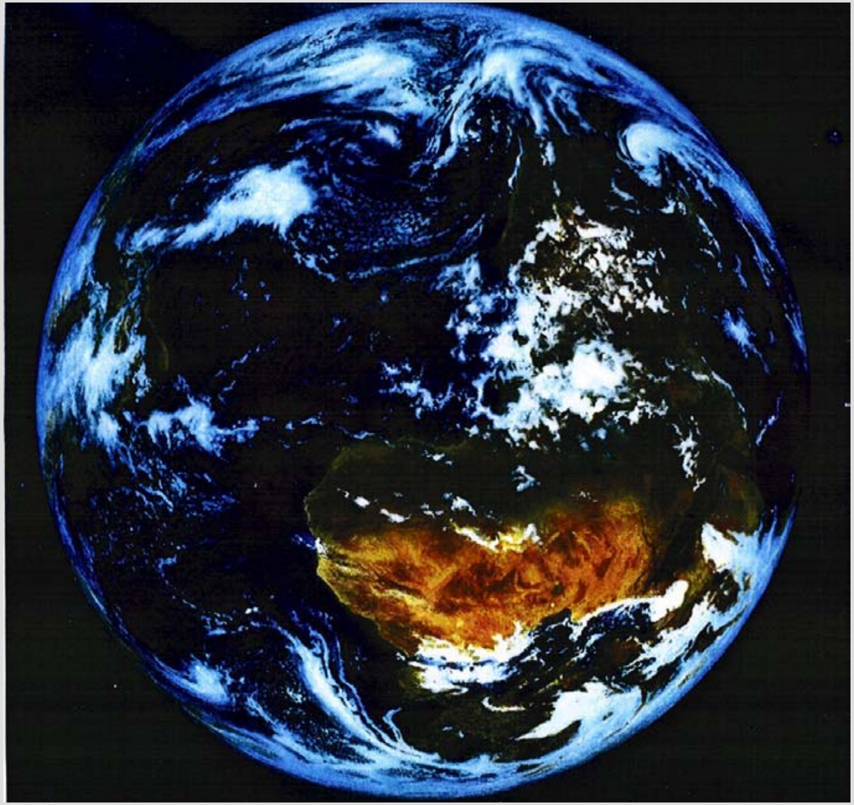
Combustion Generated Aerosol Precursors



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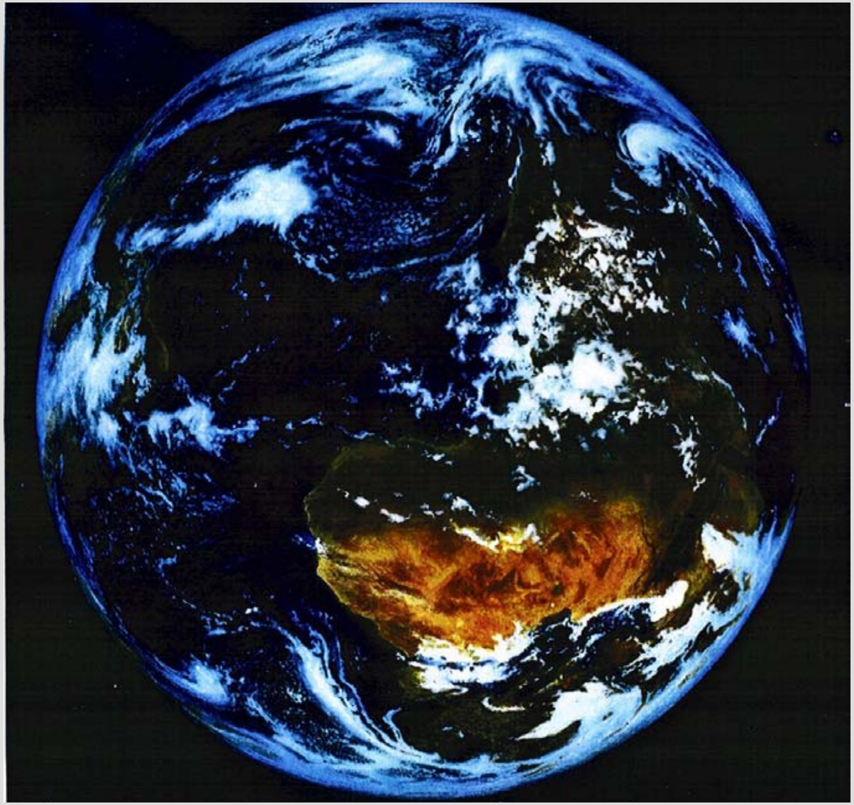
th ETH Conf. on *Combustion Generated Nanoparticles* ,Zürich 16-18 August 2004

Combustion Generated Aerosol Precursors



Potential
Influence

on

CLOUDS

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Aerosol-Precursor Measurements

- GASES
- IONS

Aerosol Precursor Measurements: Environments

- Free Atmosphere

Aerosol Precursor Measurements: Environments

- Free Atmosphere
- Atmospheric Boundary Layer

Aerosol Precursor Measurements: Environments

- Free Atmosphere
- Atmospheric Boundary Layer
- Air Craft Wakes (in flight)

Aerosol Precursor Measurements: Environments

- Free Atmosphere
- Atmospheric Boundary Layer
- Air Craft Wakes (in flight)
- Air Craft Engine Exhaust (at ground level)

Aerosol Precursor Measurements: Environments

- Free Atmosphere
- Atmospheric Boundary Layer
- Air Craft Wakes (in flight)
- Air Craft Engine Exhaust (at ground level)
- Ship Plumes

Aerosol Precursor Measurements: Environments

- Free Atmosphere
- Atmospheric Boundary Layer
- Air Craft Wakes (in flight)
- Air Craft Engine Exhaust (at ground level)
- Ship Plumes
- Burner Exhaust (laboratory)

Aerosol Precursor Measurements: Environments

- Free Atmosphere
- Atmospheric Boundary Layer
- Air Craft Wakes (in flight)
- Air Craft Engine Exhaust (at ground level)
- Ship Plumes
- Burner Exhaust (laboratory)
- Flow Reactor (laboratory)

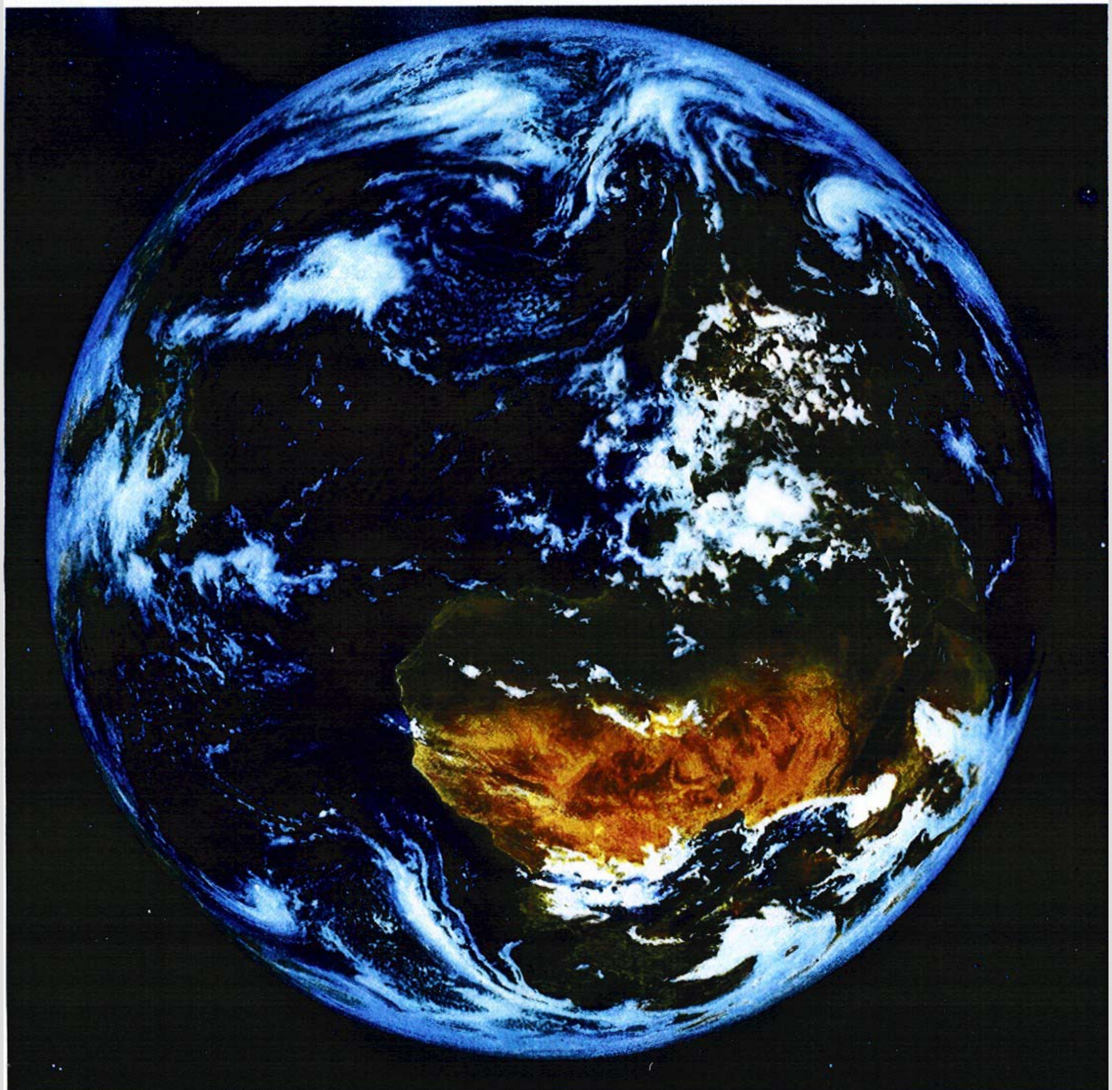
Aerosol Precursor Measurements:
Environments

- Free Atmosphere
- Atmospheric Boundary Layer
- Air Craft Wakes (in flight)
- Air Craft Engine Exhaust (at ground level)
- Ship Plumes
- Burner Exhaust (laboratory)
- Flow Reactor (laboratory)

Does Air Traffic Influence the ATMOSPHERE ?

- TRACE GASES
- AEROSOL
- CLOUDS
- CLIMATE

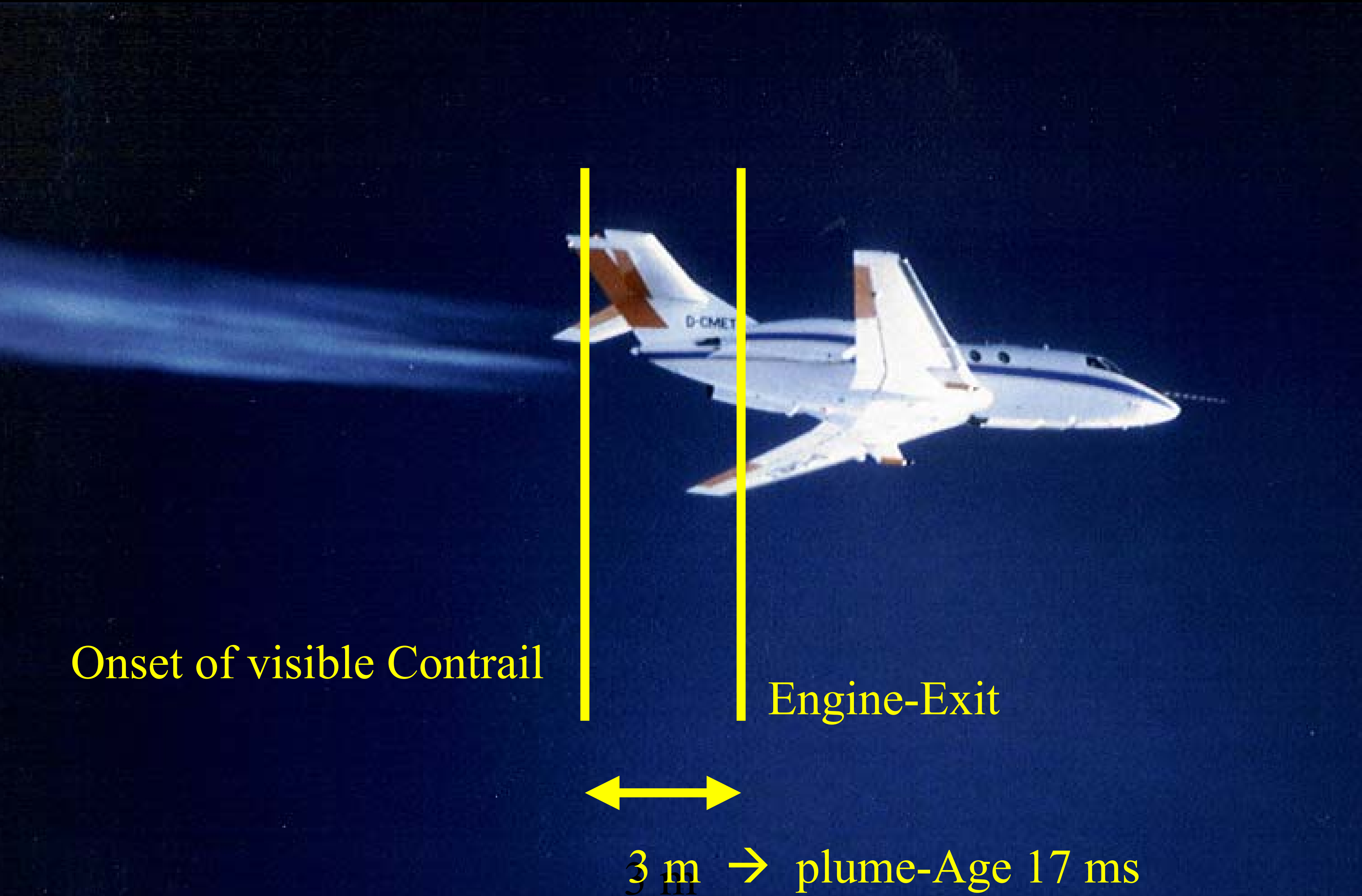
Does Air Traffic influence Clouds ?



CONDENSATION TRAIL

Most striking Manifestation of an
Air Traffic Influence on
Atmospheric Clouds


D-CMET



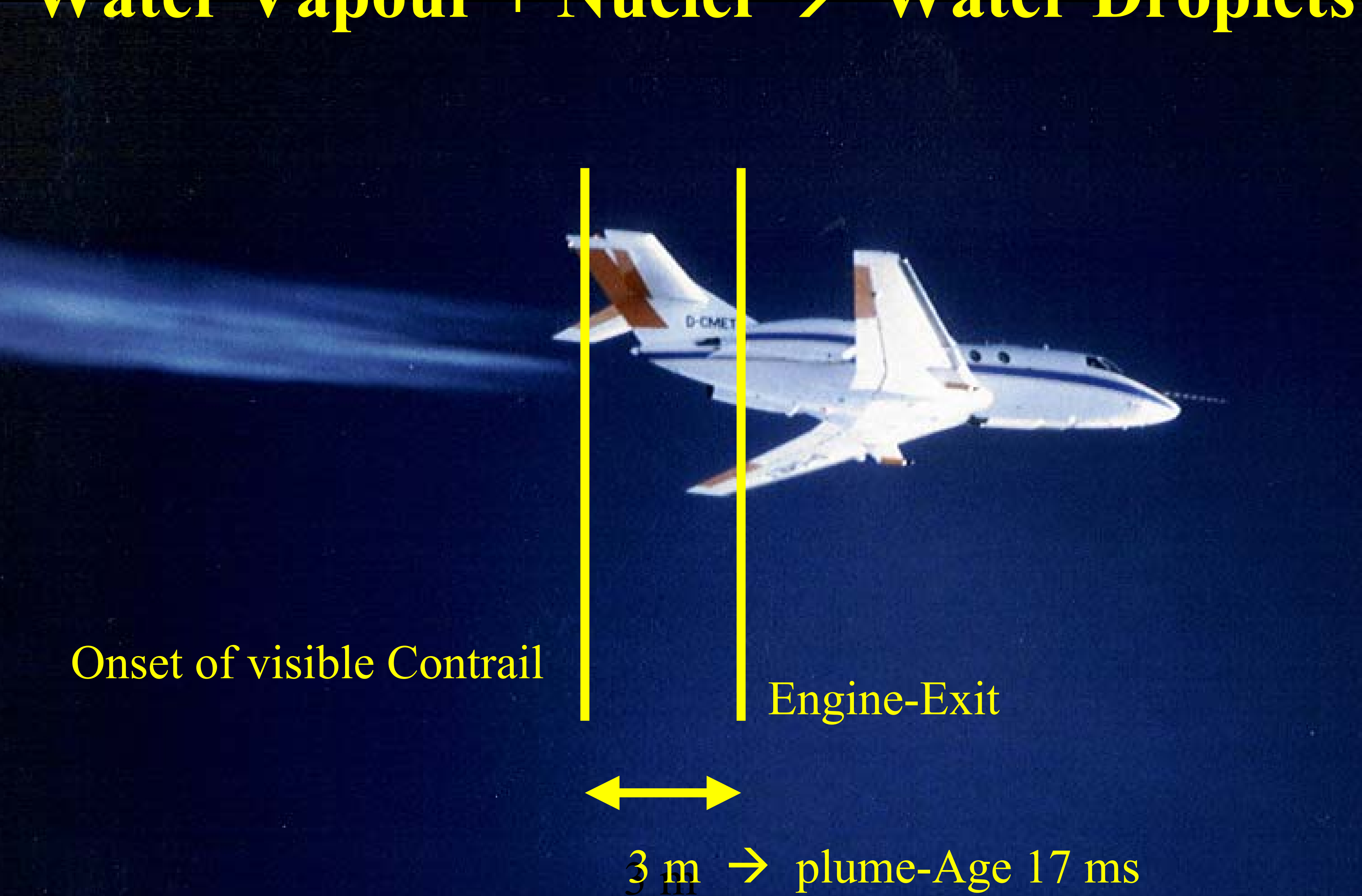
Onset of visible Contrail

Engine-Exit

3 m → plume-Age 17 ms

3 m

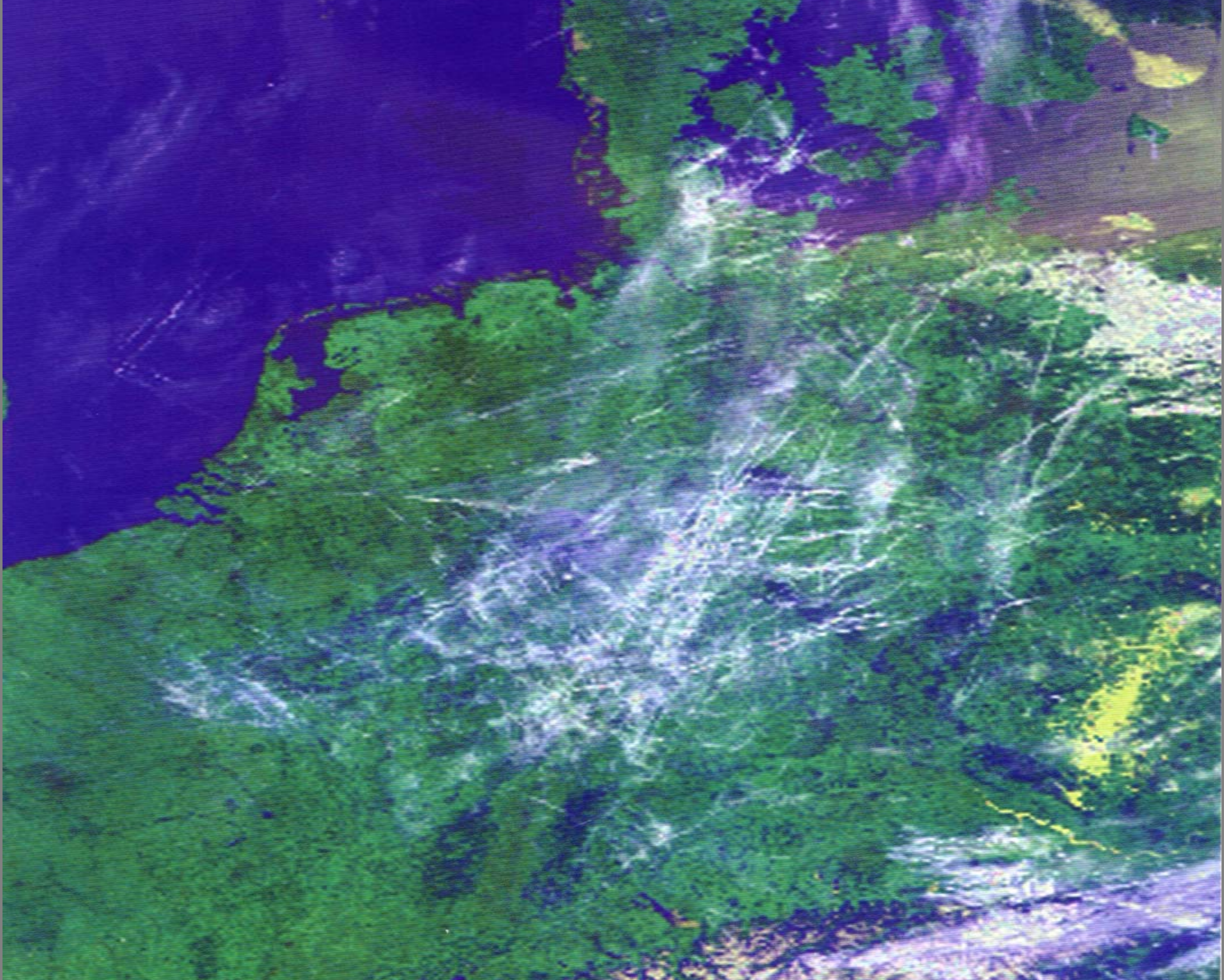
Water Vapour + Nuclei → Water Droplets

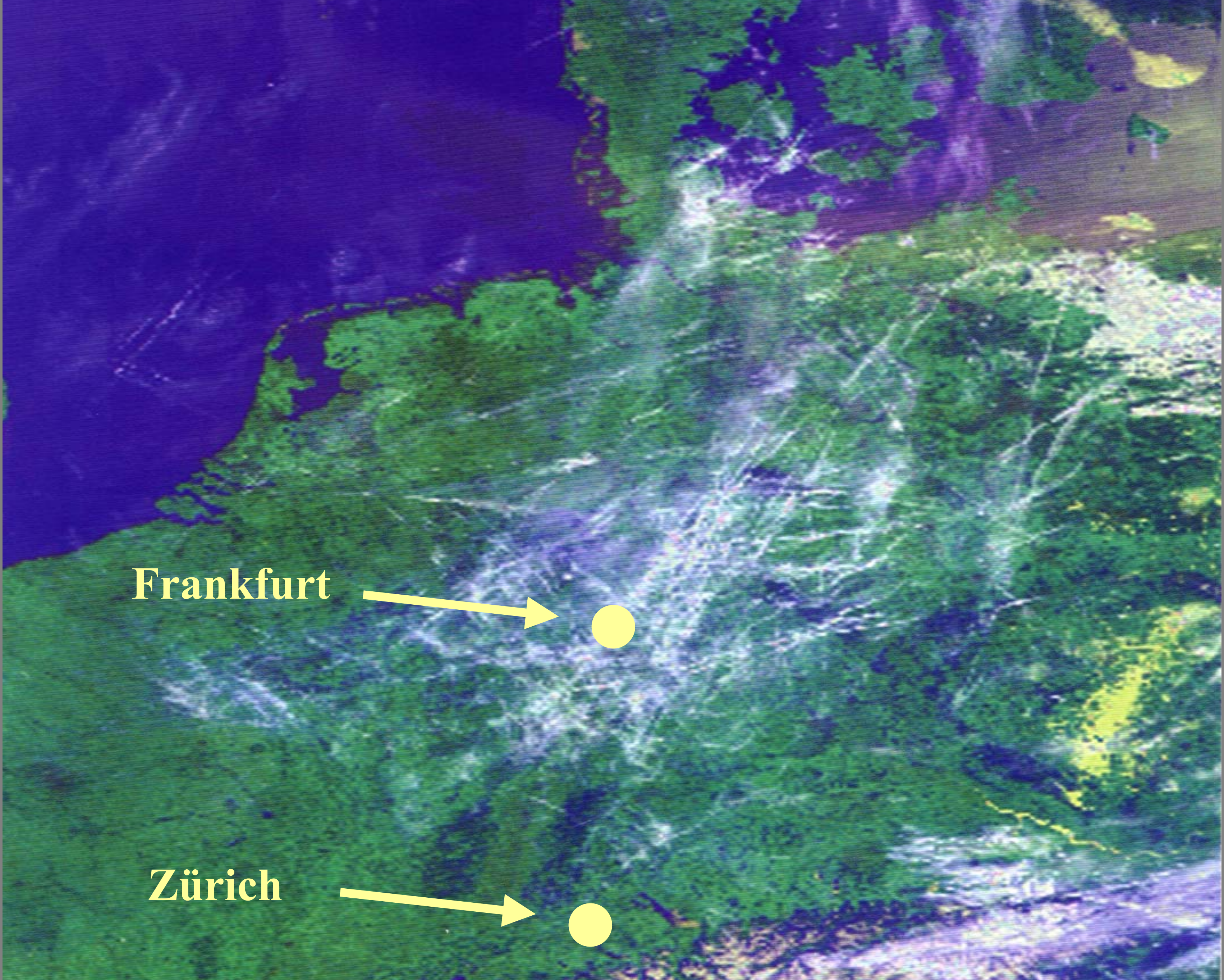


Onset of visible Contrail

Engine-Exit

3 m → plume-Age 17 ms




Frankfurt
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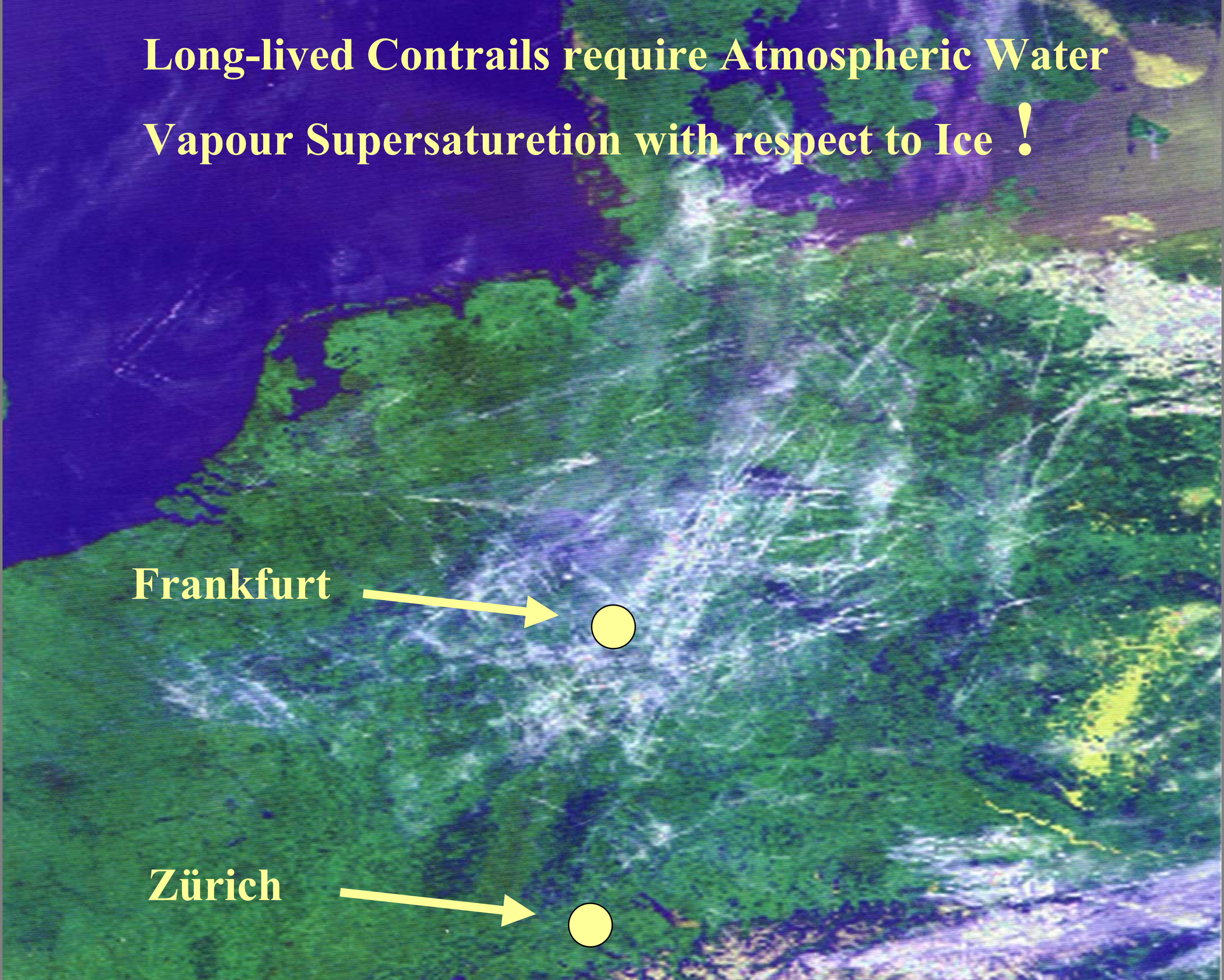
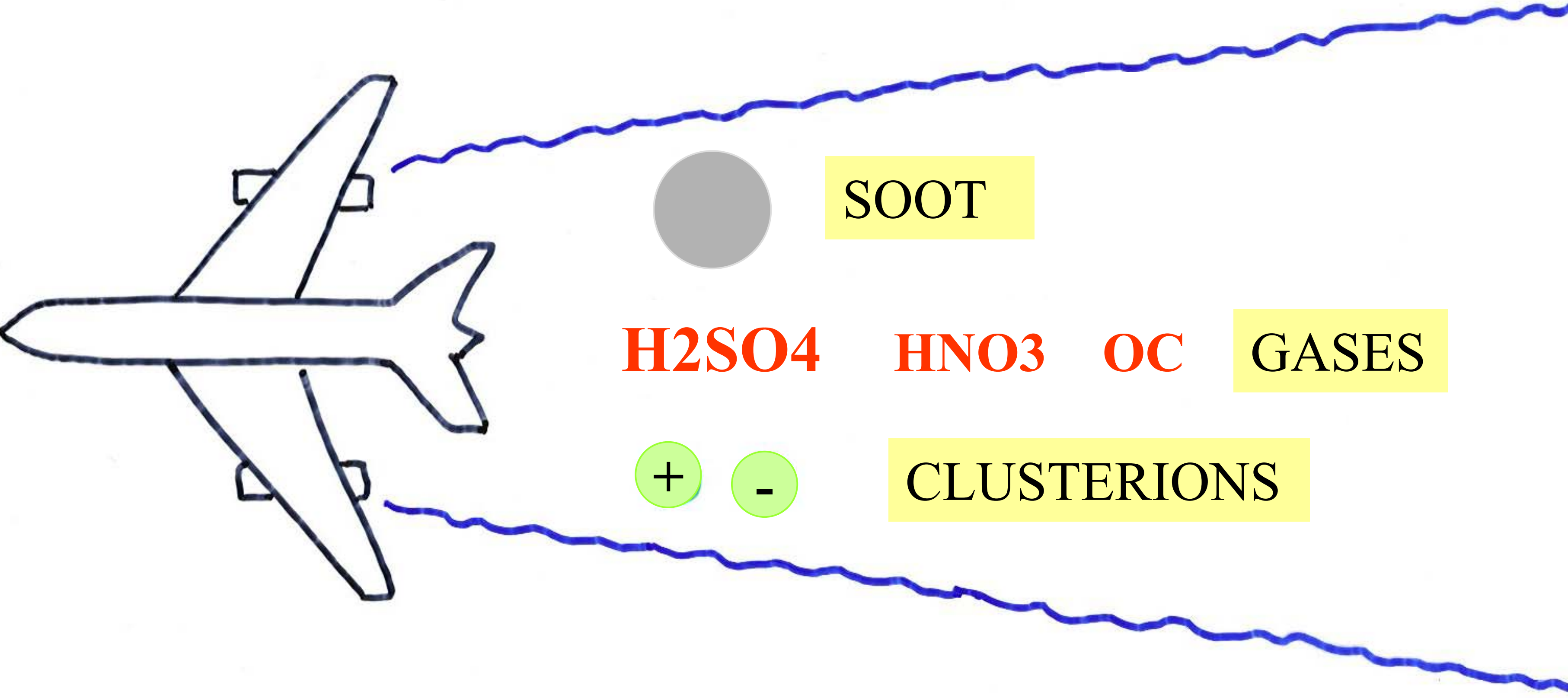
Long-lived Contrails require Atmospheric Water Vapour Supersaturetion with respect to Ice !



Aerosol-Precursors and Primary Aerosol in the Early Aircraft-Wake



SOOT

H2SO4 **HNO3** **OC** GASES

\+ -

CLUSTERIONS

SULFURIC ACID MOLECULE
H_2SO_4

- Most important property : large **GA**
  → proton transfer to other molecule with large **PA**
  (example **H_2O)** → strong **H-Bond**
  → Gas-Phase Hydrates $H_2SO_4(H_2O)_n$

SULFURIC ACID MOLECULE
H_2SO_4

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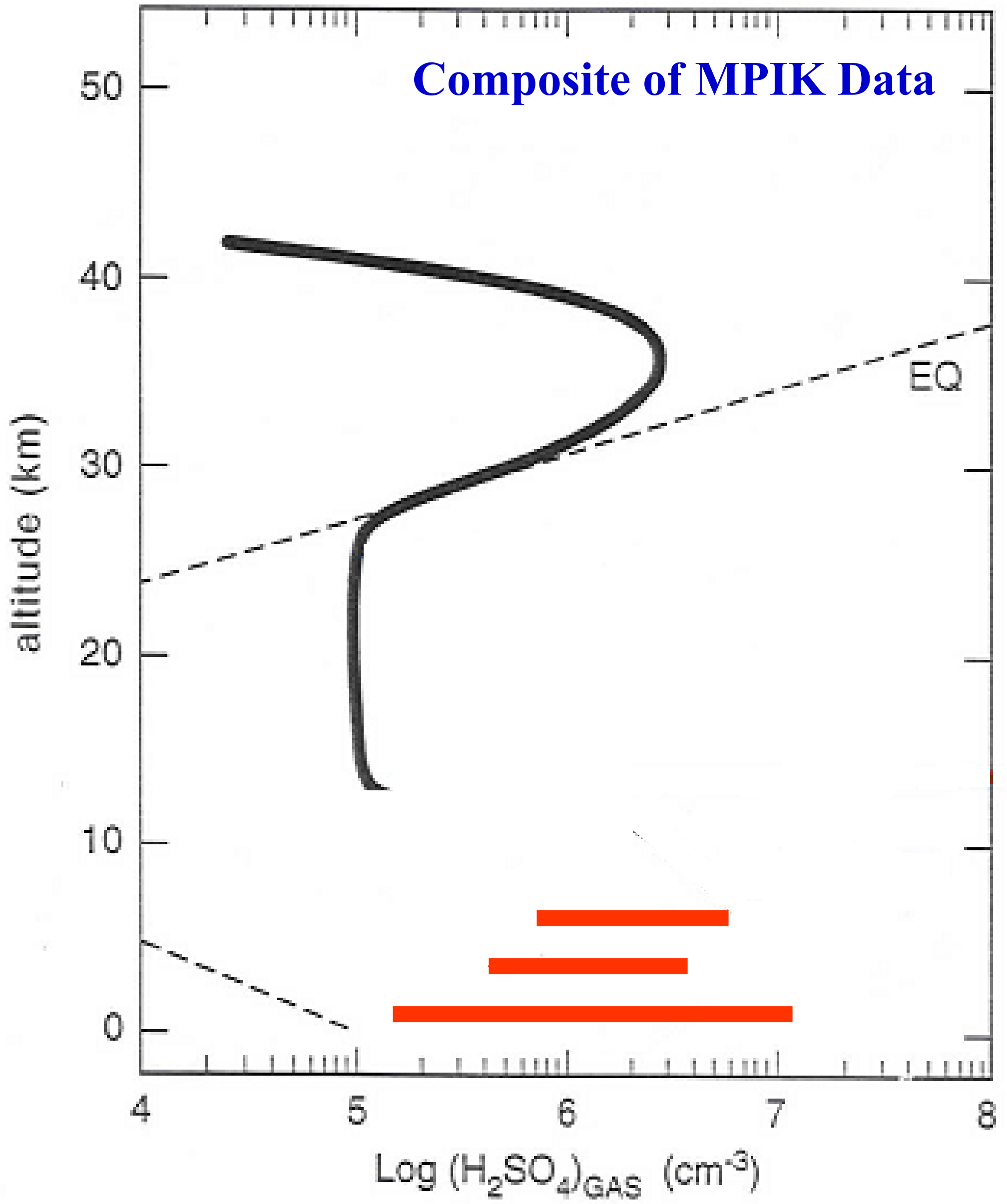
  → Gas-Phase Hydrates $H_2SO_4(H_2O)_n$

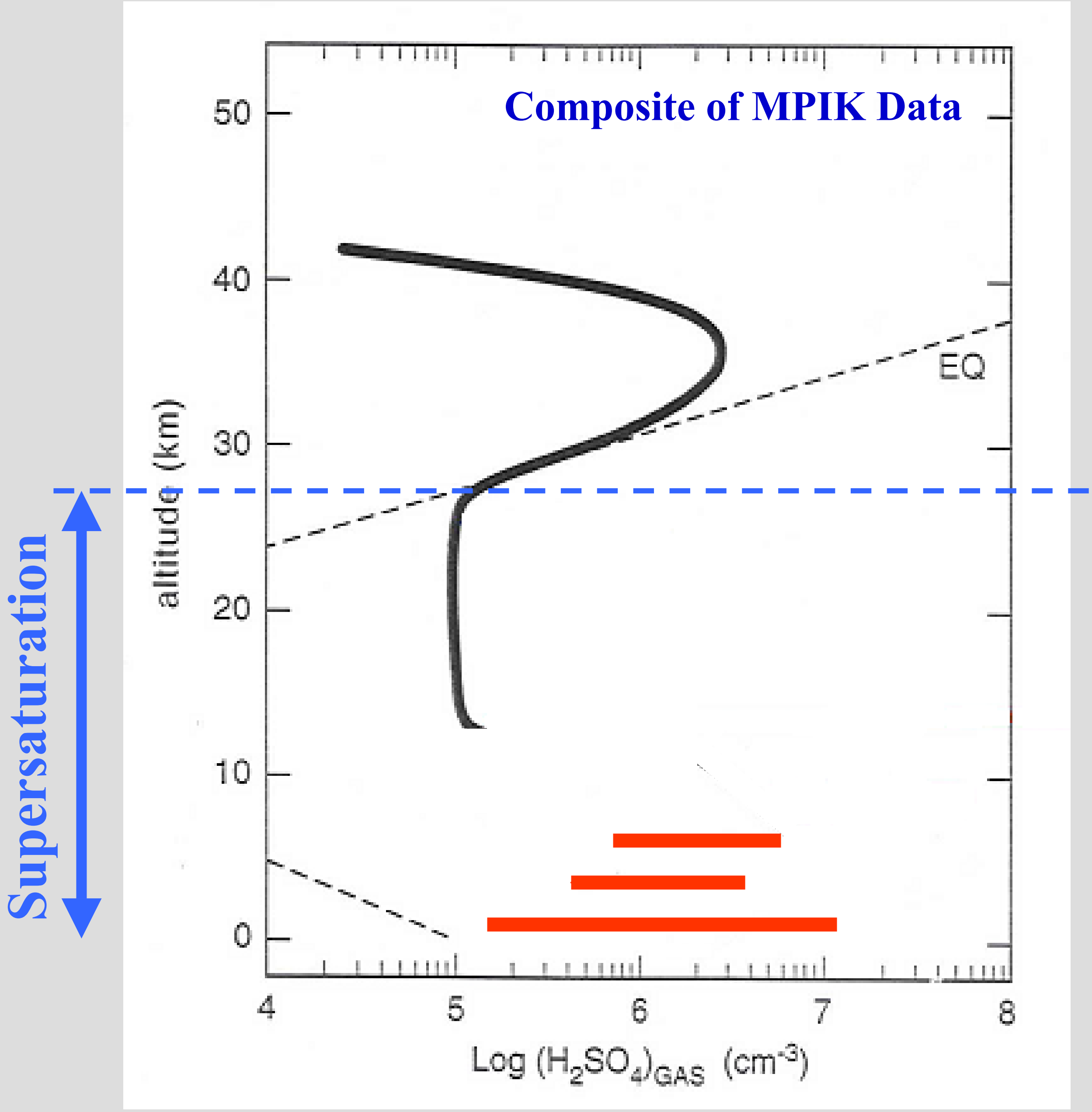
- Atmosphere :
  Primary H_2SO_4 released from combustion
  Secondary H_2SO_4 formed in Atmosphere from SO_2
  → Supersaturation → **H_2SO_4-H_2O Condensation**

Gaseous Sulfuric Acid
in the Atmosphere

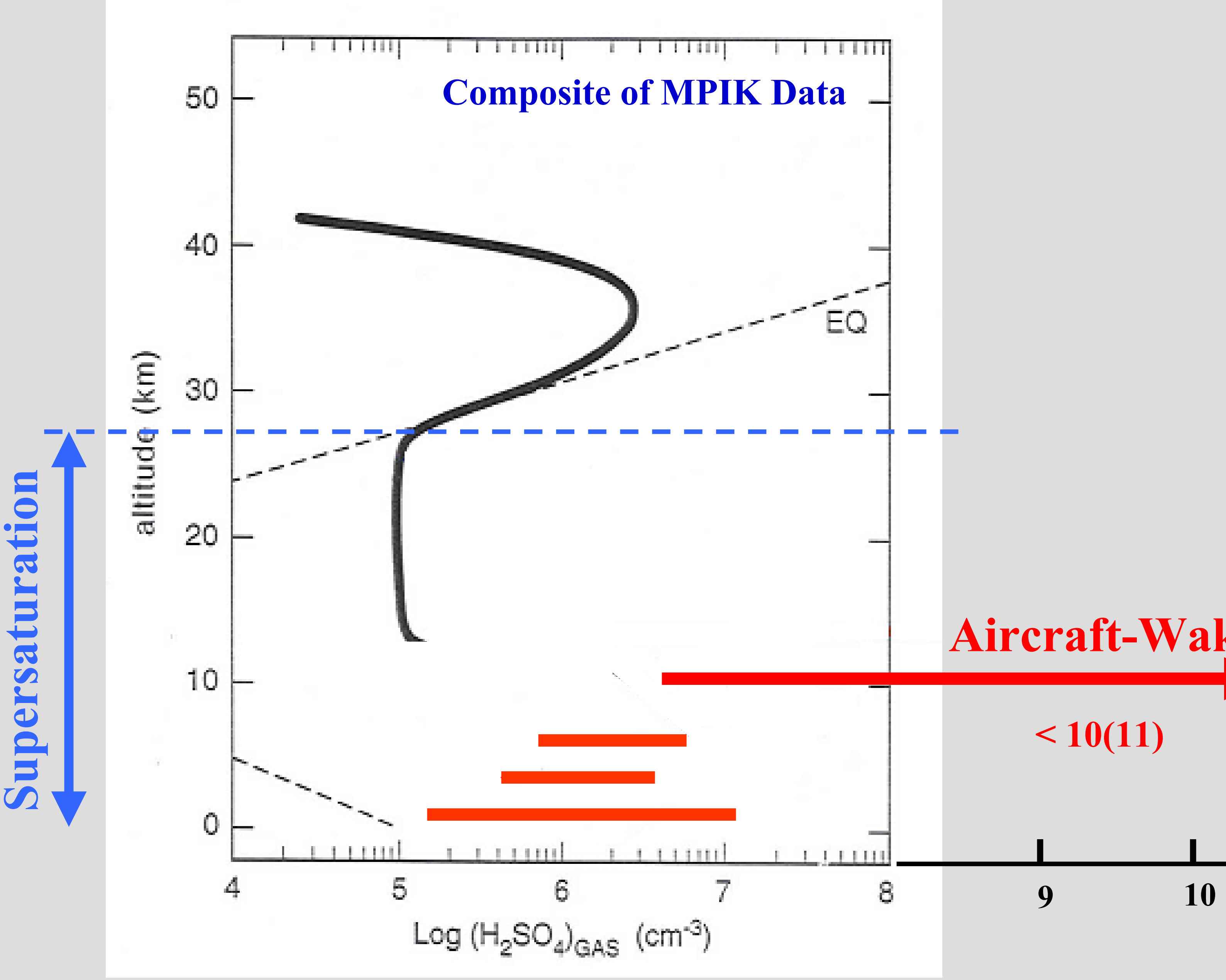
ATMOSPHERIC GASEOUS SULFURIC ACID



ATMOSPHERIC GASEOUS SULFURIC ACID



ATMOSPHERIC GASEOUS SULFURIC ACID



Aircraft Engine Exhaust

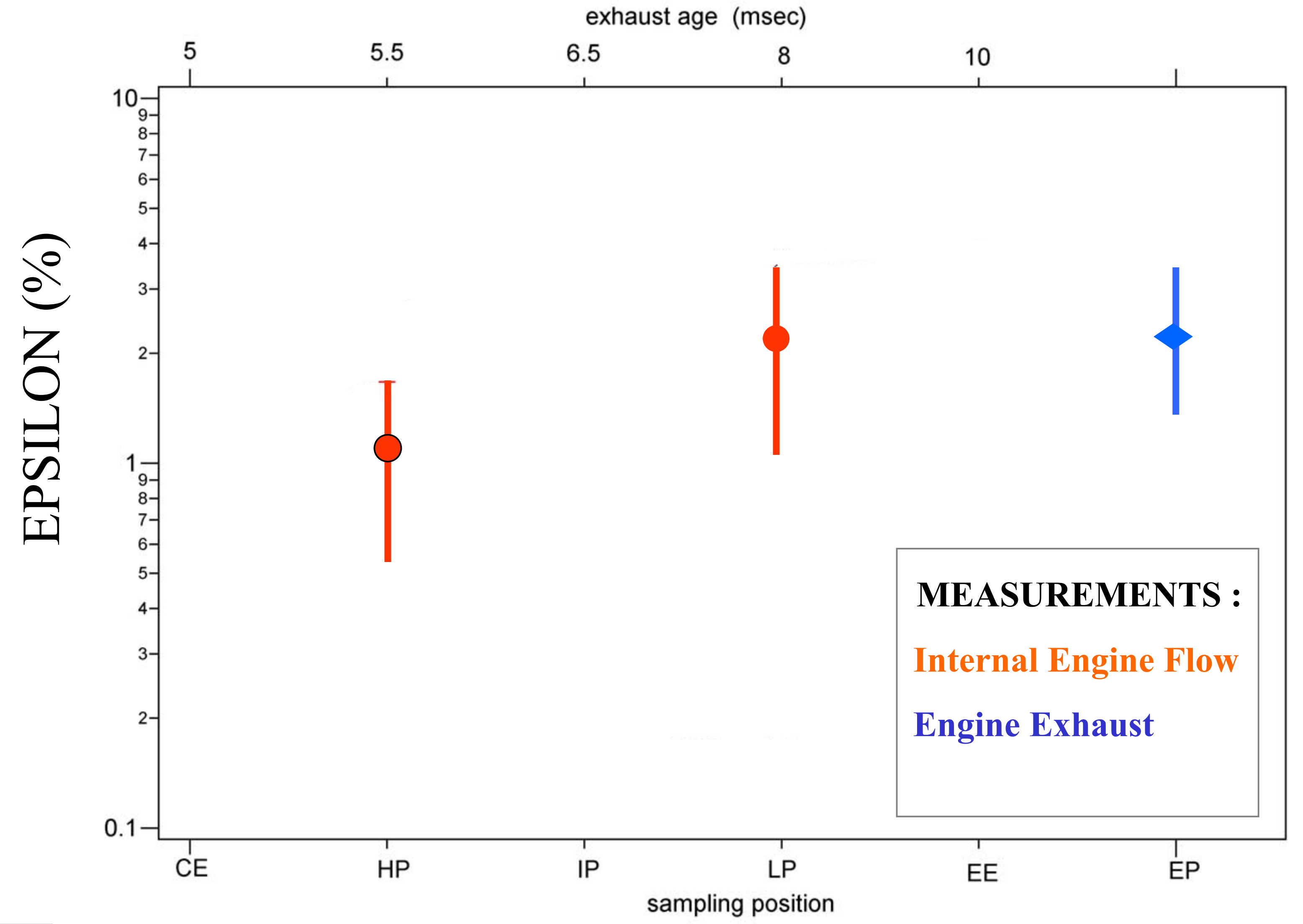
Gaseous Sulfuric Acid

Measurements at Ground-Level

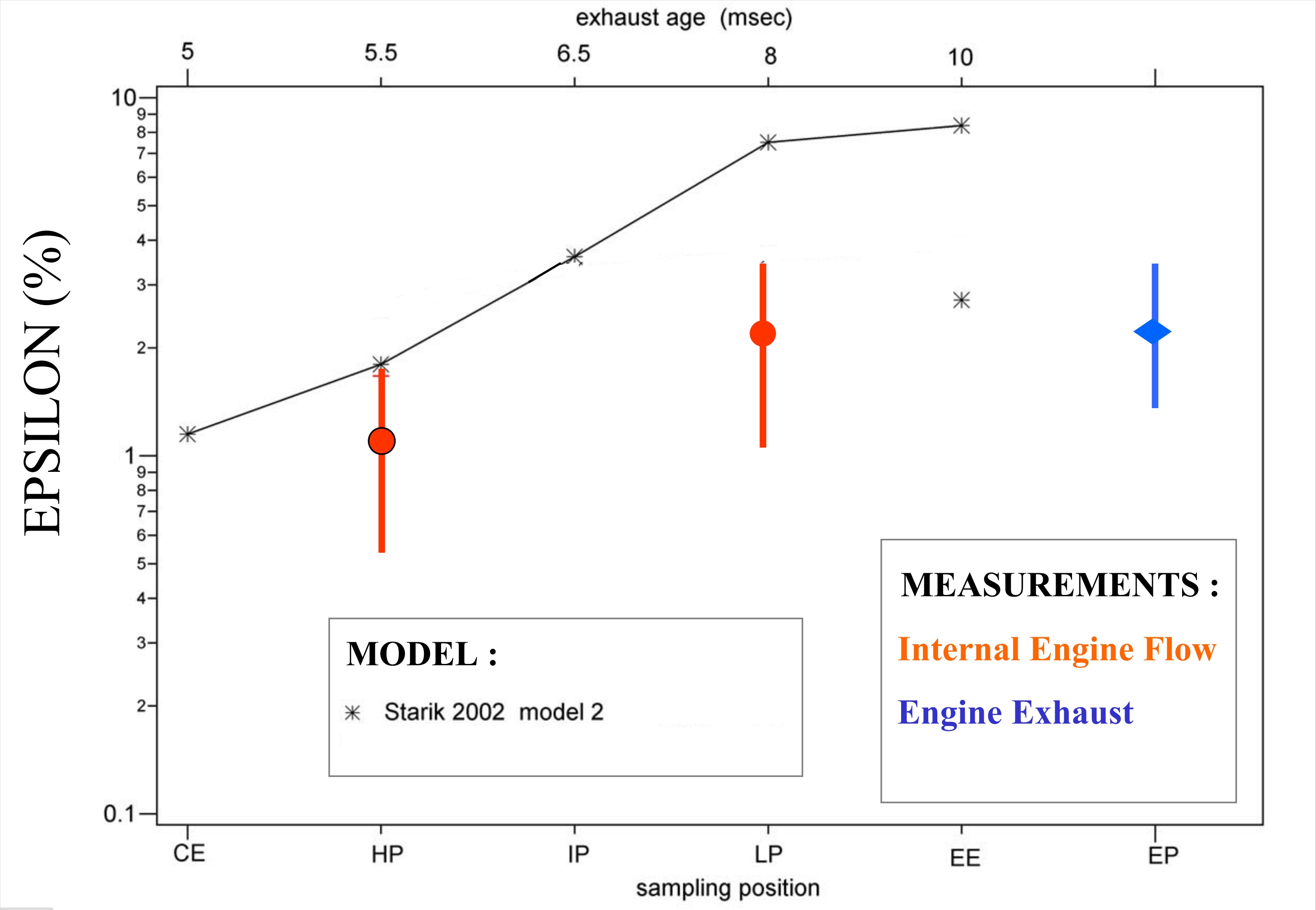
CIMS
(Chemical Ionization Mass Spectrometry)

CIMS-Apparatus equipped with
Quadrupole Ion Trap Mass Spectrometer
→ Improved Species Identification

EPSILON = (SO3 + H2SO4) / S



EPSILON = (SO3 + H2SO4) / S



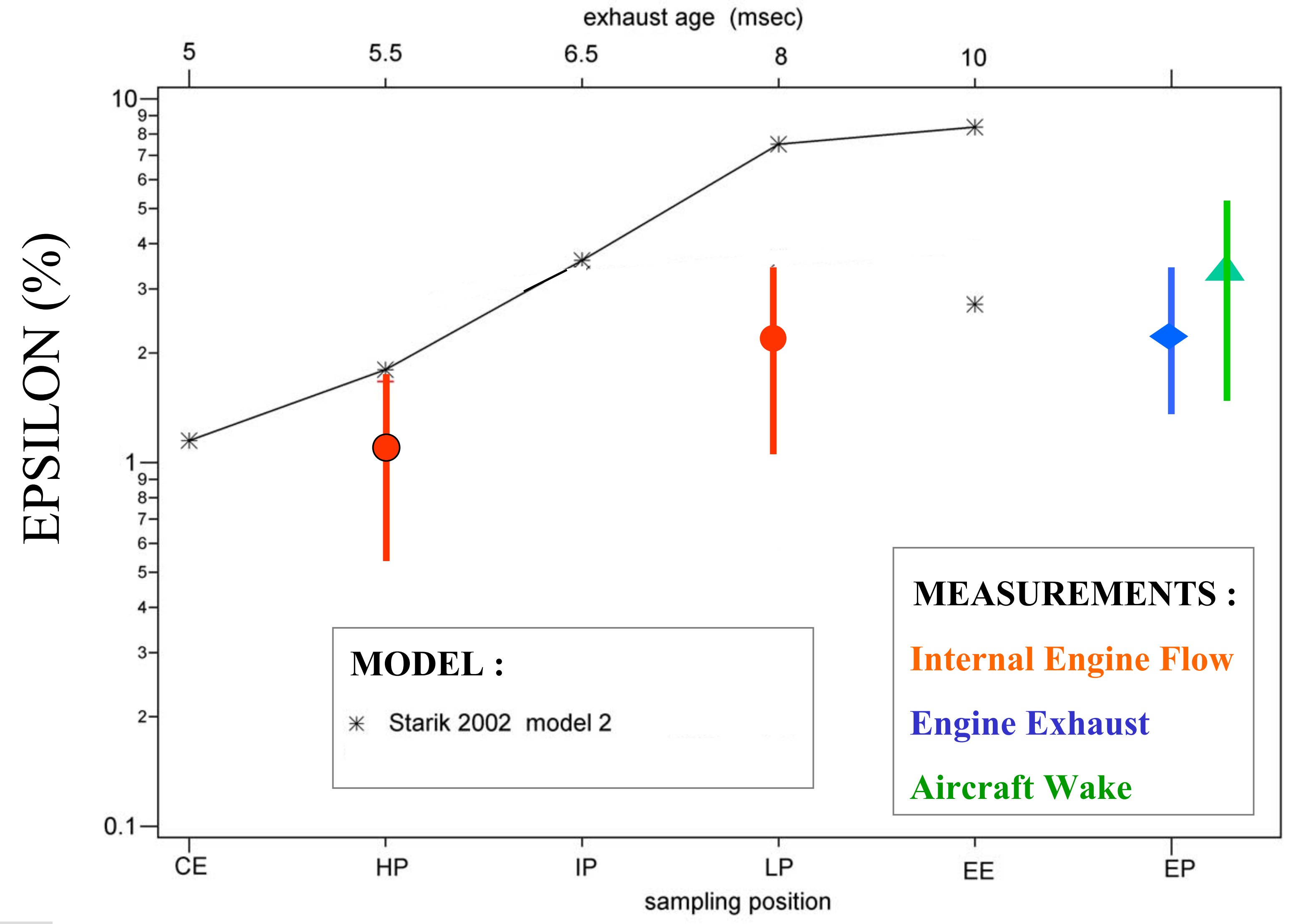
Aircraft Wake

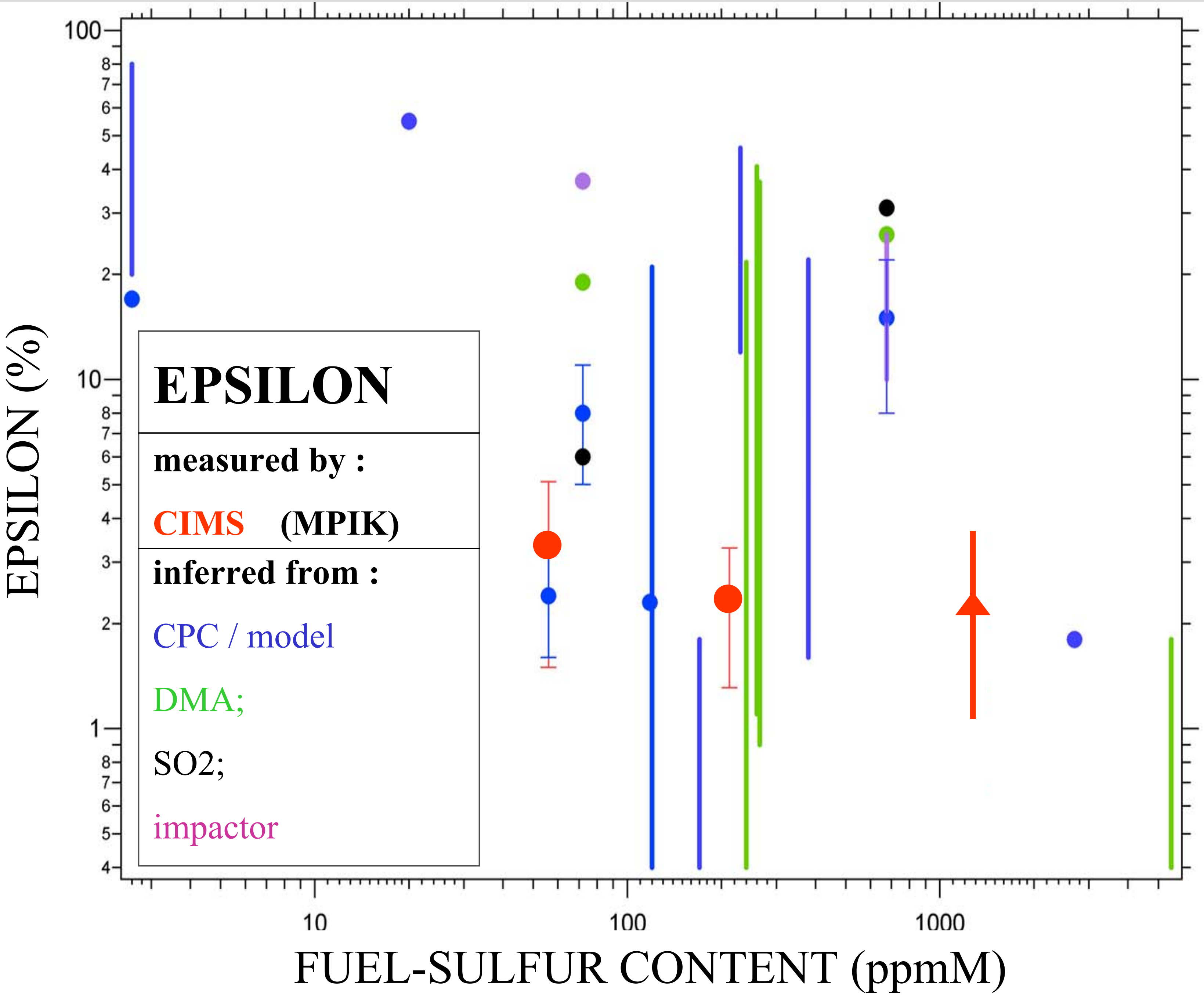
Gaseous Sulfuric Acid
Measurements

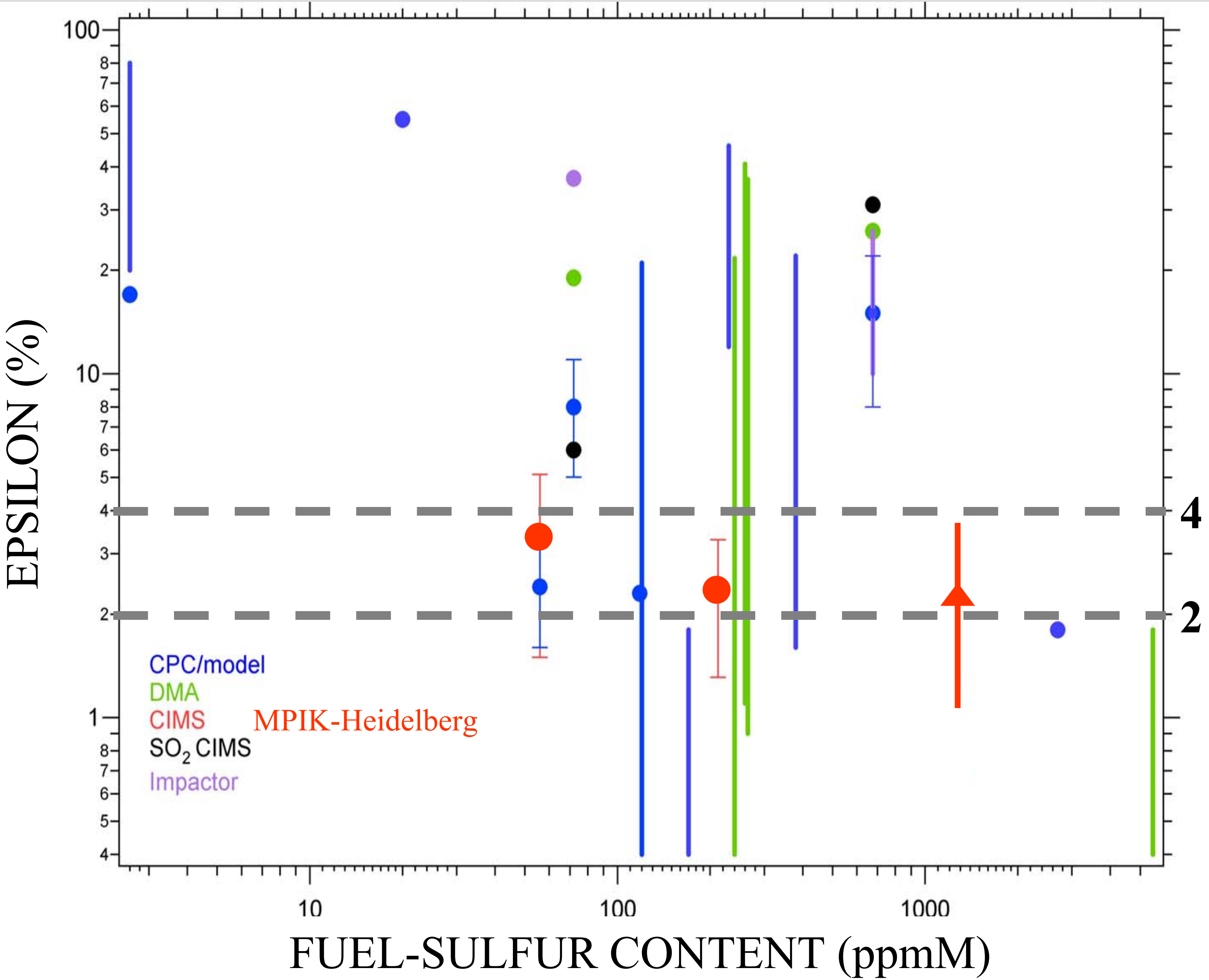

DLR
D-CMET
DLR - IPA


F-GMGB
F-GALP
GEHLMAX
DLR

EPSILON = (SO_3 + H_2SO_4) / S




EPSILON
measured by :
CIMS (MPIK)
inferred from :
CPC / model
DMA;
SO2;
impactor
EPSILON (%)
100
8
7
6
5
4
3
2
10
8
7
6
5
4
3
2
1
8
7
6
5
4
10
100
1000
FUEL-SULFUR CONTENT (ppmM)


EPSILON (%)
100
10
1
8
7
6
5
4
3
2
FUEL-SULFUR CONTENT (ppmM)
10
100
1000
4
2
CPC/model
DMA
CIMS
SO_2 CIMS
Impactor
MPIK-Heidelberg

EMISSION INDEX (mg / kg)

For modern engine and FSC=400 (100-3000) ppmM

H2SO4 - CONDENSATE	73 (18-550)
SOOT	10
COND. HC.	10

Gaseous Sulfuric Acid

Processes in

Aircraft Wake

Gaseous Sulfuric Acid Formation and Loss in Aircraft Engine Exhaust

SO_2

HSO_3

O_2

SO_3

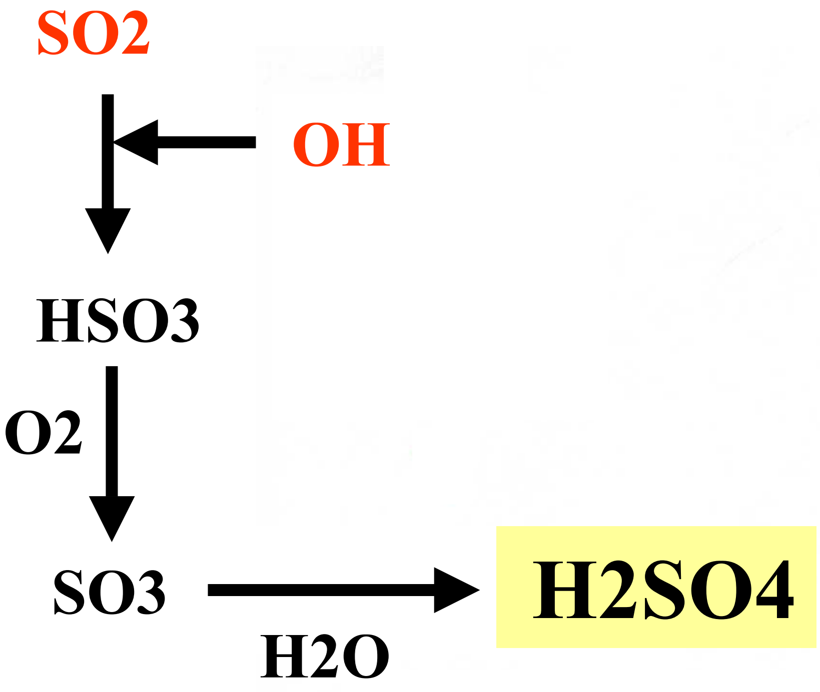
H_2O

H_2SO_4

From

COMBUSTOR

Gaseous Sulfuric Acid Formation and Loss in Aircraft Engine Exhaust



SO2

OH

HSO3

O2

SO3

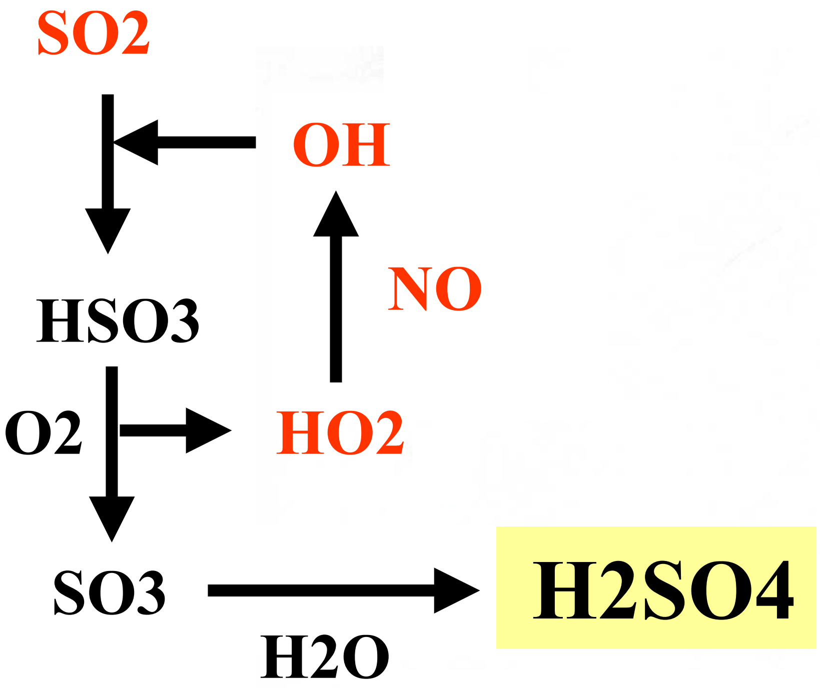
H2O

H2SO4

From

COMBUSTOR

Gaseous Sulfuric Acid Formation and Loss in Aircraft Engine Exhaust



SO2

OH

NO

HSO3

O2

HO2

SO3

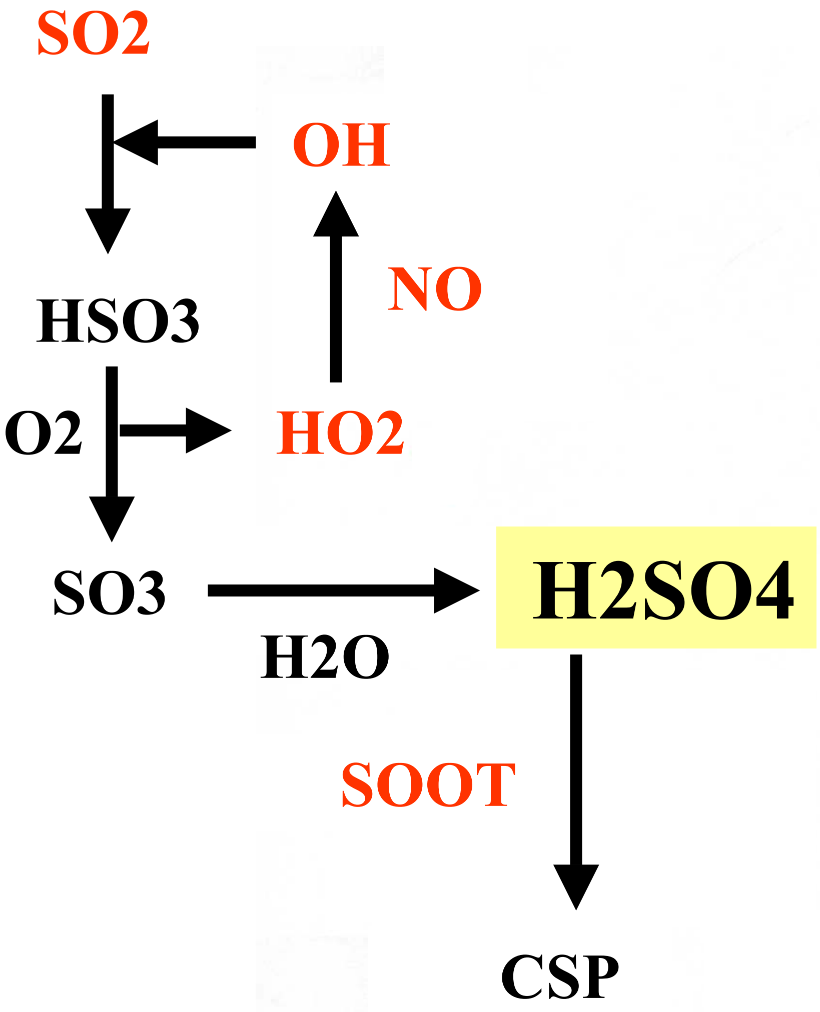
H2SO4

H2O

From

COMBUSTOR

Gaseous Sulfuric Acid Formation and Loss in Aircraft Engine Exhaust



SO2

OH

HSO3

NO

O2

HO2

SO3

H2O

H2SO4

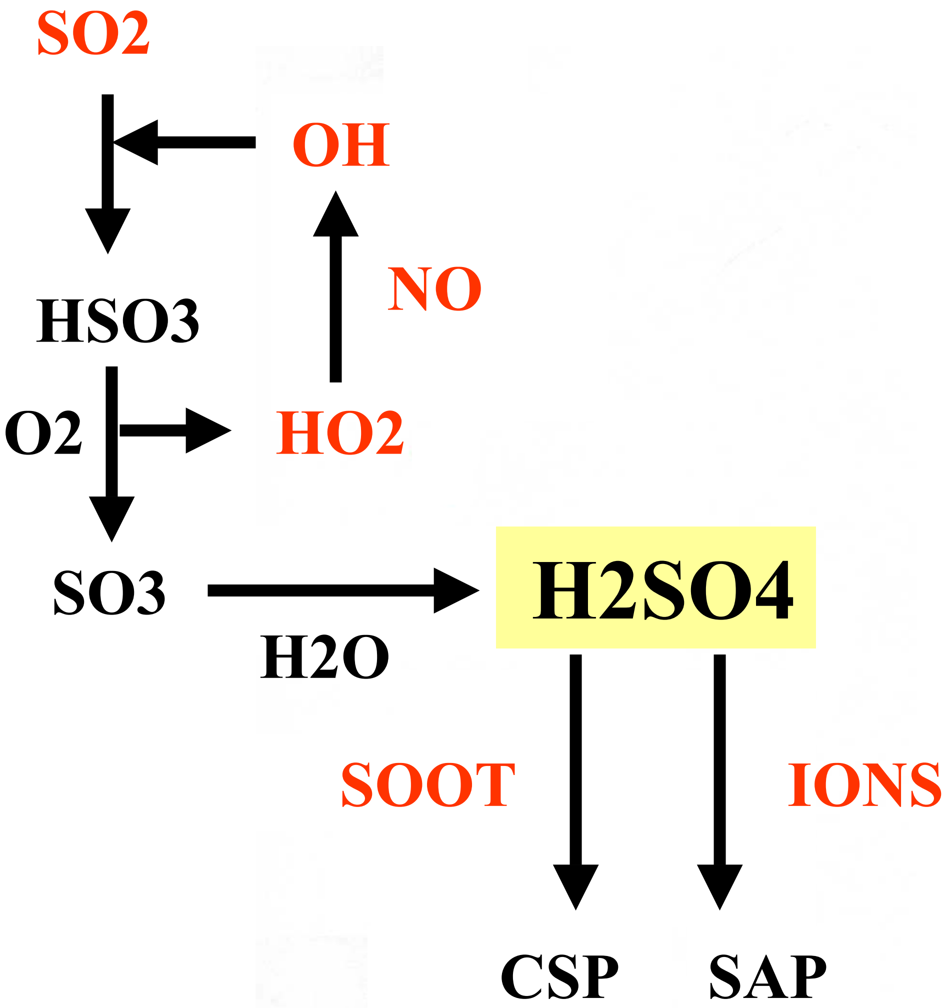
SOOT

CSP

From

COMBUSTOR

Gaseous Sulfuric Acid Formation and Loss in Aircraft Engine Exhaust



SO2

OH

NO

HSO3

O2

HO2

SO3

H2O

H2SO4

SOOT

IONS

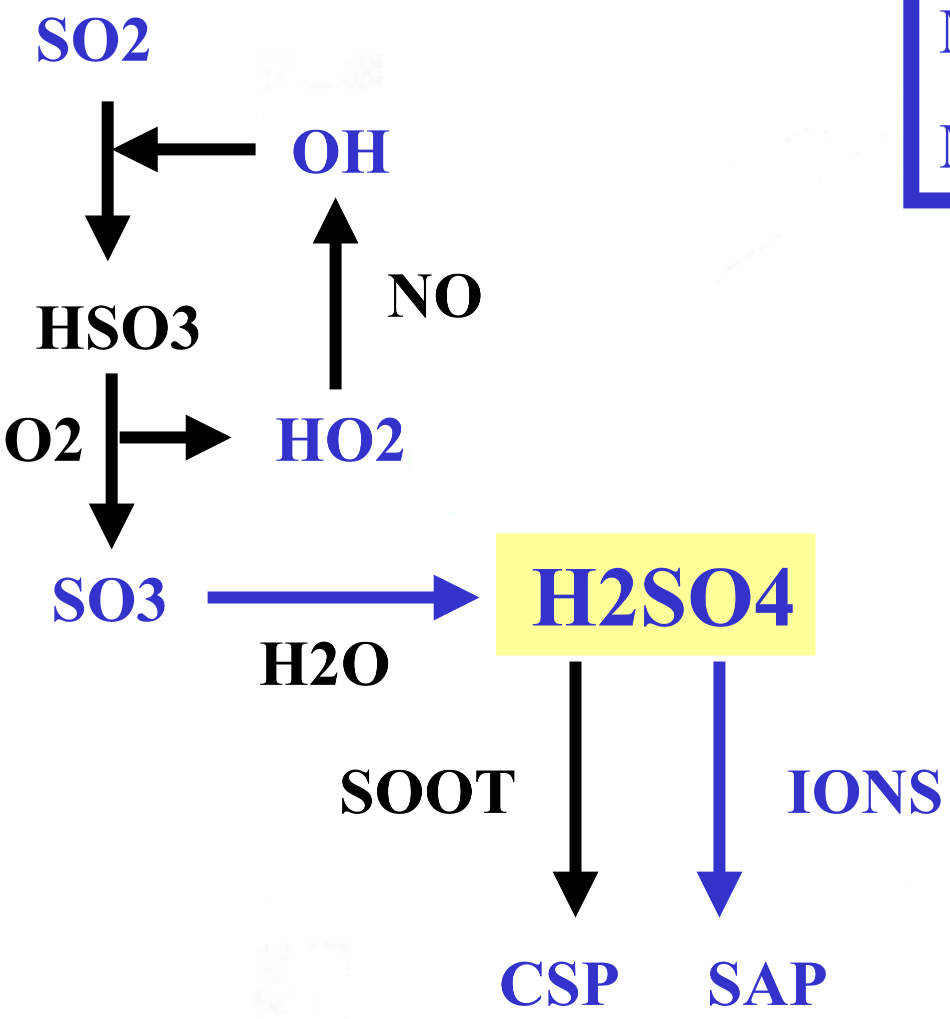
CSP

SAP

From

COMBUSTOR

Gaseous Sulfuric Acid Formation and Loss in Aircraft Engine Exhaust



SO2

OH

NO

HSO3

O2

HO2

SO3

H2O

H2SO4

SOOT

IONS

CSP

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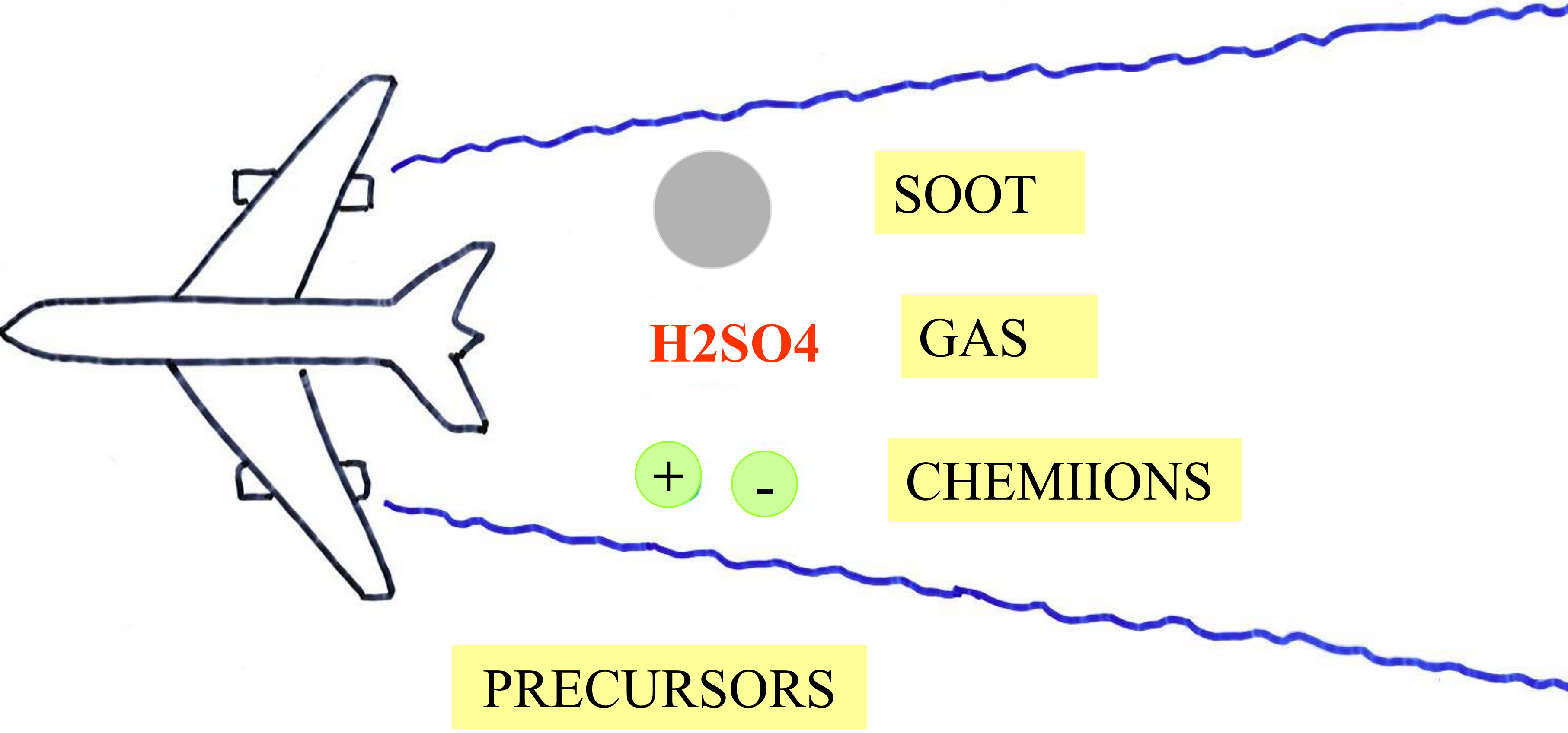
Mesured by

MPIK-Heidelberg

CONLUSIONS

SULFURIC ACID AEROSOL PARTICLES FROM AIRCRAFT



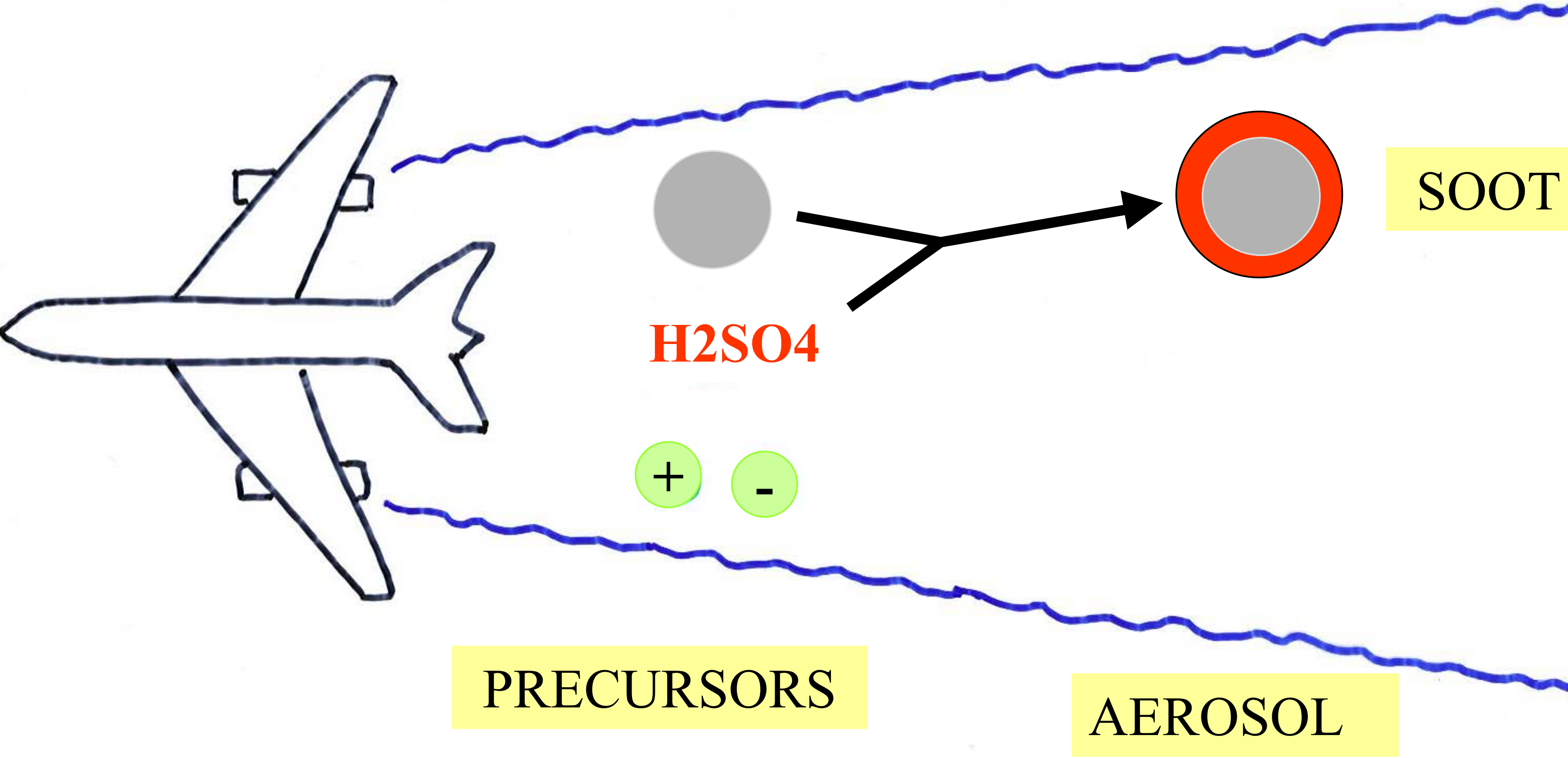
SOOT

H2SO4 GAS

+ - CHEMIIONS

PRECURSORS

SULFURIC ACID AEROSOL PARTICLES FROM AIRCRAFT



SOOT

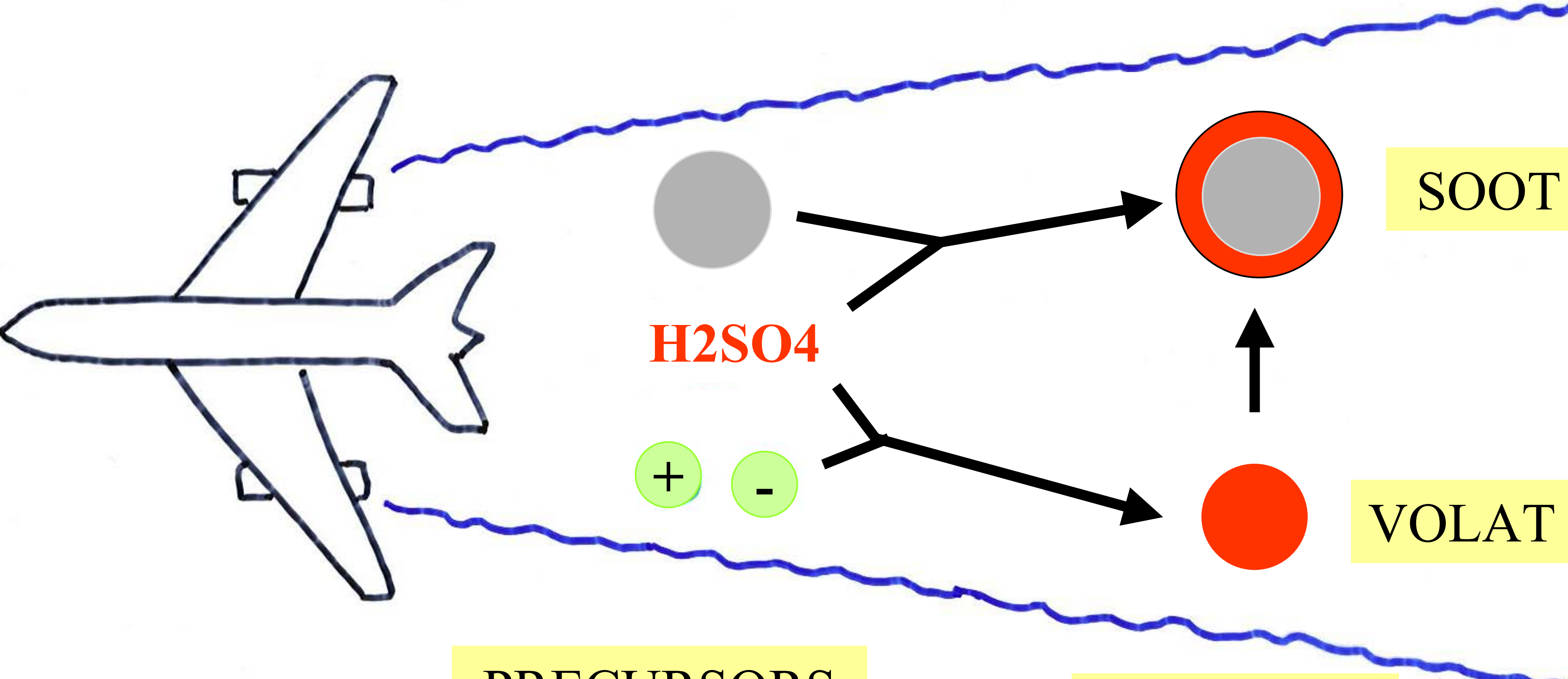
H2SO4

\+ -

PRECURSORS

AEROSOL

SULFURIC ACID AEROSOL PARTICLES FROM AIRCRAFT



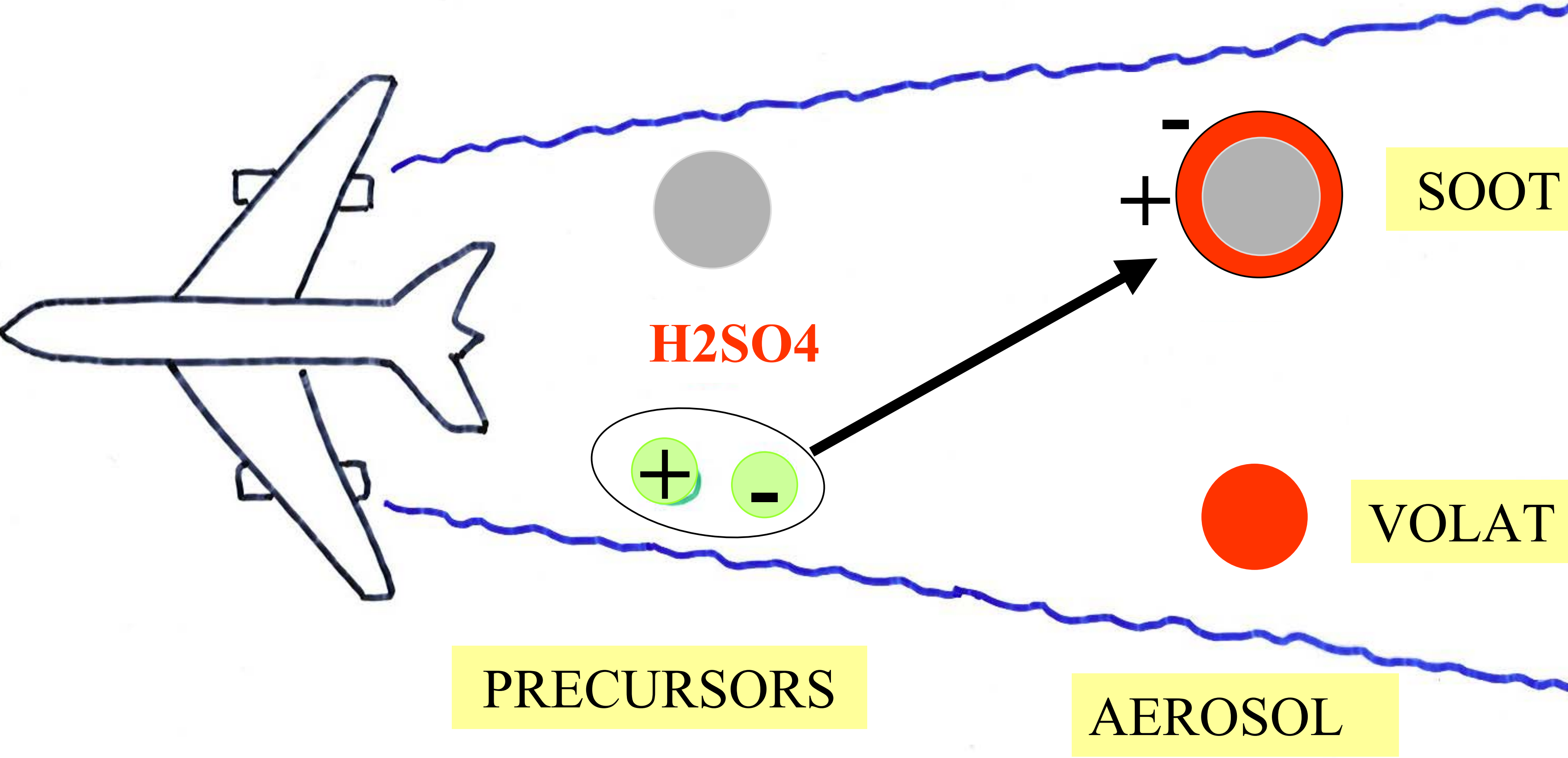
SOOT

VOLAT

PRECURSORS

AEROSOL

SULFURIC ACID AEROSOL PARTICLES FROM AIRCRAFT



H2SO4

+

-

PRECURSORS

+

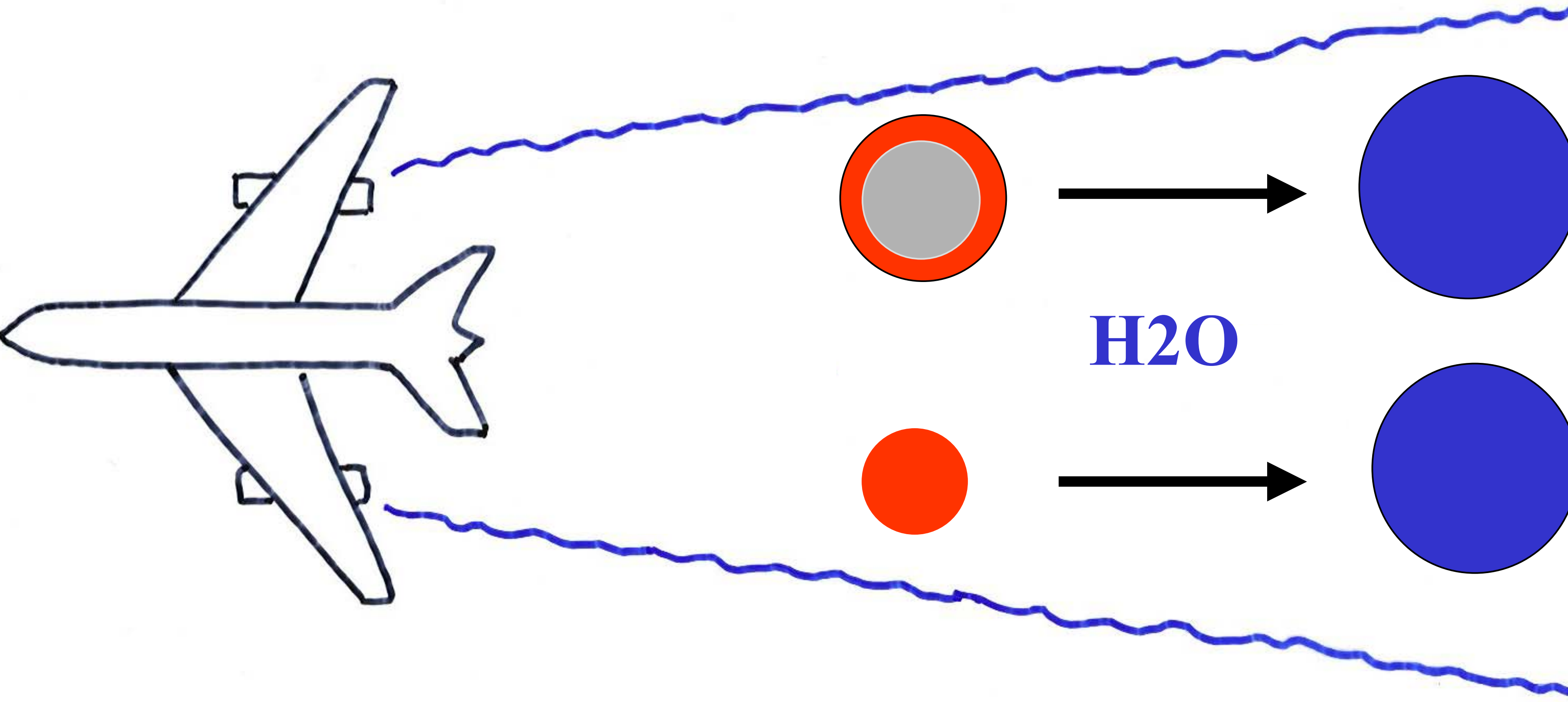
-

SOOT

VOLAT

AEROSOL

Sulfuric Acid Aerosols act as **Water Vapour Condensation Nuclei**



WATER DROPLETS

Aircraft Generated Sulfuric Acid

- May promote **Contrail** Formation
- May promote Atmospheric **CCN** Formation

Acknowledgement
Contributions by our GROUP MEMBERS

(2000-2004 , **2004 only**)

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