Chemical characterization of atmospheric aerosol: mass closure

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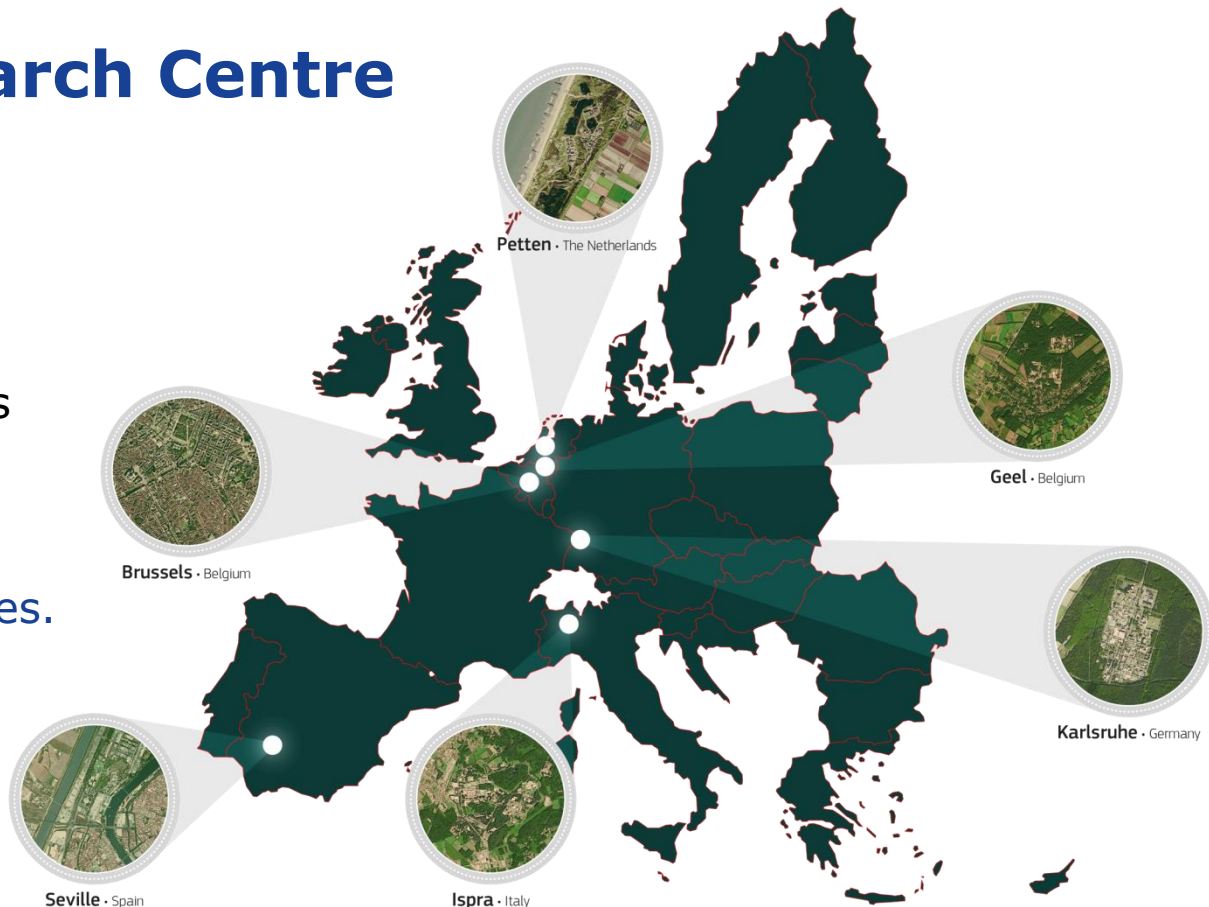
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The Joint Research Centre at a glance

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

Petten · The Netherlands

Geel · Belgium

Brussels · Belgium

Karlsruhe · Germany

Seville · Spain

Ispra · Italy

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

1. The collection of particles on a substrate $\Rightarrow$ sampling artifacts

2. Subsequent analytical measurements $\Rightarrow$ possible analytical biases

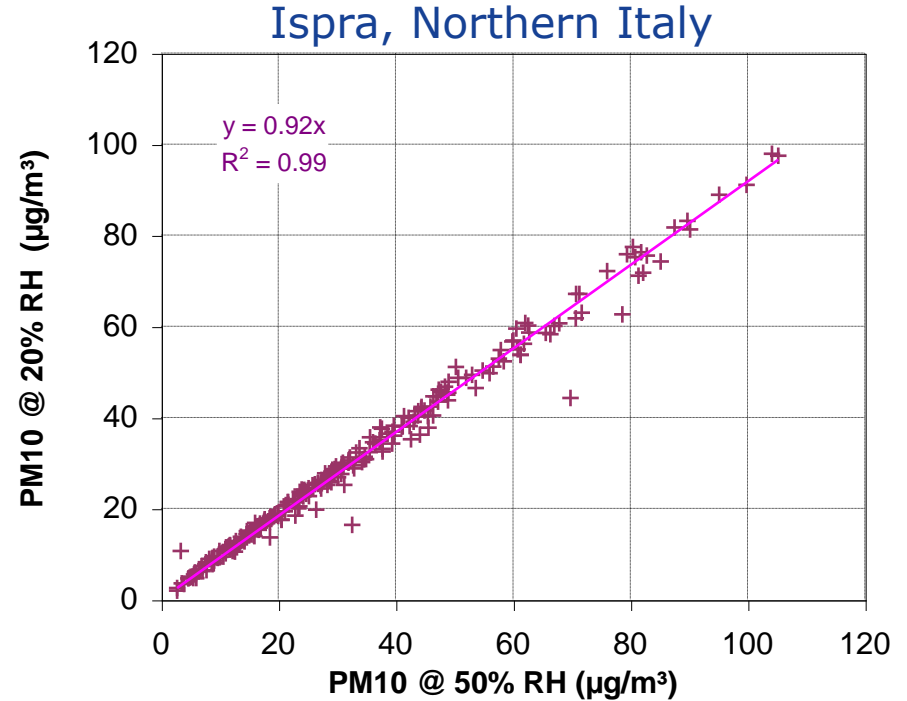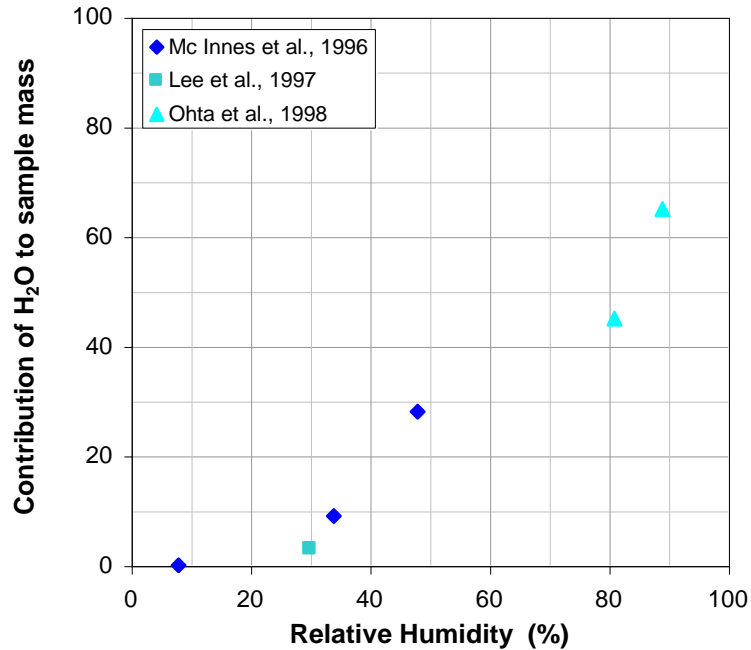**Testing "mass closure" is a powerful tool to assess measurement quality.**

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PM mass concentration is **the** aerosol related variable submitted to regulations:

- USA: annual $PM_{2.5}$ standard = 12 µg/ m³, 24-hour $PM_{2.5}$ standard = 35 µg/m³.
- Mexico: annual $PM_{2.5}$ standard = 12 µg/ m³, 24-hour $PM_{2.5}$ standard = 45 µg/m³.
- Brazil: annual PM_{10} standard = 50 µg/ m³, 24-hour $PM_{2.5}$ standard = 150 µg/m³.
- EU: annual $PM_{2.5}$ standard = 25 µg/ m³, 24-hour PM_{10} standard = 50 µg/m³.

Particulate matter mass concentration determination:

- Gravimetric analyses (recommended):
    - micro-balance with sufficient sensitivity (< 1 µg)
    - equilibration of the sample with the measurement enclosure conditions
        → 24 hr @ RH = 20 ±5% (NB: European EN12341: 24 hr @ 45% RH)
    - electrostatic charges on filters to be removed
        → corona discharge or radioactive source.

- On-line methods (if equivalence with gravimetric methods has been proven):
- TEOM (Tapered Element Oscillating Microbalance)
- β-ray attenuation instruments

PM mass concentration: effect of RH on gravimetric analyses

Left chart: Contribution of H_2O to sample mass vs Relative Humidity (%). Legend: Mc Innes et al., 1996; Lee et al., 1997; Ohta et al., 1998.

Right chart: Ispra, Northern Italy. PM10 @ 20% RH ($\mu g/m^3$) vs PM10 @ 50% RH ($\mu g/m^3$). $y = 0.92x$, $R^2 = 0.99$.

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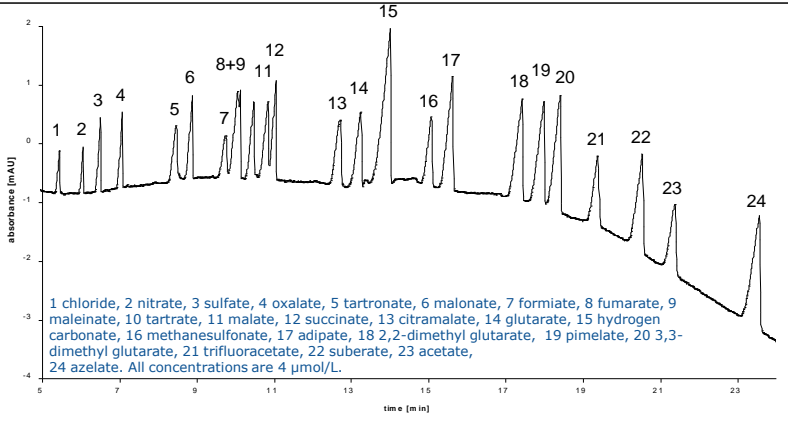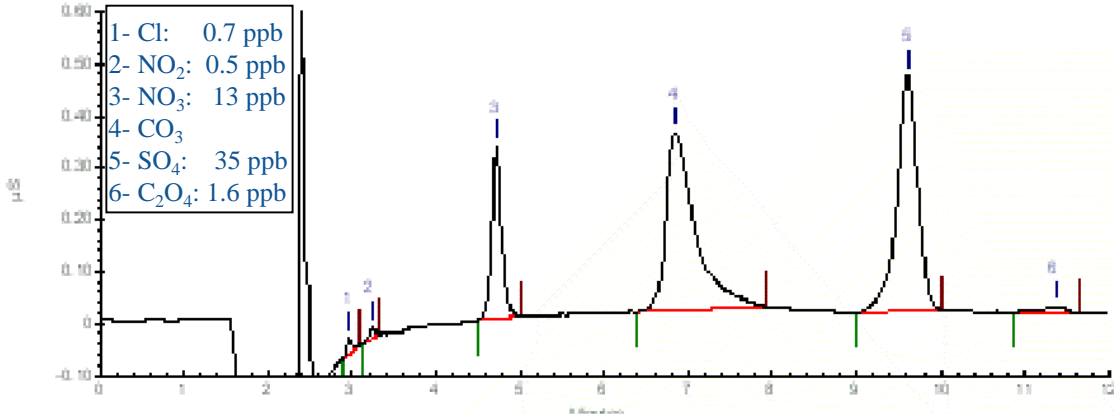Particulate matter chemical composition:

1. water soluble: inorganic ions + soluble organics

2. volatile and / or oxidisable to CO_2: carbonaceous matter

3. refractory: mineral species and elements

Particulate matter chemical composition determination: water soluble ions

- extraction: 97 – 100% after 30 min US bath if filter kept below the water surface
- take care of contamination
- bacteria "eat" NH_4^+

- ion chromatography

- capillary electrophoresis

1- Cl: 0.7 ppb
2- NO_2: 0.5 ppb
3- NO_3: 13 ppb
4- CO_3
5- SO_4: 35 ppb
6- C_2O_4: 1.6 ppb

1 chloride, 2 nitrate, 3 sulfate, 4 oxalate, 5 tartronate, 6 malonate, 7 formiate, 8 fumarate, 9 maleinate, 10 tartrate, 11 malate, 12 succinate, 13 citramalate, 14 glutarate, 15 hydrogen carbonate, 16 methanesulfonate, 17 adipate, 18 2,2-dimethyl glutarate, 19 pimelate, 20 3,3-dimethyl glutarate, 21 trifluoracetate, 22 suberate, 23 acetate, 24 azelate. All concentrations are 4 µmol/L.
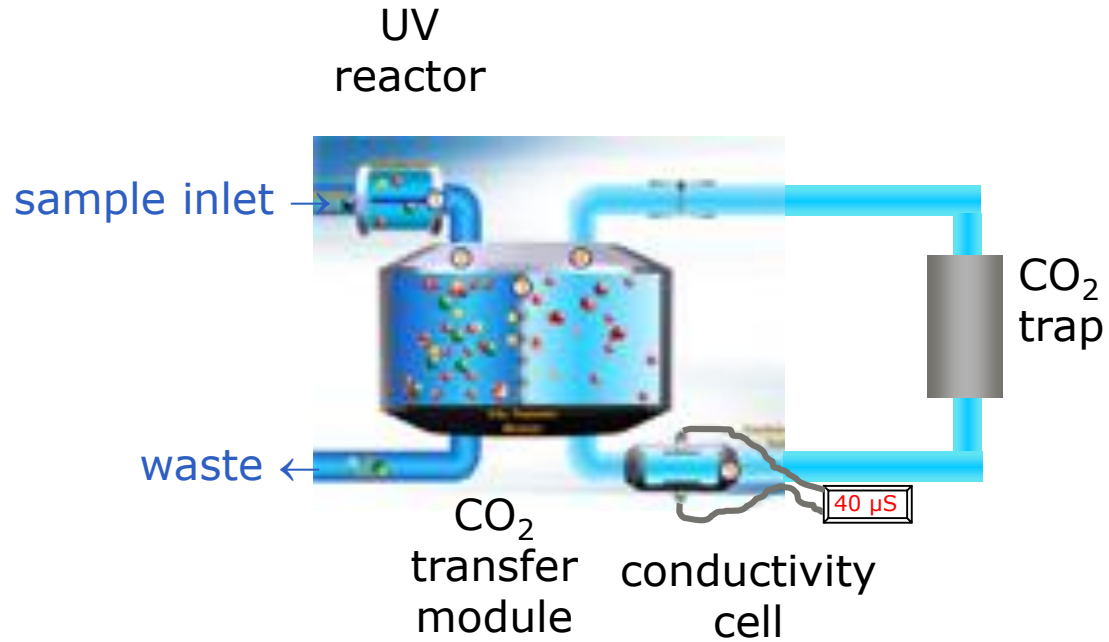
Particulate matter chemical composition: organic matter speciation

Chemical mass balance in impactor stage 0.14 - 0.42 um in Melpitz (Neusuess et al., 2000)
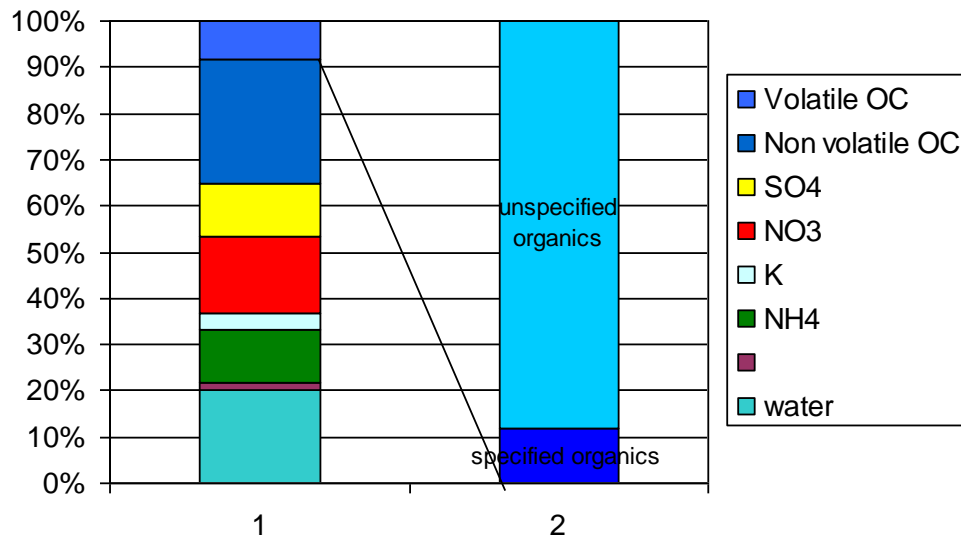
Particulate matter chemical composition: water soluble carbon determination

UV reactor

sample inlet →

CO$_2$ trap

waste ←

CO$_2$ transfer module

conductivity cell

40 µS

Particulate matter chemical composition determination: carbonaceous content

Volatilisation and / or combustion to CO_2
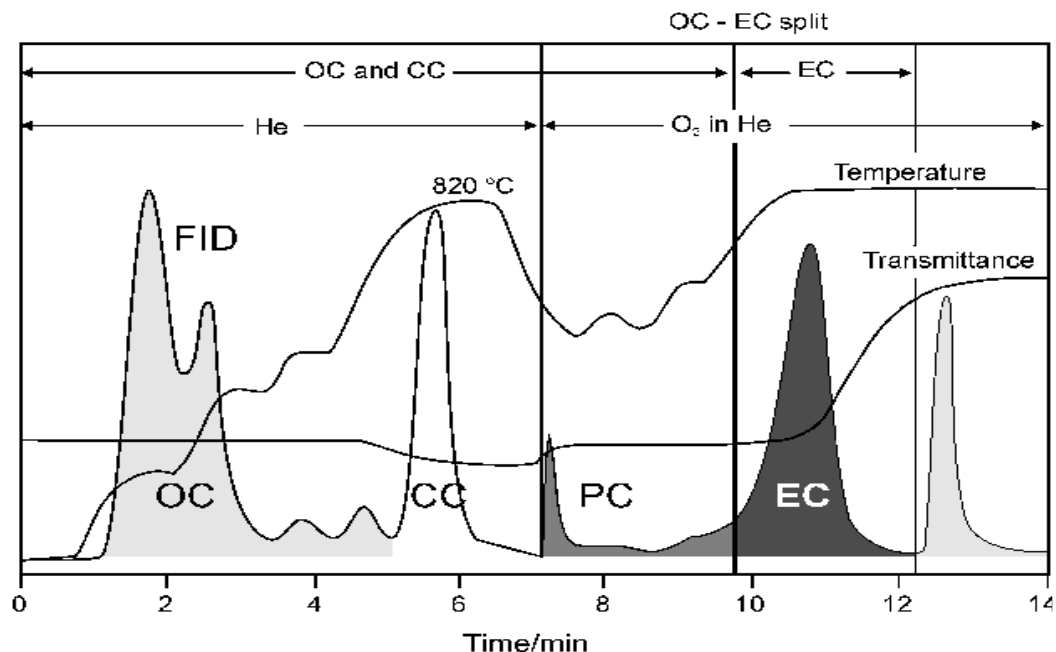
- lack of precise definition of atmospheric EC (split?)
- conversion of OC to EC during analyses (charring) must be accounted for.

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Particulate matter chemical composition: mineral species and elements

- total mineral mass: ashing ashless filter + weighing

- elemental composition

XRF   Non-Dispersive X-ray Fluorescence Spectrometry.
INAA   Instrumental Neutron Activation Analysis.
PIXE   Proton Induced X-ray Emissions Spectrometry.
EXAFS   Extended X-ray Absorption Fine Structure Spectroscopy
ICP/AES Inductively Coupled Plasma with Atomic Emission Spectroscopy
ICP/MS Inductively Coupled Plasma with Mass Spectroscopy
AAS   Atomic Absorption Spectrophotometry.
  +   Several others

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Reliability and limitation of analytical procedures

1. Detection limit
   The method detection limit is the smallest atmospheric concentration which can be distinguished from the blank's contribution:

$$MDL = t\,\sigma\,/\,V$$

   t = the Student's t value at e.g. 99% confidence level with n-1 levels of freedom (n = nb of blanks)

   σ = std deviation of replicate analyses of blanks

   V = air sample volume

2. Precision
   • based on replicate determinations (repeatability)

3. Accuracy
   • needs certified standards (e.g. NIST, JRC)
   • interlaboratory comparison robust averages often used as assigned values (reproducibility)

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Elemental analyses: minimum detection limits

Species	Minimum detection limit in ng/m³					
	ICP/AES	AA Flame	AA Furnace	INAA	PIXE	XRF
Be	0.06	2	0.05	NA	NA	NA
Na	NA	0.2	0.005	2	60	NA
Mg	0.02	0.3	0.004	300	20	NA
Al	20	30	0.01	24	12	5
Si	3	85	0.1	NA	9	3
P	50	100000	40	NA	8	3
Si	10	NA	NA	6000	8	2
Cl	NA	NA	NA	5	8	5
K	NA	2	0.02	24	5	3
Ca	0.04	1	0.05	94	4	2
Sc	0.06	50	NA	0.001	NA	NA
Ti	0.3	95	NA	65	3	2
V	0.7	52	0.2	0.6	3	1
Cr	2	2	0.01	0.2	2	1
Mn	0.1	1	0.01	0.12	2	0.8
Fe	0.5	4	0.02	4	2	0.7
Co	1	6	0.02	0.02	NA	0.4
Ni	2	5	0.1	NA	1	0.4
Cu	0.3	4	0.02	30	1	0.5
Zn	1	1	0.001	3	1	0.5
Ga	42	52	NA	0.5	1	0.9
As	50	100	0.2	0.2	1	0.8
Se	25	100	0.5	0.06	1	0.6
Br	NA	NA	NA	0.4	1	0.5
Rb	NA	NA	NA	6	2	0.5
Sr	0.03	4	0.2	18	2	0.5
Y	0.1	300	NA	NA	NA	0.6
Zr	0.6	1000	NA	NA	3	0.8
Mo	5	31	0.02	NA	5	1
Pd	42	10	NA	NA	NA	5
Ag	1	4	0.005	0.12	NA	6
Cd	0.4	1	0.003	4	NA	6
In	63	31	NA	0.006	NA	8
Sn	21	31	0.2	NA	NA	8
Sb	31	31	0.2	0.06	NA	9
In	NA	NA	NA	1	NA	NA
Cs	NA	NA	NA	0.03	NA	NA
Ba	0.05	8	0.04	6	NA	25
La	10	2000	NA	0.05	NA	30
Au	2.1	21	0.1	NA	NA	2
Hg	26	500	21	NA	NA	1
Tl	42	21	0.1	NA	NA	1
Pb	10	10	0.05	NA	3	1
Ce	52	NA	NA	0.06	NA	NA
Sm	52	2000	NA	0.01	NA	NA
Eu	0.08	21	NA	0.006	NA	NA
Hk	16	2000	NA	0.01	NA	NA
Ta	26	2000	NA	0.02	NA	NA
W	31	1000	NA	0.2	NA	NA
Th	63	NA	NA	0.01	NA	NA
U	21	25000	NA	NA	NA	1

NA: not available
Based on 30 m³ samples collected on 47 mm filters

Chemical mass closure:

sum of the quantified aerosol components' concentrations
vs
independently measured PM mass concentration
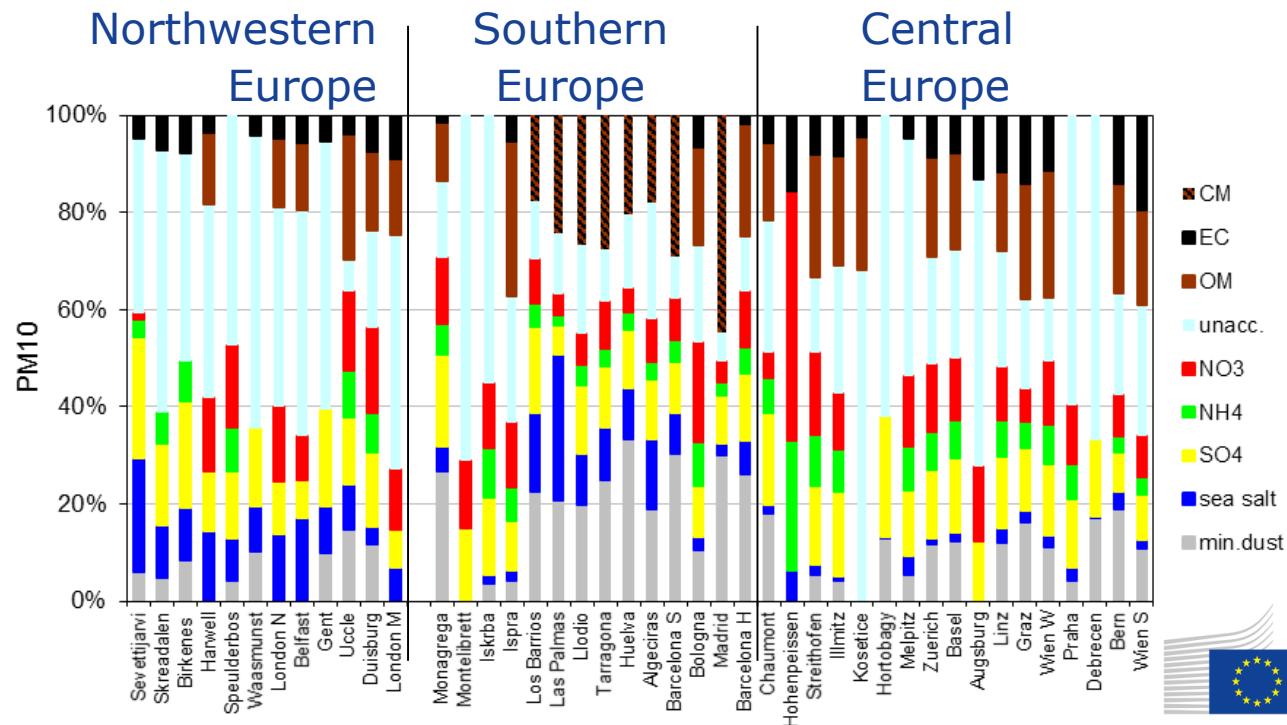
Chemical mass closure:

sum of the quantified aerosol components' concentrations (c_i)

vs

independently measured PM mass concentration (C)

$$\sum c_i \ = \ C$$

i.e.

$$|\sum c_i \ - \ C| \ < \ S(\sum c_i \ - \ C)$$

where S = uncertainty of the difference
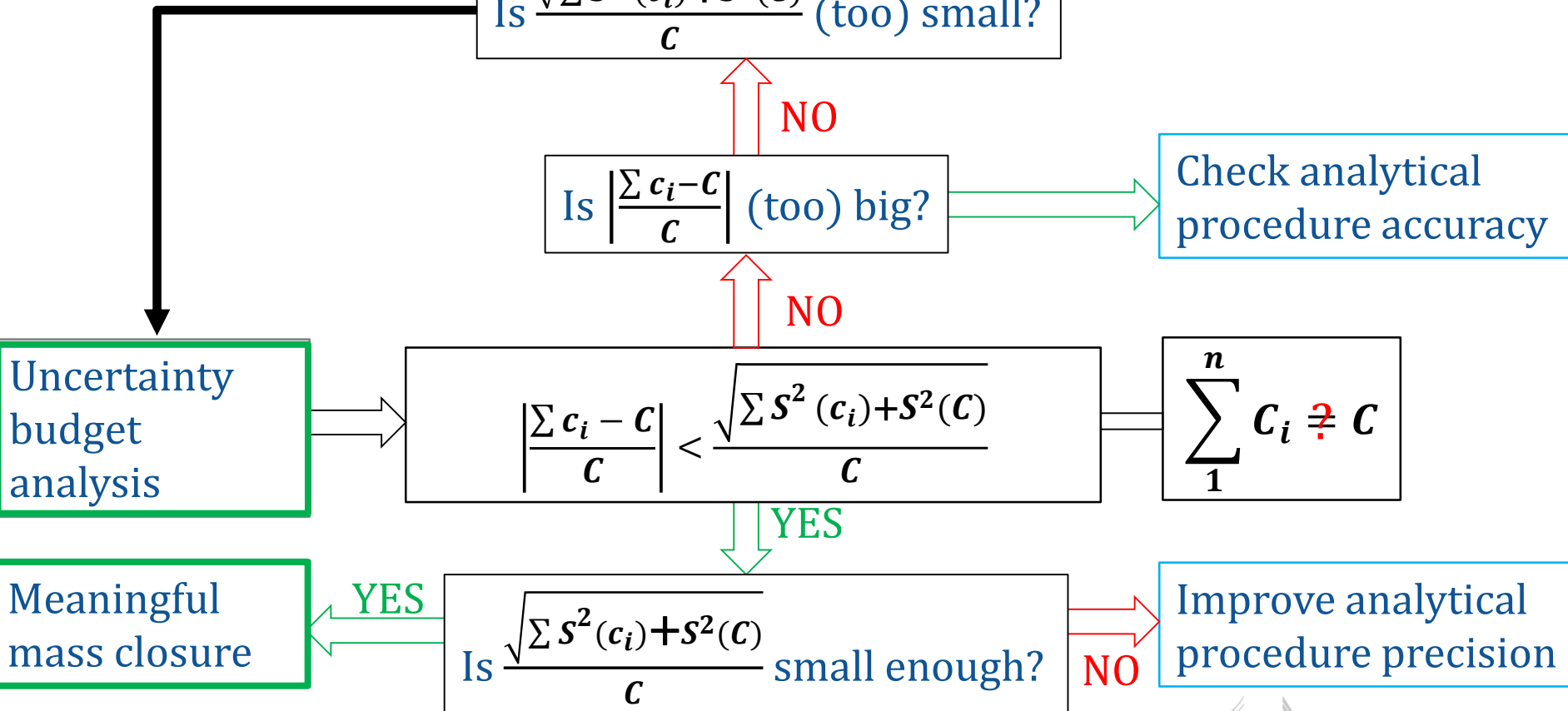
Law of propagation of errors (independent variables x_i):

$$S^2(f(x_1,\dots,x_i,\dots,x_n)) \approx \sum(\partial f/\partial x_i)^2 \ S^2(x_i)$$

where $S(x_i)$ = uncertainty of the (measured) variable x_i

Applied to mass closure (assuming that c_i and C are independent variables):

$$S^2(c_1+c_2+\dots+c_n \ - \ C) \approx S^2(c_1)+S^2(c_2)+\dots+ \ S^2(c_n)+S^2(C)$$

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Chemical mass closure?

Is $\dfrac{\sqrt{\sum S^2\,(c_i)+S^2(C)}}{C}$ (too) small?

NO

Is $\left|\dfrac{\sum c_i-C}{C}\right|$ (too) big?

Check analytical procedure accuracy

NO

$\left|\dfrac{\sum c_i - C}{C}\right| < \dfrac{\sqrt{\sum S^2\,(c_i)+S^2(C)}}{C}$

$\displaystyle\sum_{1}^{n} C_i \overset{?}{=} C$

Uncertainty budget analysis

YES

Meaningful mass closure

YES

Is $\dfrac{\sqrt{\sum S^2\,(c_i)+S^2(C)}}{C}$ small enough?

NO

Improve analytical procedure precision

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Chemical mass closure exercise output:

Even if ions, OC, EC, dust (i.e. sum of refractory species) and total mass
are measured accurately from a single filter, reasons why $\sum c_i < C$ can be:
• water, contributing to the aerosol mass, has not been measured.
• the organic-mass-to-organic-carbon ratio is underestimated.

Even if mass closure is satisfactory (*i.e.* $\sum c_i = C$ within uncertainties),
this does not mean anything about sampling artifacts if components'
and total mass concentrations have been measured from a single filter.

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