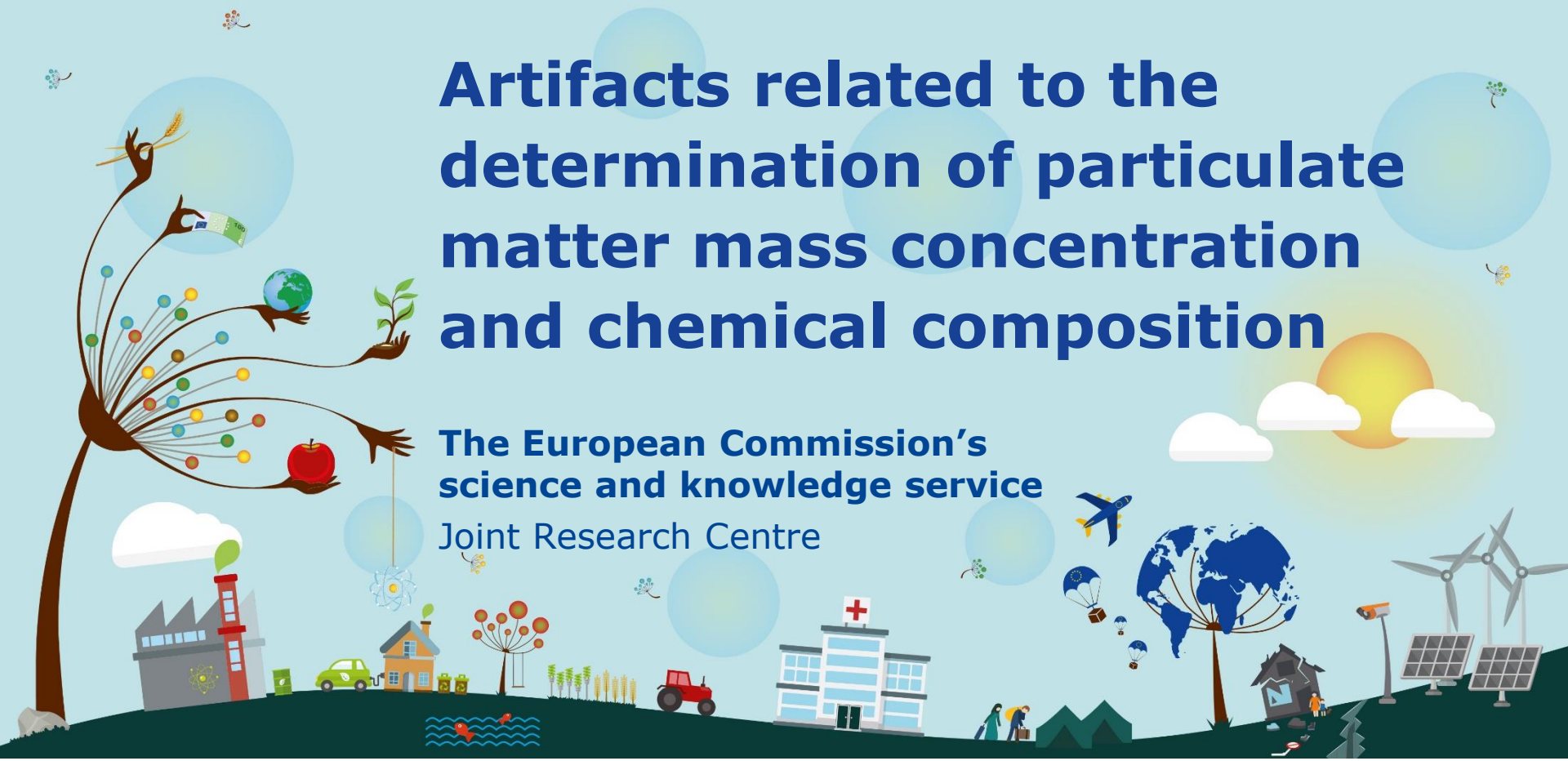
Artifacts related to the determination of particulate matter mass concentration and chemical composition



The European Commission's science and knowledge service

Joint Research Centre

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Artifacts related to the determination of particulate matter mass concentration and chemical composition

J.P. Putaud

Dir. for Energy, Transport and Climate

Air & Climate Unit

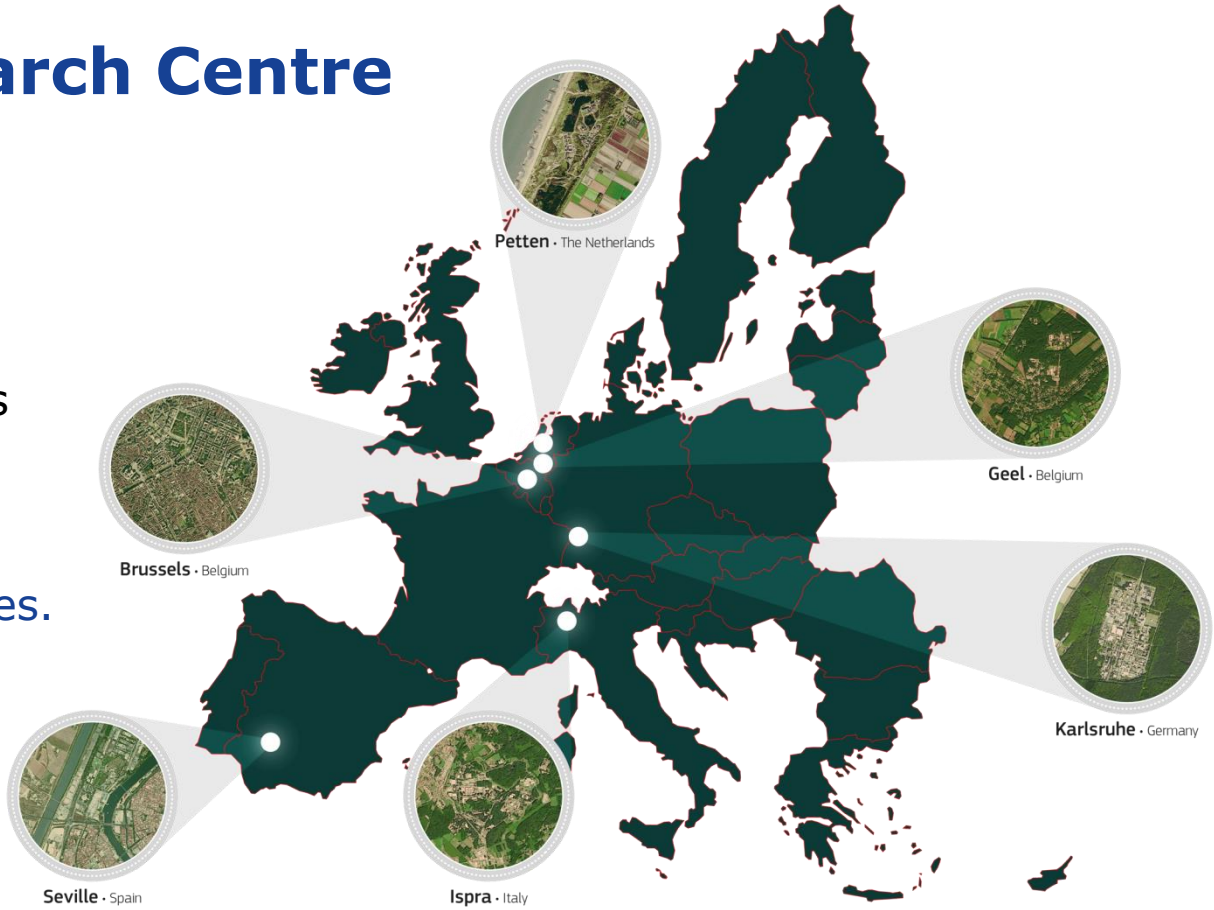
ACTRiS

ECAC

European Commission

The Joint Research Centre at a glance

3000 staff
Almost 75% are scientists and researchers.
Headquarters in Brussels and research facilities located in 5 Member States.



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The determination of particulate matter mass and constituents' concentrations often implicates:

1. The collection of particles on a substrate ⇒ sampling artifacts

2. Subsequent analytical measurements ⇒ possible analytical biases

Alternative methods are now available.

Positive and negative sampling artifacts

- **negative artifacts**: particulate matter volatilised from sampling substrates: NH_4NO_3, PAHs and other organics

+ **positive artifacts**: gas phase species adsorbed or absorbed onto / into sampling substrates:
  - HNO_3 (glass, cellulose ester and cellulose filters)
  - SO_2 (glass, cellulose filters)
  - (probably polar) VOCs (quartz)

Positive and negative sampling artifacts

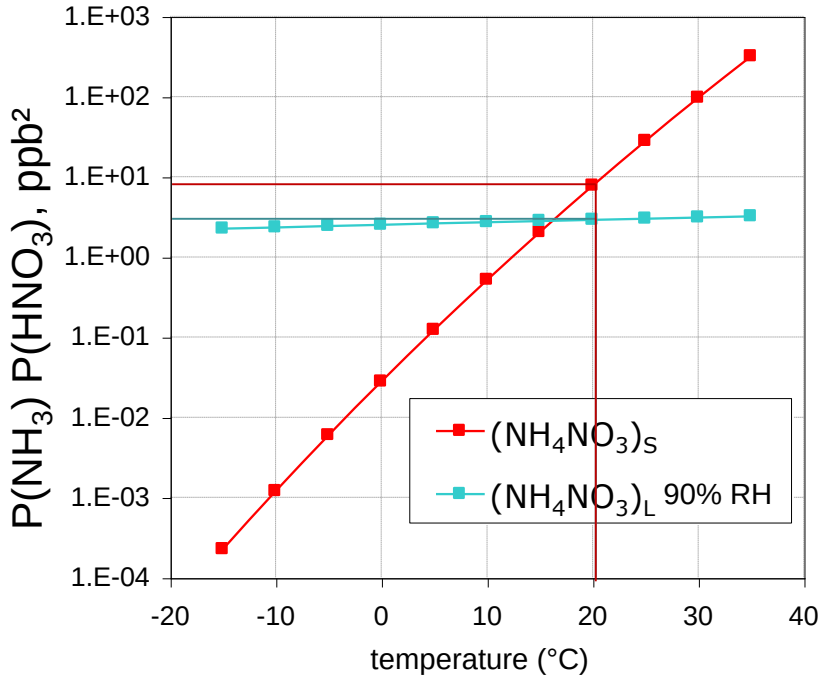
regard semi-volatile material (present in both the condensed and gaseous phases)

- Z_S or $Z_L \rightleftharpoons Z_G$
- XY_S or $XY_L \rightleftharpoons X_G + Y_G$

Gas / particulate phase equilibrium, NH_4NO_3

$(NH_4NO_3)_S \rightleftharpoons NH_3 + HNO_3$ $\quad K_p(T) = P(NH_3)\,P(HNO_3)$

$(NH_4NO_3)_L \rightleftharpoons NH_3 + HNO_3$ $\quad K_p(T) = \dfrac{P(NH_3)\,P(HNO_3)}{[NH_4^+{}_L]\,[NO_3^-{}_L]}$



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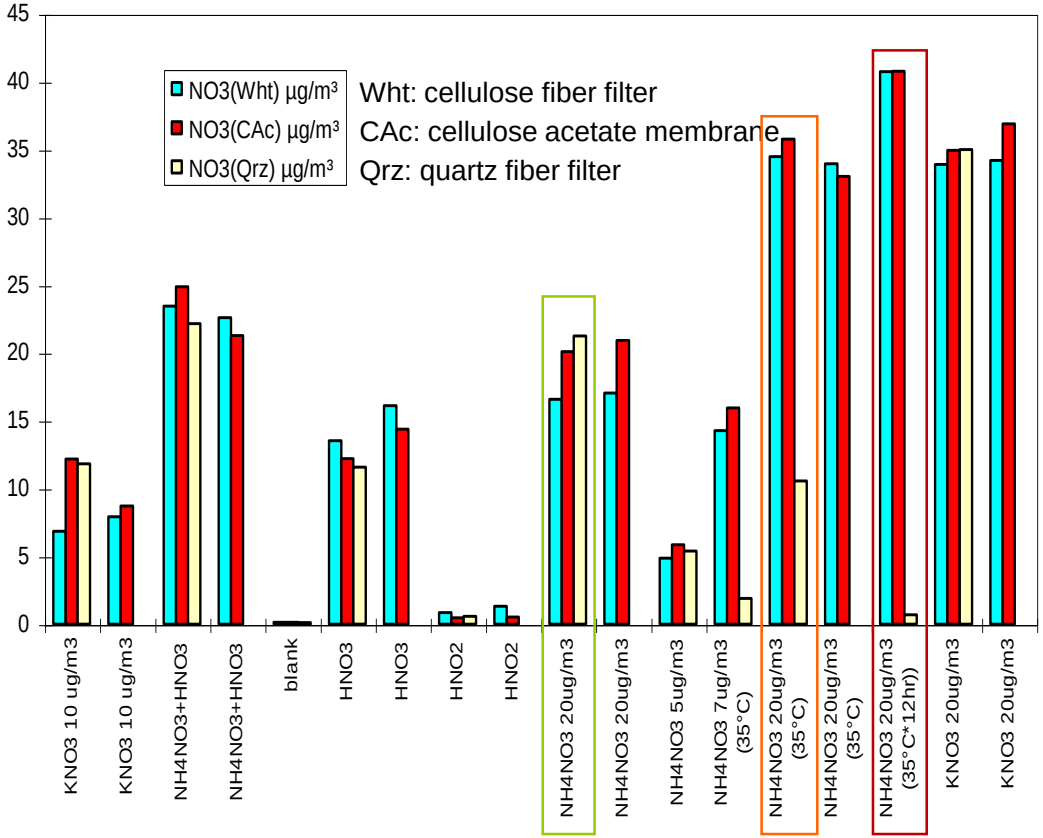
Sampling artifacts magnitude for NH_4NO_3:

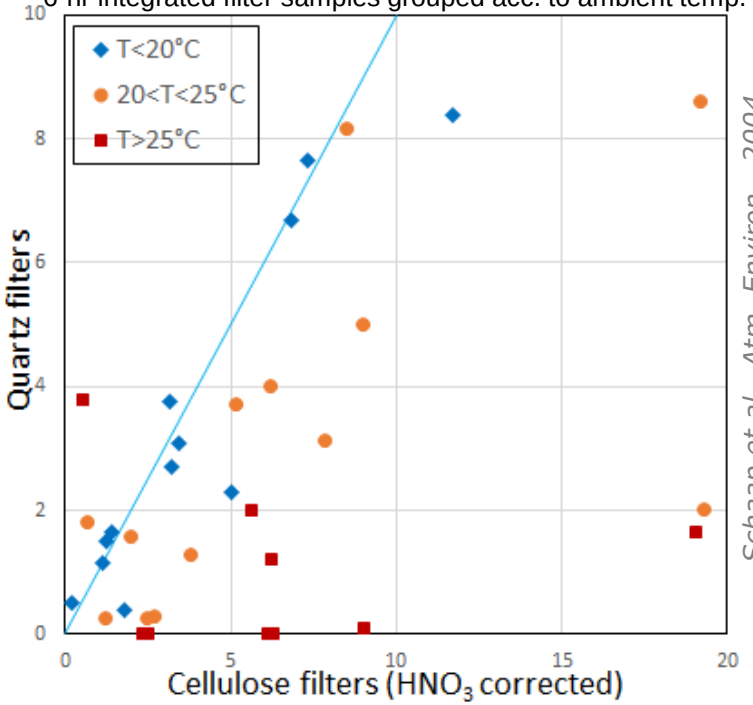
ECN Petten wind tunnel, June 1997



NH_4NO_3 concentrations (µg/m³)

Milano, May – June 1998

6-hr integrated filter samples grouped acc. to ambient temp.



Schaap et al., Atm. Environ., 2004

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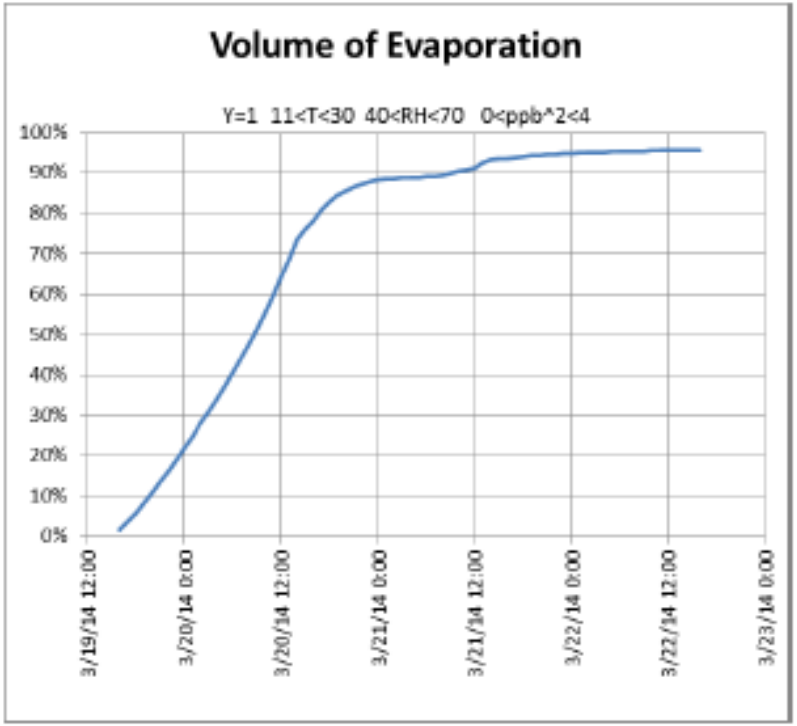
Sampling artifacts magnitude for NH_4NO_3:

Applied 497 ug NH4NO3 (9 ug/m³ at 2.3 m³/h for 24 hr)

Evaporated 477 ug

Residue 4%



Courtesy R. Otjes

ECN

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Evaporation rate for NH_4NO_3:

• Under severe conditions (high temperature, low RH, low gas phase concentrations), NH_4NO_3 may evaporate from filters up to 40 µg/hr for loadings > 100 - 300 µg.

• For loadings < 100 – 300 µg, NH_4NO_3 evaporation slows down.
Residual evaporation rate up to 3 µg/hr.

• Independently of particle diameters (between 0.5 and 2.5 µm), the evaporation rate for dry and wet NH_4NO_3 particles is about -0.1 nm (diameter) / s.

Harrison et al., Atm. Environ., 1990

Gas / Particle phase equilibrium for organics

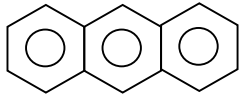
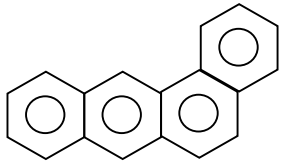
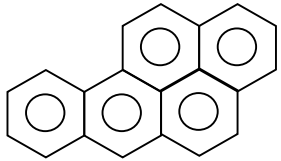
$$1/K_p(T) = \frac{[X_P]}{[X_G]\,[PM]} = \frac{As\ T}{1600\ P^\circ}\ \exp\frac{\Delta H}{RT}$$

Specific surface concentration of sorption sites

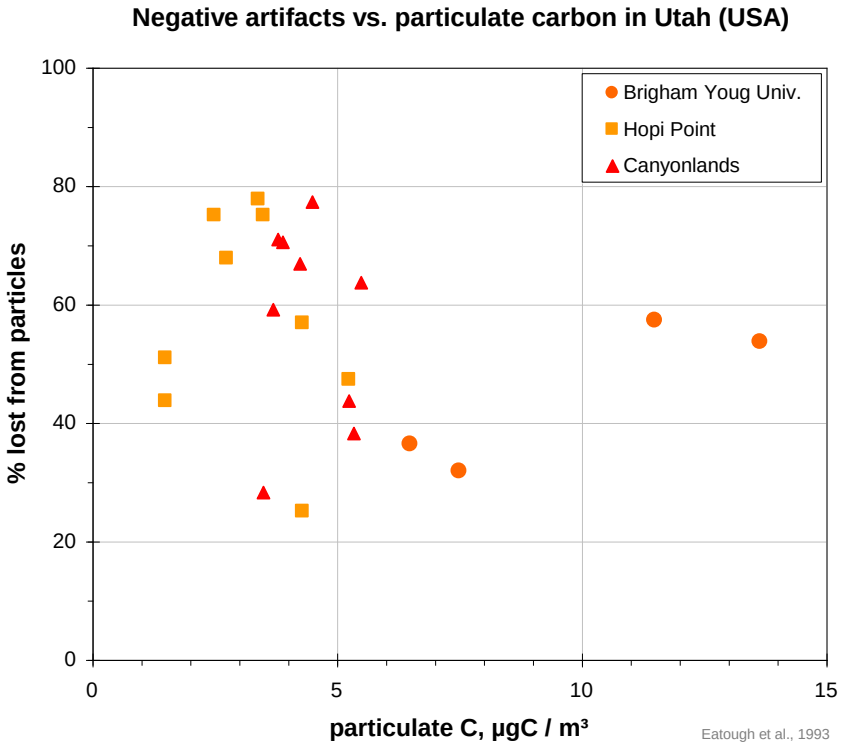
Enthalpy of desorption - volatilization

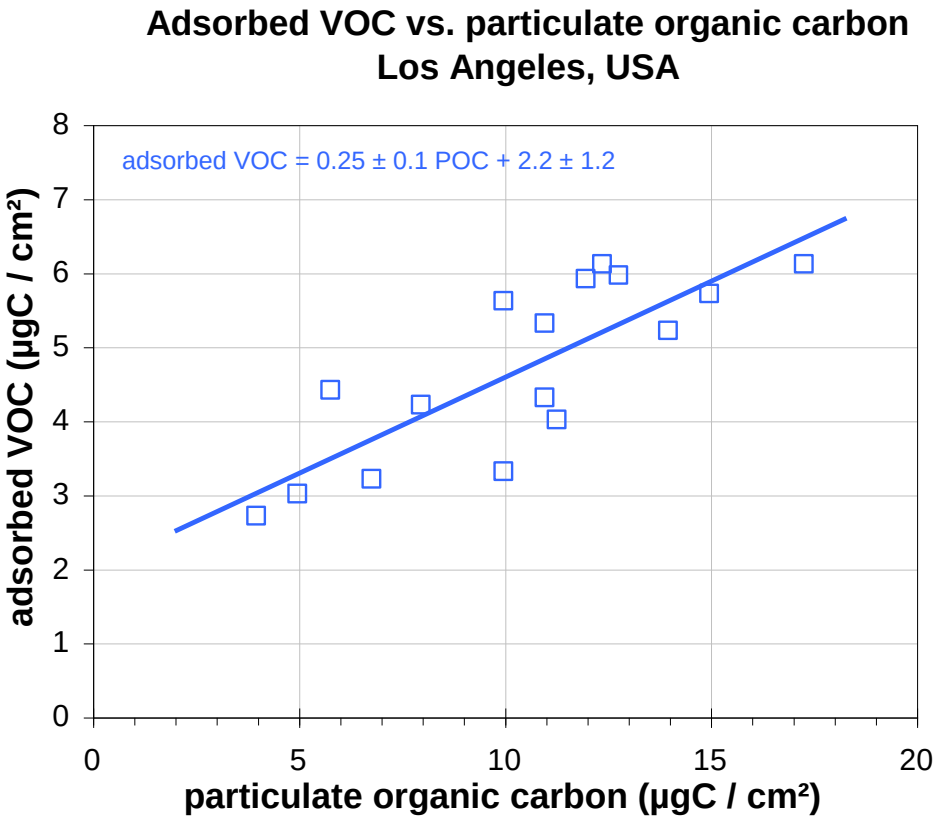
Temperature

Saturating vapor pressure

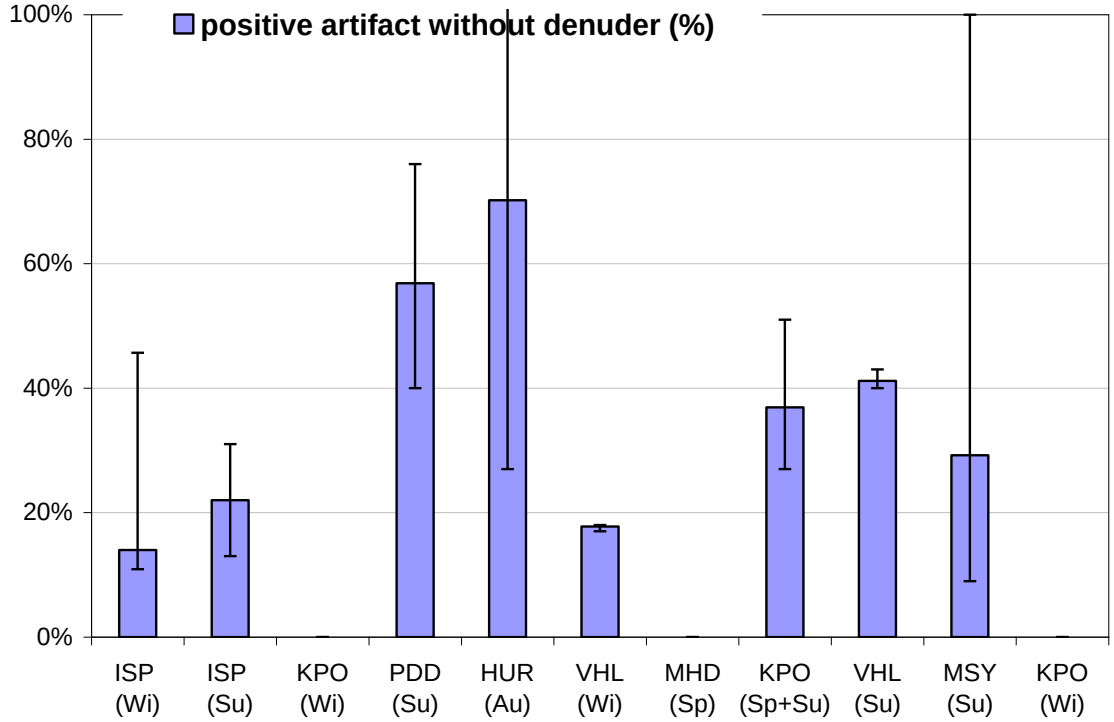
		X_P / X_G (20°C)
Anthracene		0.0033
Benzo[a]fluorene		0.19
Benzo[a]pyrene		27

Positive and negative sampling artifacts for organic carbon: USA





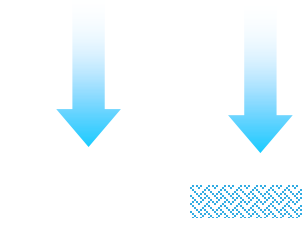
Positive and negative sampling artifacts for organic carbon: Europe



Cavalli et al., Atm. Environ., 2016

European Commission

Addressing positive sampling artifacts (OC)



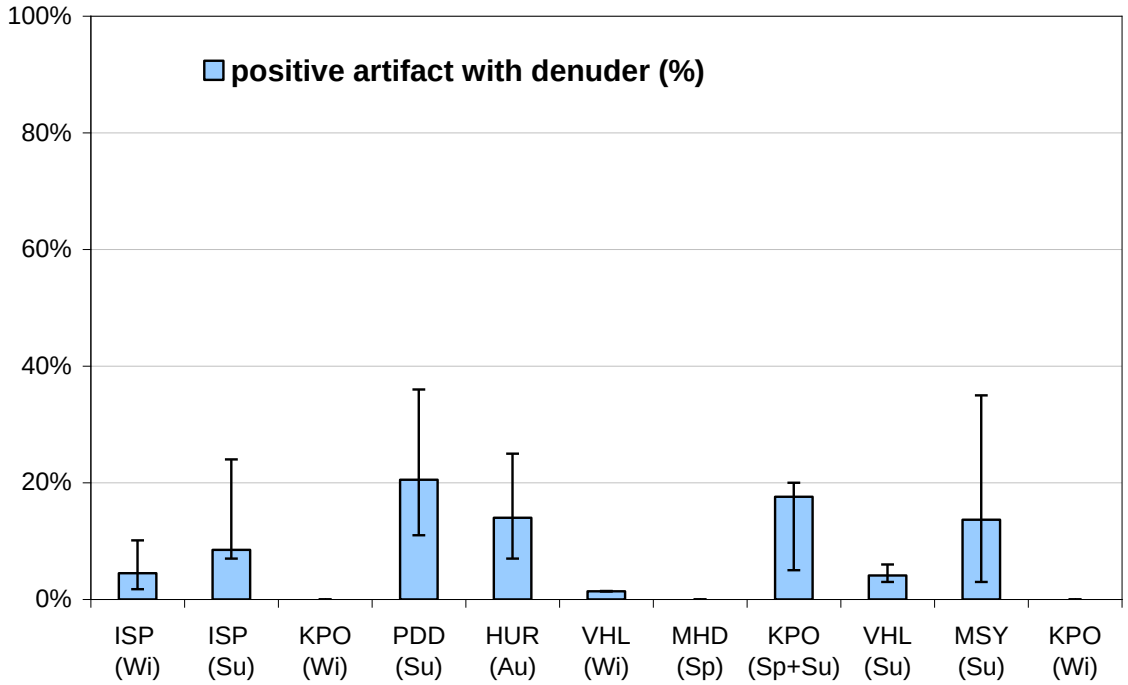
Assess positive artifacts → multi-filter

"positive artifact free" OC = OC1 – OC2

Mitigate positive artifacts → denuder

Quartz fiber filter for subsequent analyses

Positive and negative sampling artifacts for organic carbon: Europe



Cavalli et al., Atm. Environ., 2016

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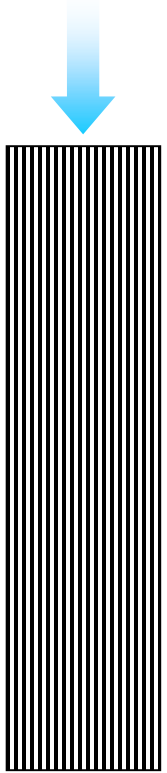
Addressing negative sampling artifacts

negative artifact ⇔ efficient denuder



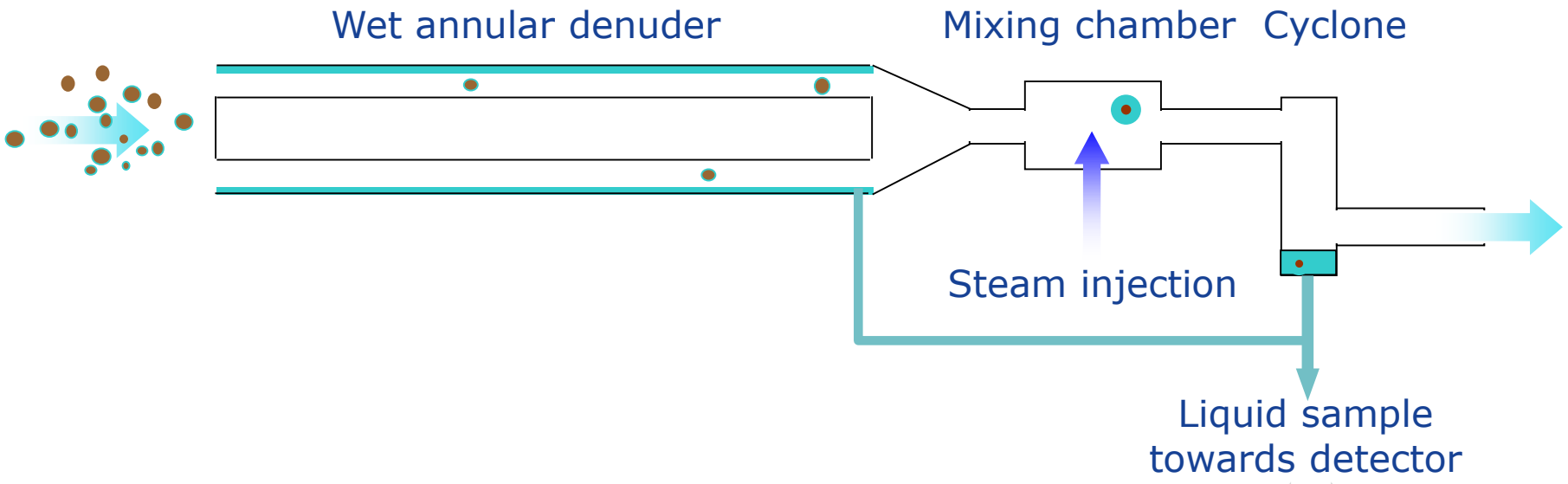
Mitigate positive artifacts → denuder

Filter for subsequent analyses

Determine negative artifacts → sorbent

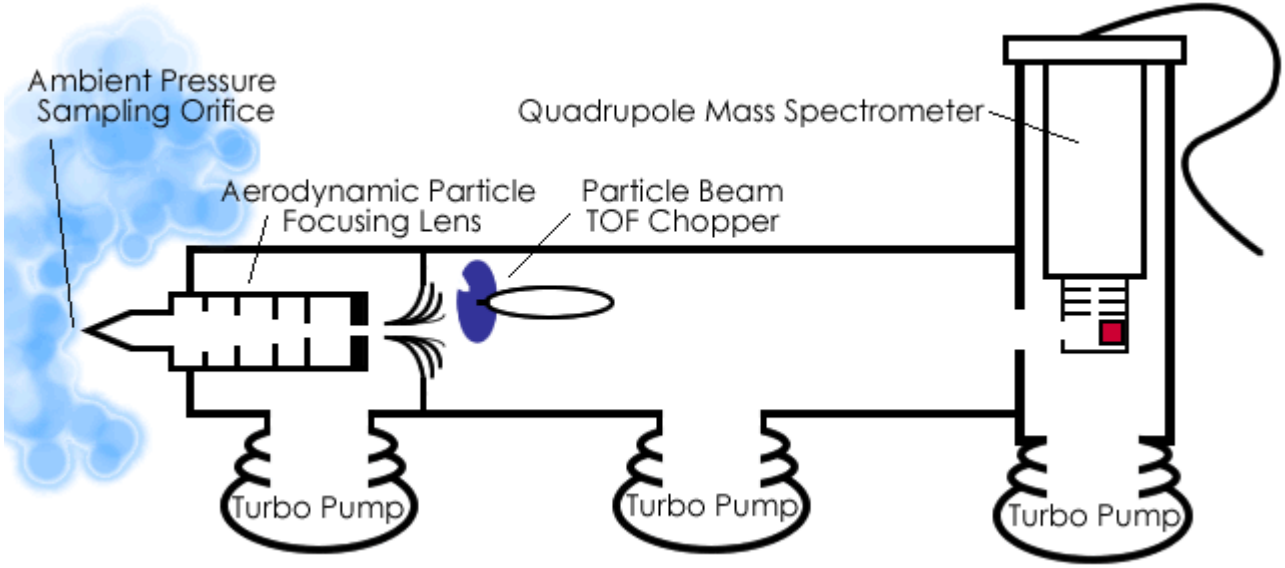
Alternative methods: on-line analyses

1. Wet Annular Denuder + Steam Jet Aerosol Collector



Alternative methods: on-line analyses

2. Aerosol Mass Spectrometer



Alternative methods: on-line analyses

3. Single Particle Mass Spectrometer

Nd:YAG – laser:

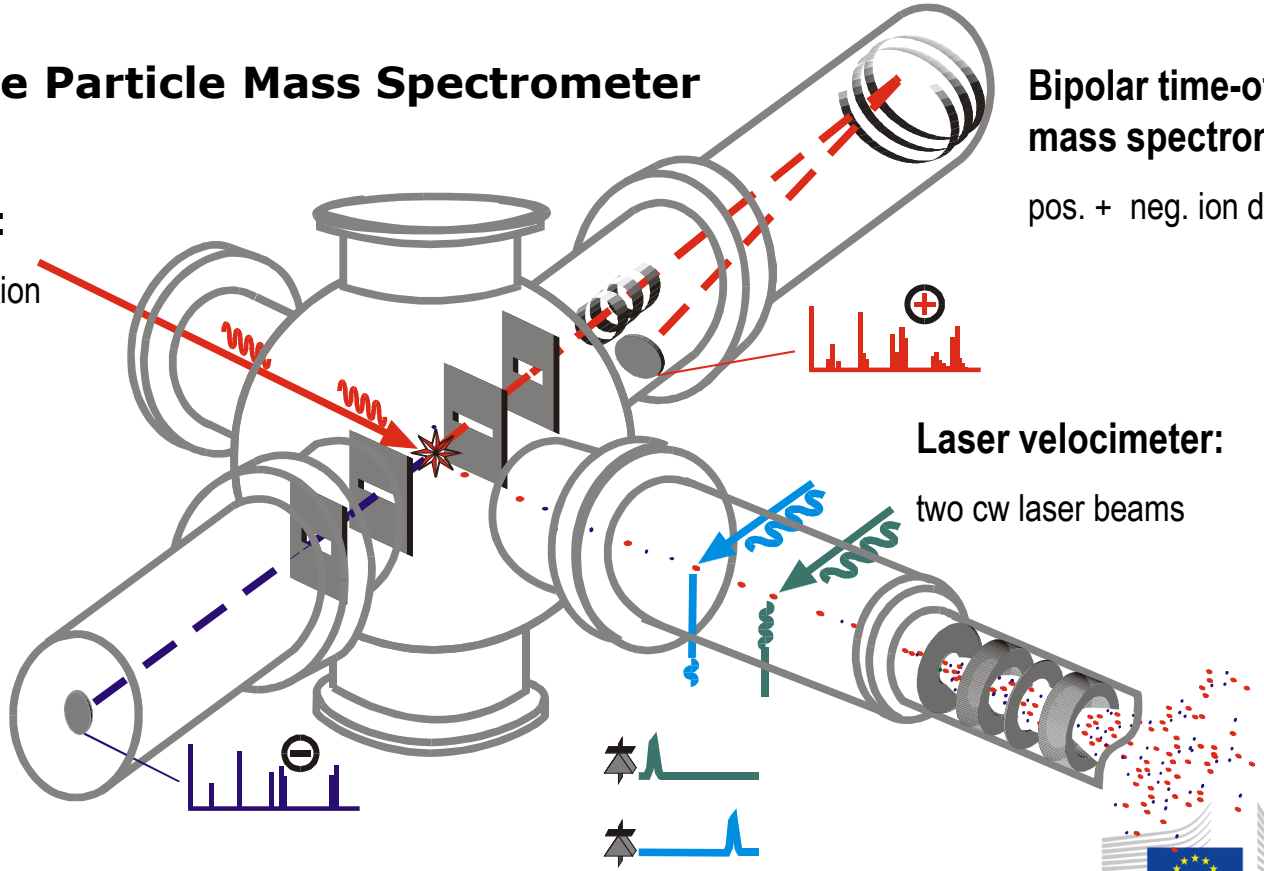
desorption / ionisation

Bipolar time-of-flight mass spectrometer:

pos. + neg. ion detection

Laser velocimeter:

two cw laser beams



Chemical sampling artifacts

regard reactive species

1. neutralisation of acidic species
2. oxidation of specific organics
3. nitrification of polyaromatic hydrocarbons (PAH)

Storage artifacts

1. significant losses of NH_4^+, Cl^-, and NO_3^- from glass and quartz fiber filters can occur during storage at room temperature

2. refrigeration at 5 °C required by European standard EN16909 (analysis of organic and elemental carbon deposited on filters)

3. I never detected any significant losses of semi-volatile species during conditioning for gravimetric analyses

Other artifacts

Analytical artifacts

- water weighing
- uncorrected charring (Organic carbon → Elemental carbon like)
- NO_2^- → NO_3^- (wet sampler)

“Calculation” artifacts

- blank subtraction if field blanks are not properly taken

Take home message

Particulate matter filter sampling and analyses ⇔ artifacts

- awareness
- mitigation
- assessment

On-line instruments with no filter are better

Still wonder about what happens inside

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