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Measurement methods for RWB Emissions:
What should be considered for a future standard?

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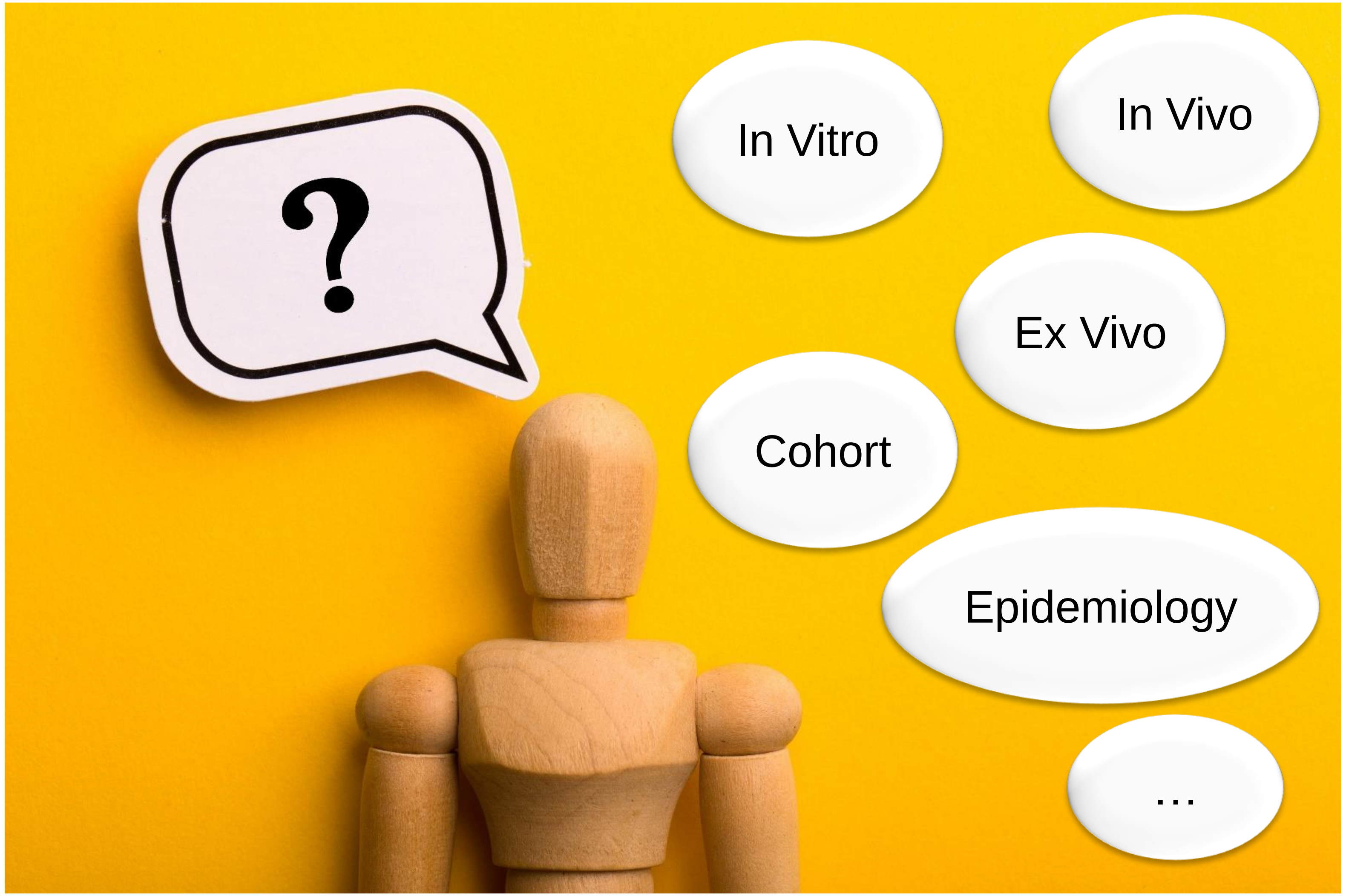
Take home message, measuring particulate matter emissions (PME)

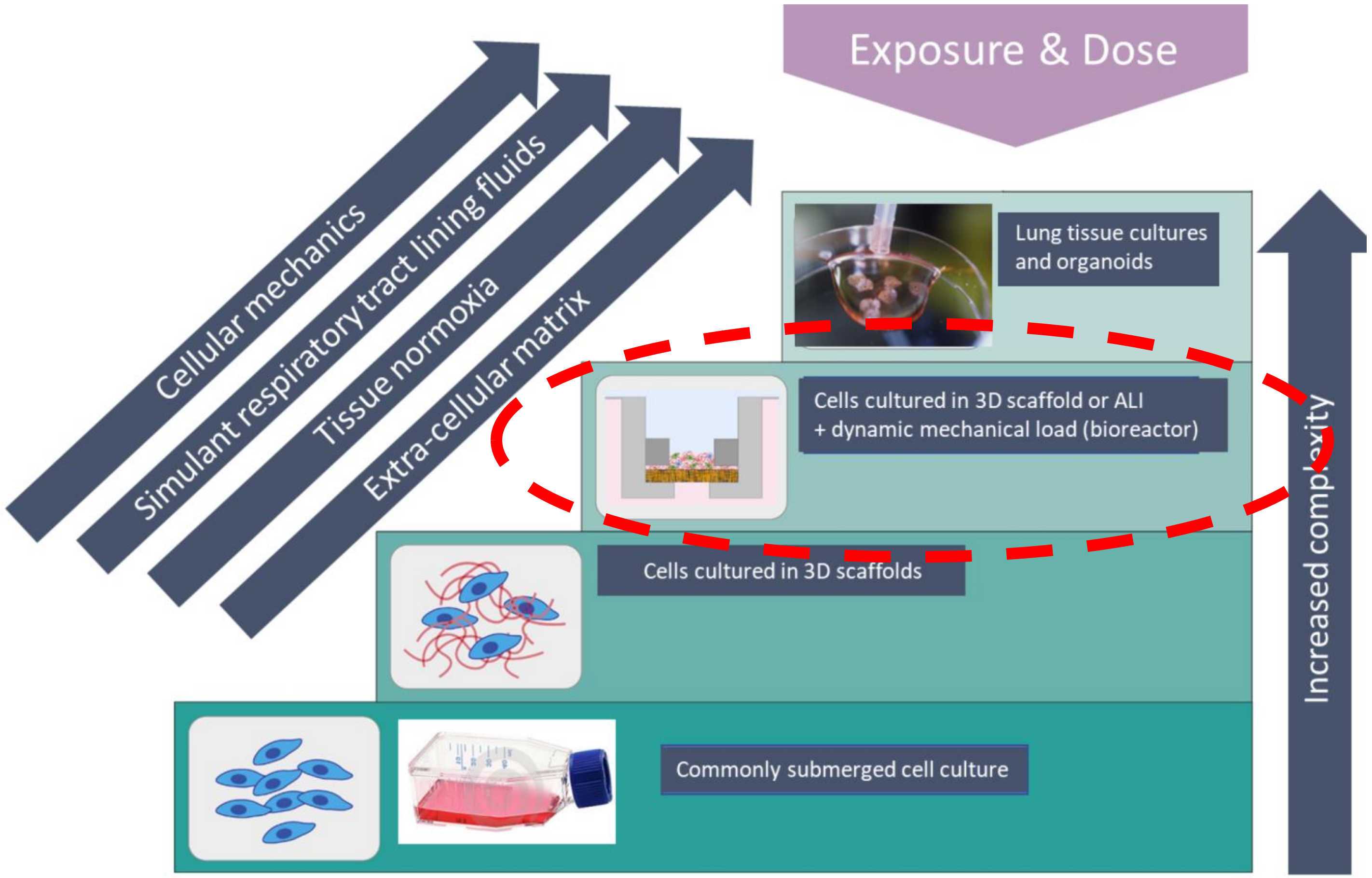
- The ideal metric describes climate and health effects of emissions.
- Health related studies look at very diverse aspects which not necessarily correlate (genotoxicity ≠ cytotoxicity ≠ oxidative stress ≠ …).
- A simple physical parameter (e.g., mass, number, surface) cannot capture the complexity of these effects.
- Quality of the combustion influences the chemical composition and thus the climate and health effects (e.g., light absorbing for climate effects, PAH content and water solubility for toxicity).
- Atmospheric processes (e.g., oxidation through O_3, OH, NO_X) can increase effective PME several fold and increase toxicity.
- The ideal metric (or combination of metrics) should at some degree differentiate composition (but also account for all PM emissions) and consider potential atmospheric processes.

Health effects



- Viability/Cell Death
- Cell Damage
- Inflammation
- Oxidative Stress
- Genotoxicity
- Decreased Lung Function
- Respiratory Symptoms
- Hospitalizations
- Increased Mortality
- …

Models with different physiological relevance (in vitro and ex vivo)



Create an aerosol standard* (in the case of AeroTox) for health effects studies

Not all cells react equally to particulate matter (PM)
- Lung region (e.g., bronchial vs alveolar)
- Health of donor
- Indicator (e.g., cell viability, cytokines, chemokines, …)

PM can be very diverse even for model cases:
- Particle size
- Composition (in AeroTox starts with ~100% elemental carbon, which is gradually coated with secondary organic aerosol [SOA])
- Different VOC Precursors of SOA (e.g., biogenic vs anthropogenic)

Source: EMPIR AeroTox Project (http://empir.npl.co.uk/aerotox/)

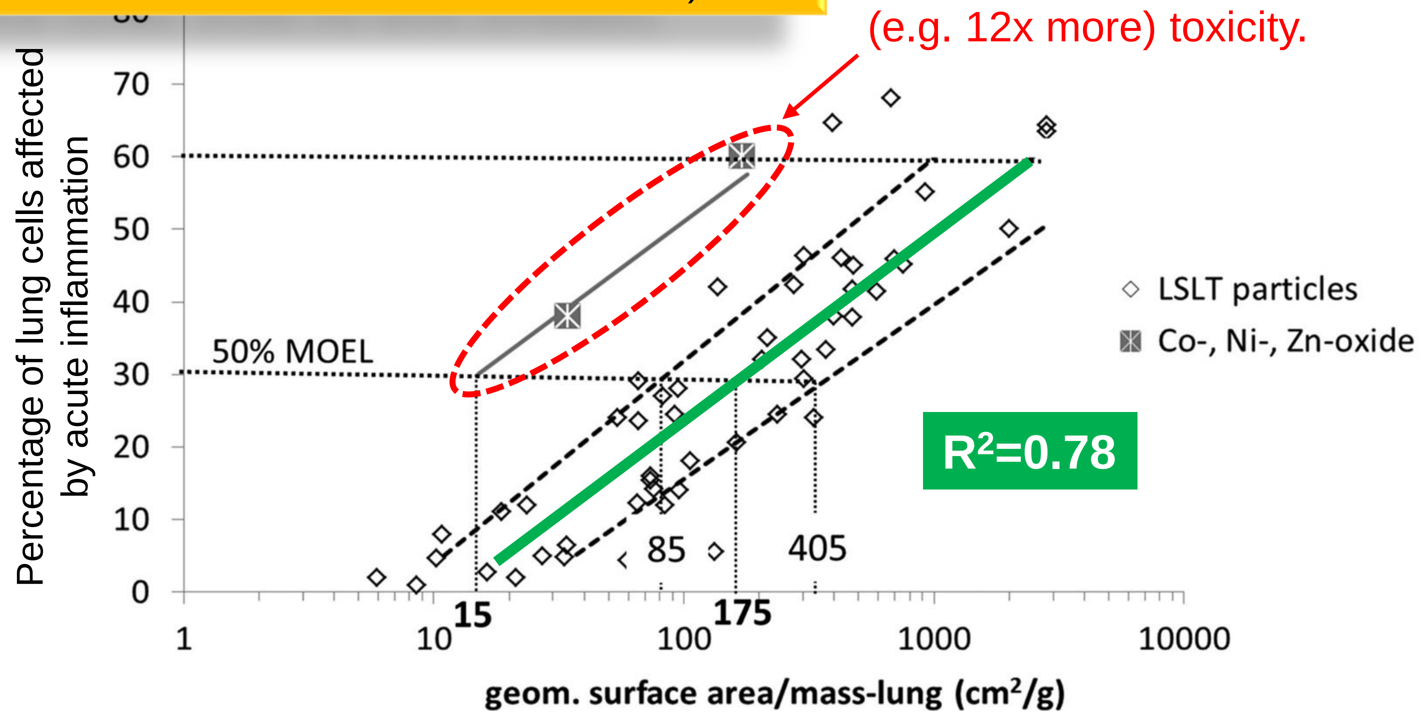
*Keller et al., Aerosol Sci. & Tech, 2022: https://doi.org/10.1080/02786826.2022.2110448

What is the best simple metric for health effects?

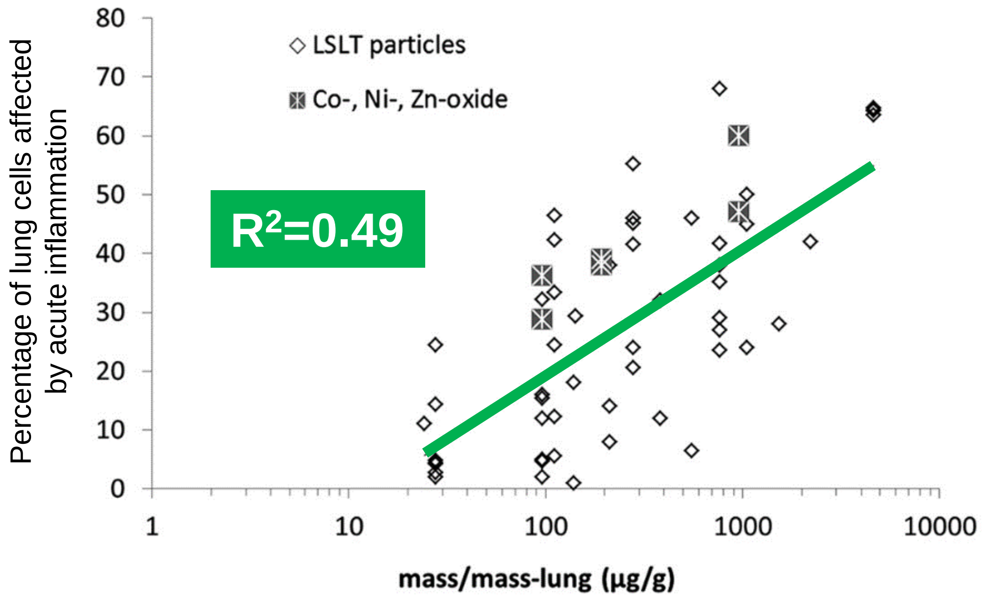
"Surface area is the biologically most effective dose metric for acute nanoparticle toxicity in the lung"

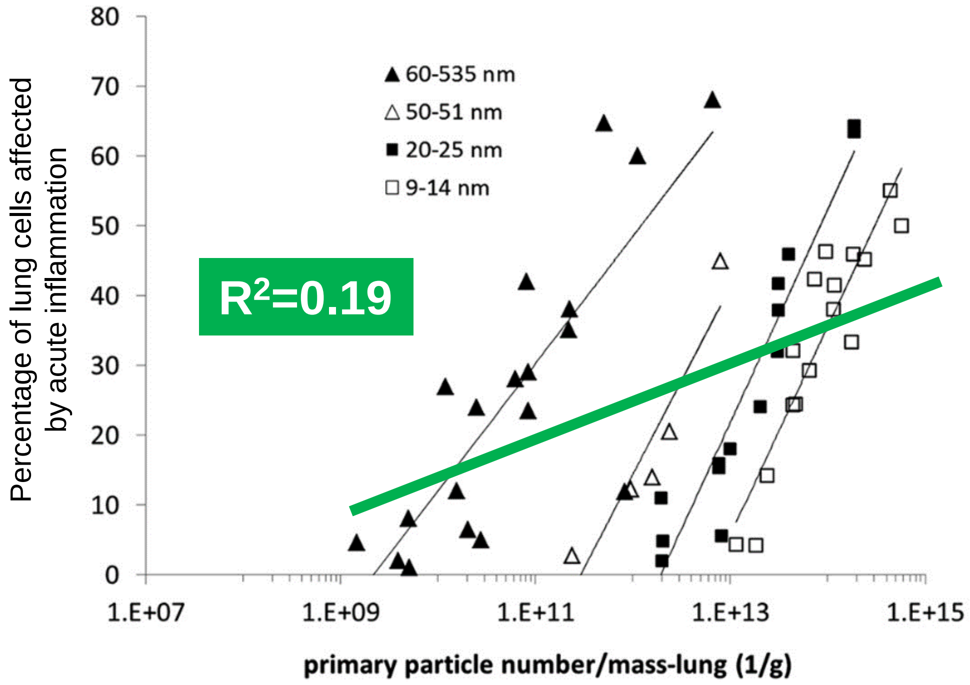
(Particle number shows the worst correlation)

None can differentiate between low and high (e.g. 12x more) toxicity.



LSLT = Low Solubility and Low Toxicity Particles
(4 very different materials)

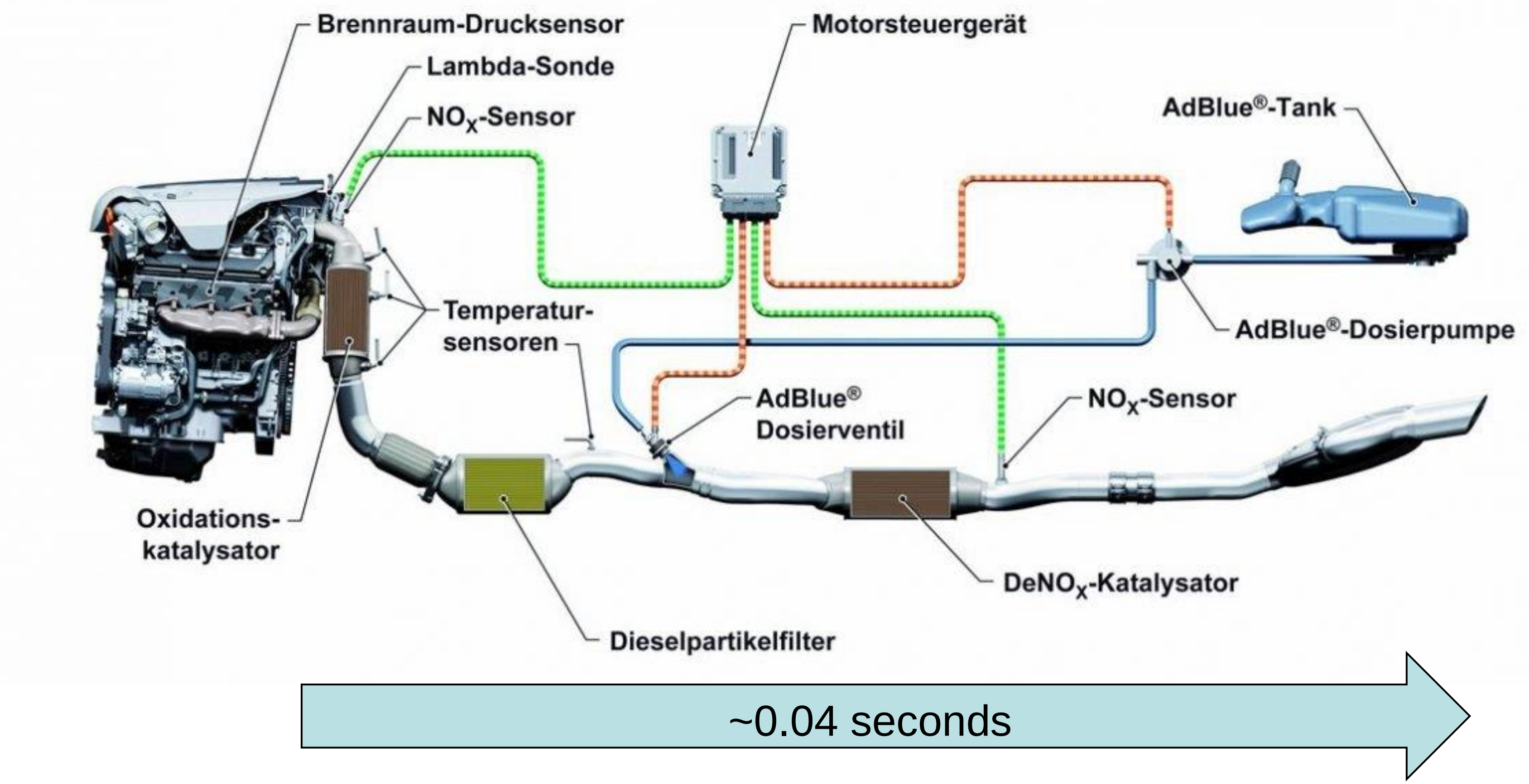




Source: Schmid and Stoeger, J. Aerosol Science 99, 2016, pp. 133-143

Particle number: vehicle vs biomass burning emissions

Image: https://www.krafthand.de/



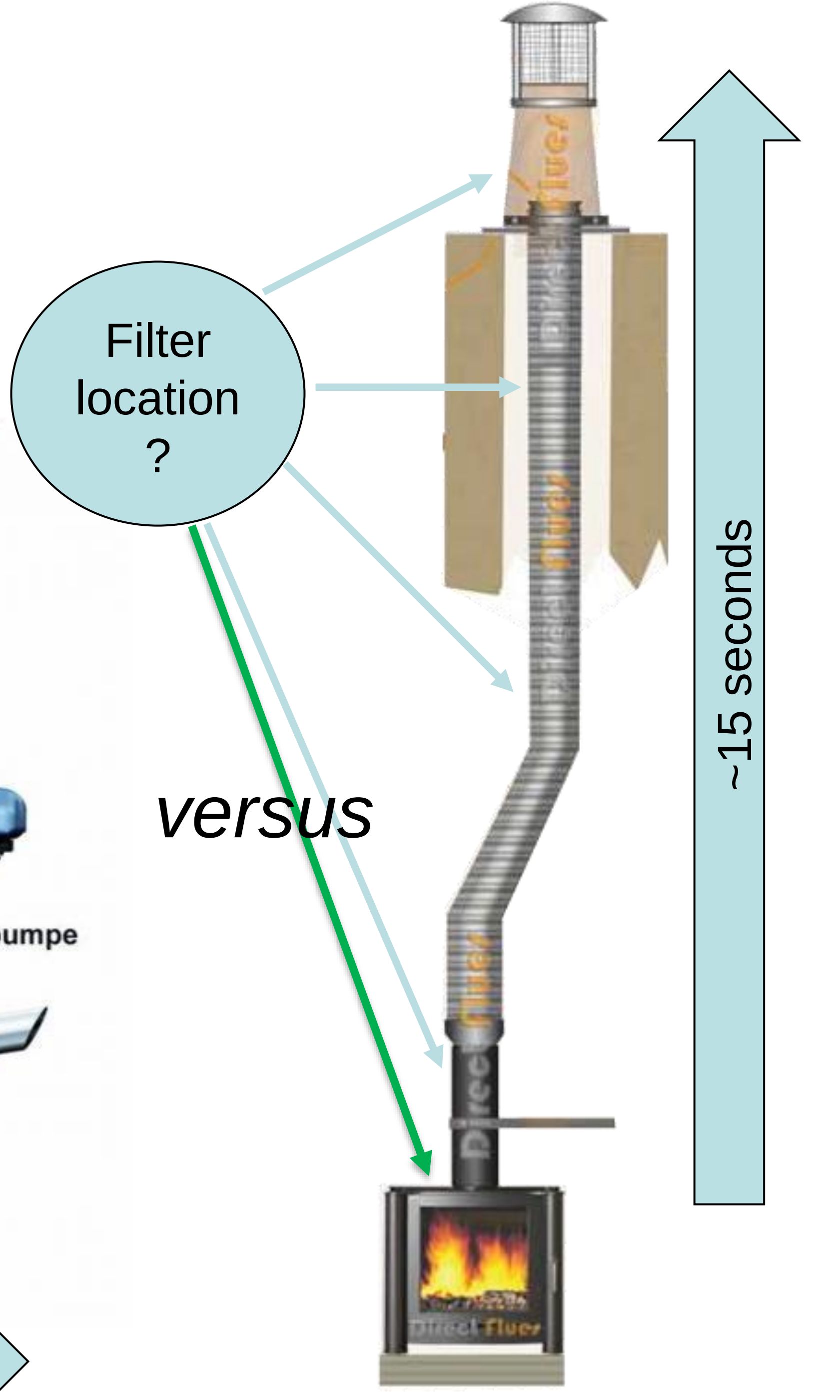
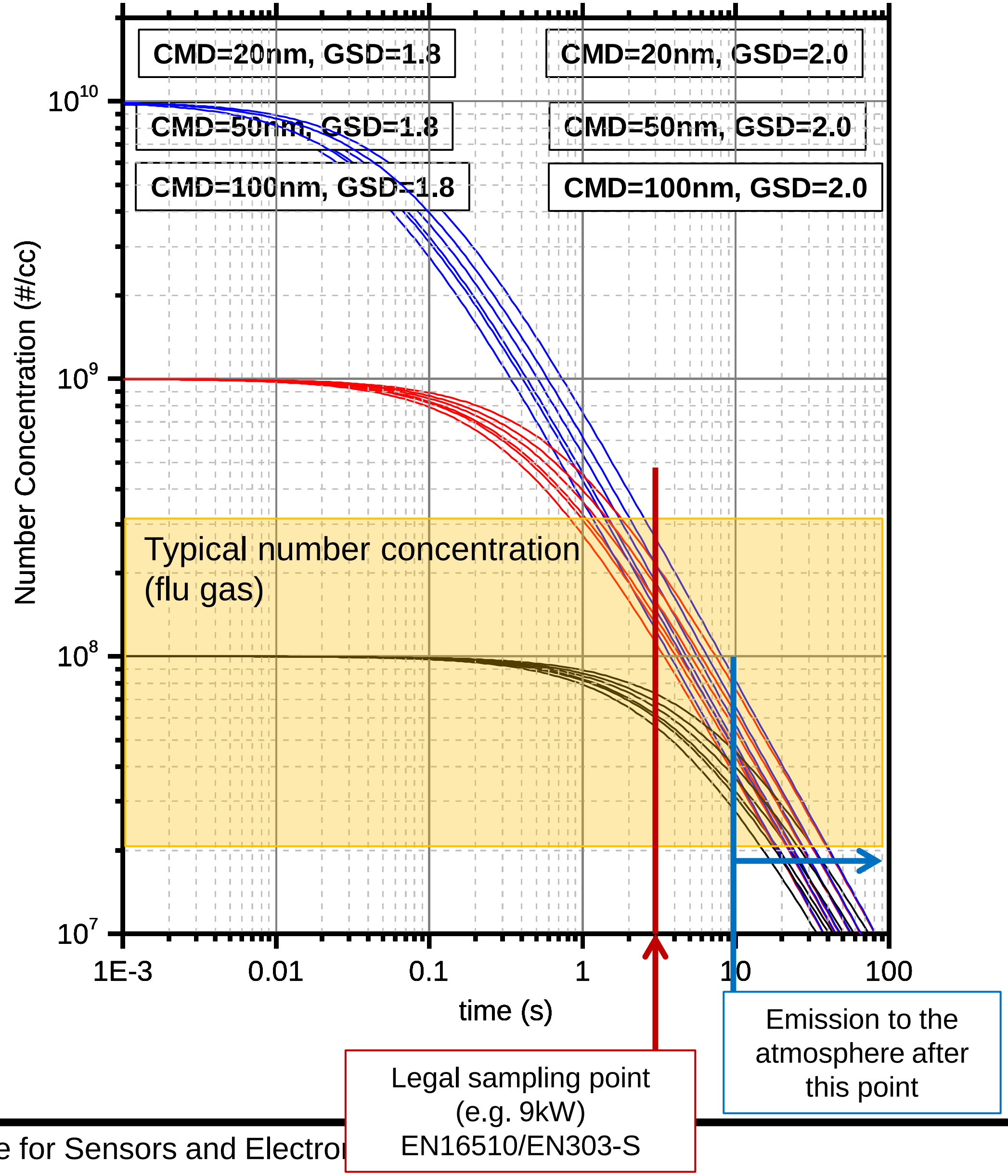


Image adapted from: http://directflues.co.uk

Particle coagulation*



For monodisperse case:

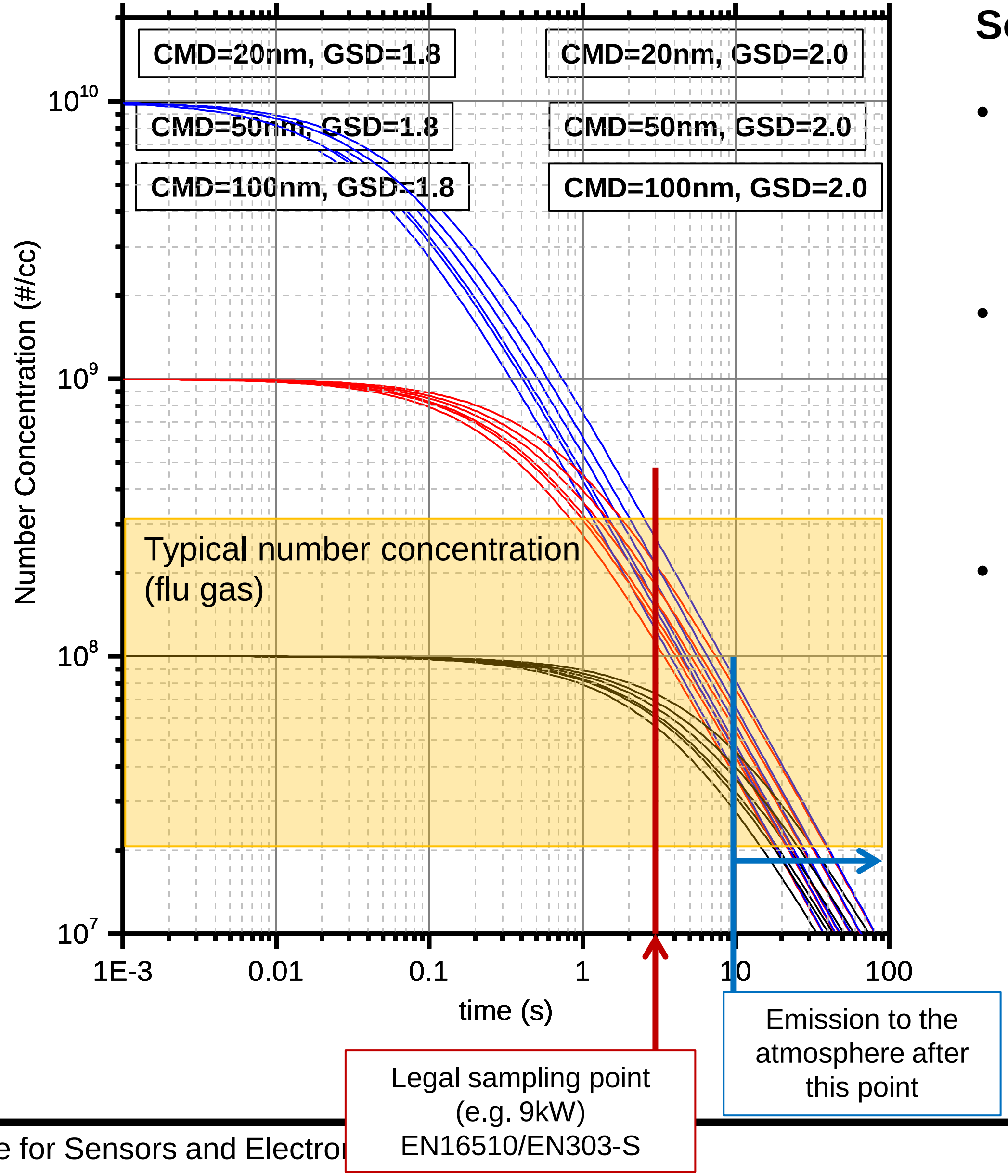
$$N(t) = \frac{N_0}{1 + N_0 K t}$$

$$d(t) = d_0 (1 + N_0 K t)^{1/3}$$

$N \rightarrow$ Number Concentration
$d \rightarrow$ Particle diameter
$K \rightarrow$ Coagulation coefficient

*Example at room temperature. Coagulation would be up to **3 times faster** at real flu gas temperatures ($K \propto T$)

Particle coagulation

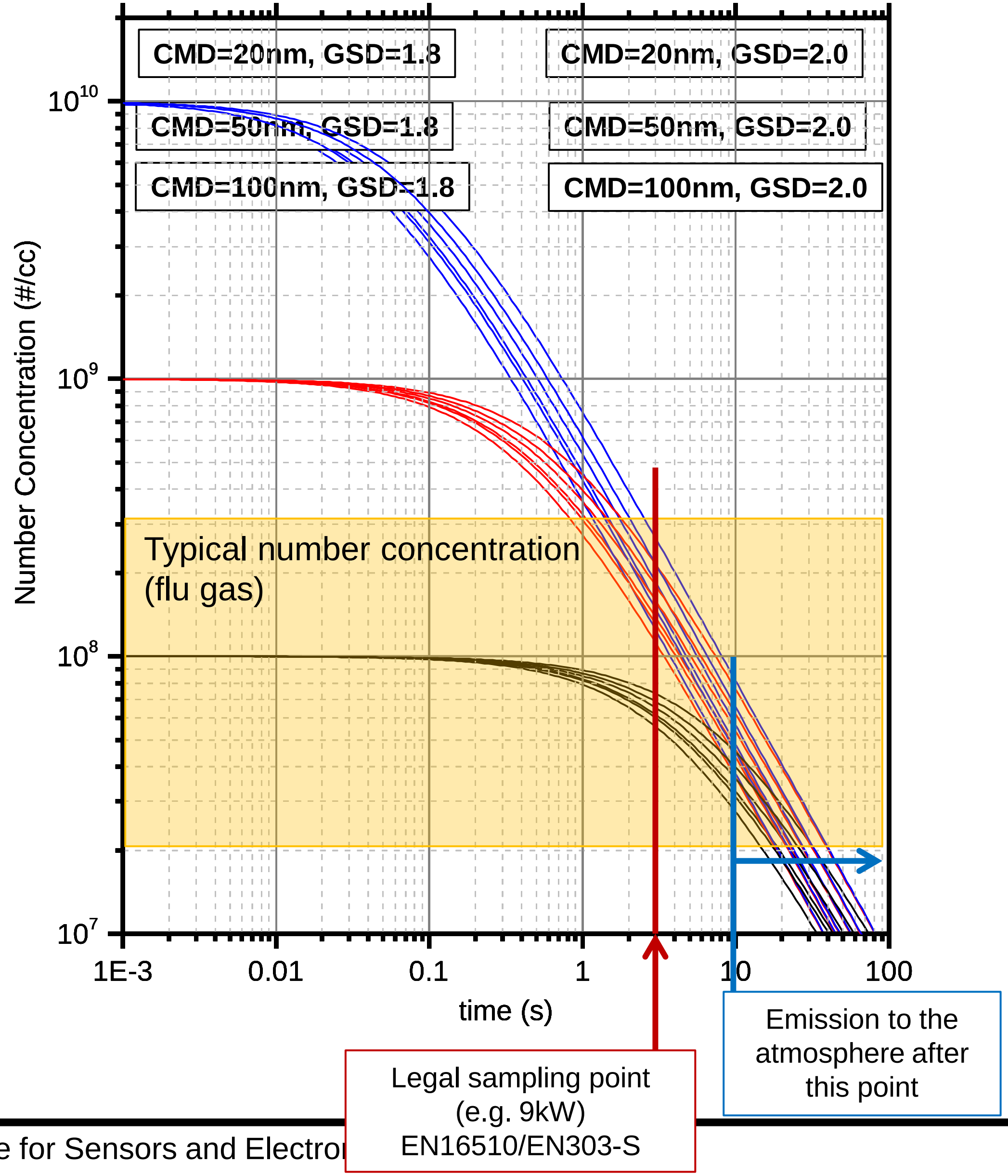


Some consequences of a number-based metric

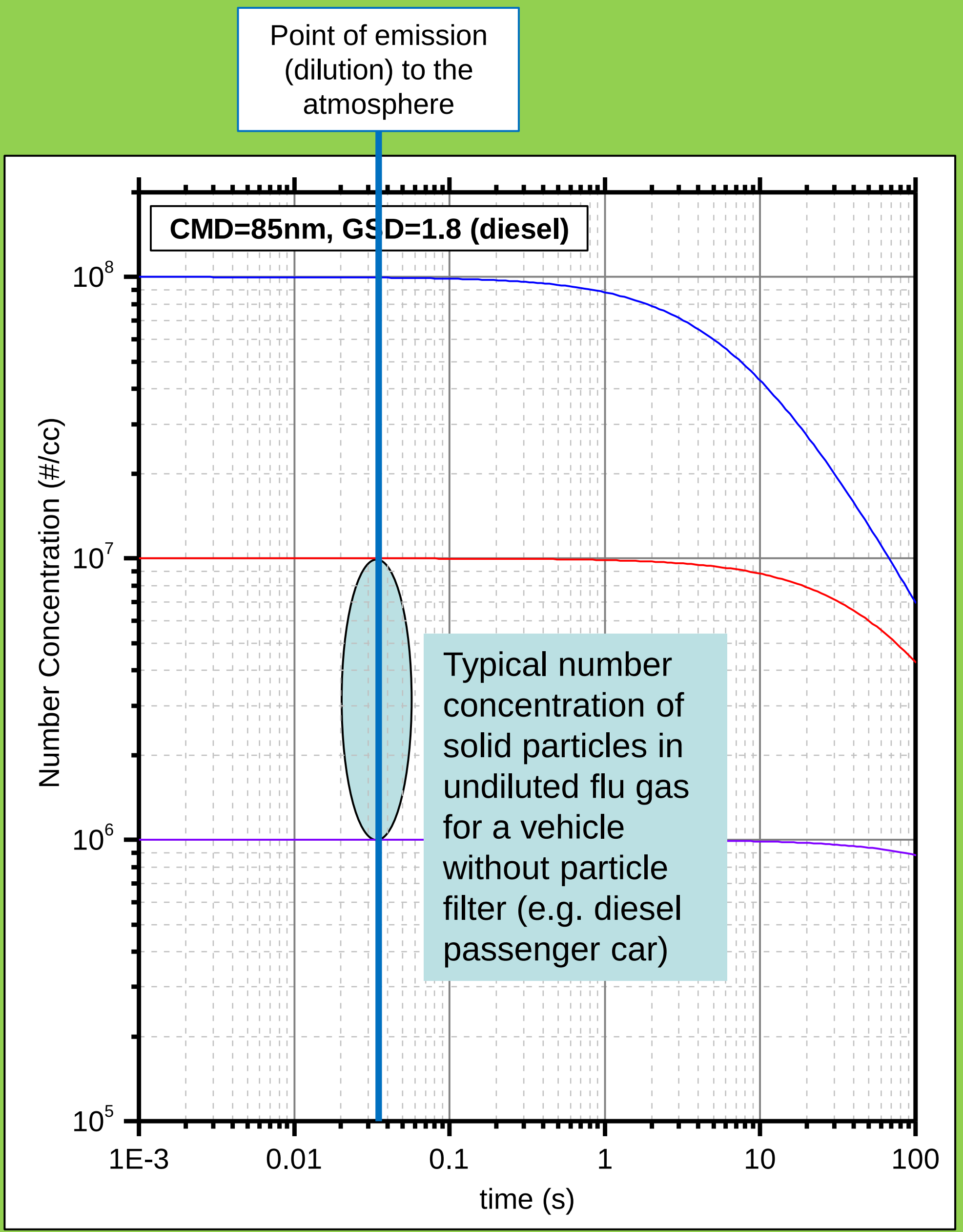
- Number has no relation with the quality of the combustion. Even clean oil boilers (mass emissions M≈1 mg/m^3_{STP} @ 3% O_2) have number concentrations N~10^7 #/cc.
- Filters and stoves would be designed/selected with the sole purpose of meeting a standard that has no useful connection to the actual emissions or to the health and climate impact.
- It will promote the placement of filters as close as possible to the end of the stack.

Conclusion: A number-based metric would kill current and future emission reduction developments that promote the use of filters integrated into the appliance, specially those situated in or near the combustion chamber.

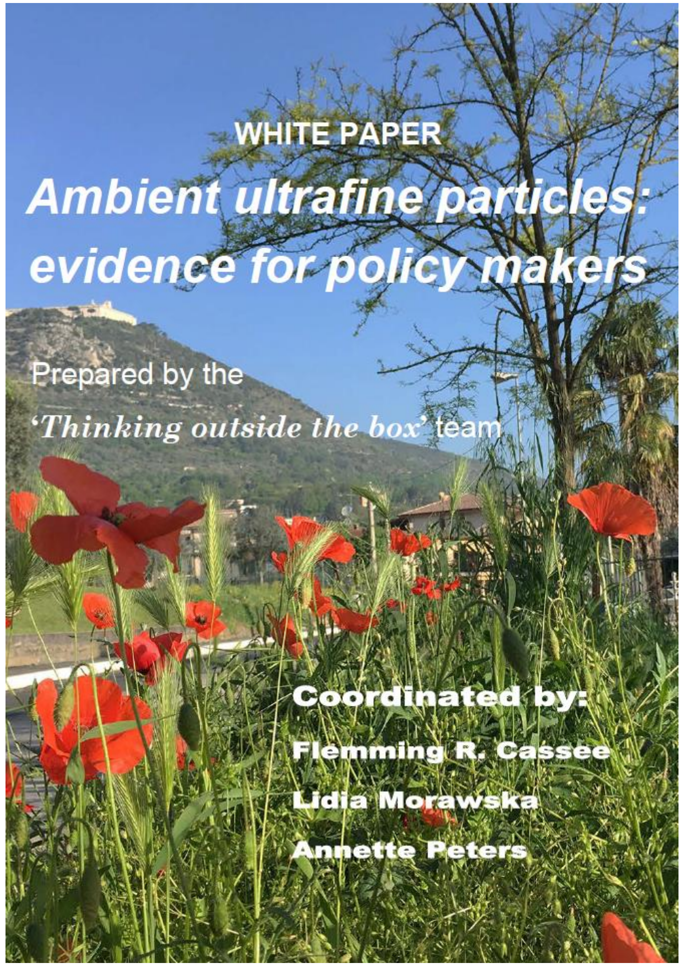
Particle coagulation



Vehicles are completely different



European Federation of Clean Air (EFCA) view on Ultrafine Particles (UFP)



PDF October 25th, 2019:
https://lnkd.in/gh7qB96

"2.3 Which metric should be used to describe UFP concentration-effect relationships?

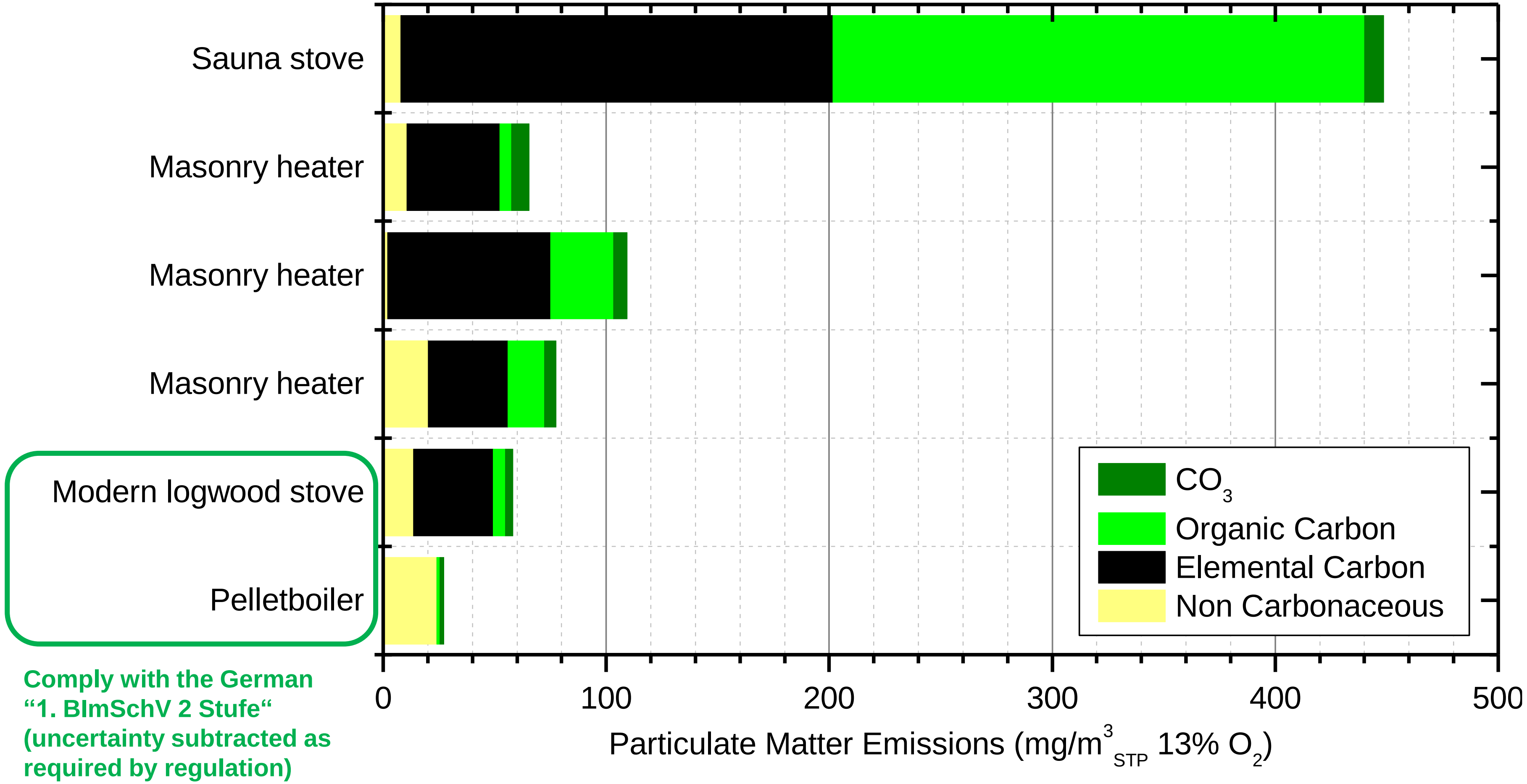
For practical reasons, using particle number as a predictor may be preferred […]over mass and surface area, especially if the particles size distribution is known. However, increased understanding of **the importance of chemical composition for toxicological effects of UFP and the use of surface area** rather than mass as dose metric may possibly shed more light on the issue."

Keep in mind that UFP refers to **ambient observations of particles smaller than 100nm (down to, 2 to 5nm), including organics and secondary particles**. The number-based emission metrics (cars and wood stoves) are for **particles larger than 23nm after removing organics and without secondary particles**. These are completely different metrics!

Other quotes from the white paper recommending a surface metric:

- "ROS production was quite well correlated with surface area rather than total particle number concentration or mass. "
- "Chronic health effects and disease prevalence also scale better with surface area dose rather than with mass"
- "It has to be noted that some studies report very strong correlation between toxicity and surface area of the particles this metric requires careful consideration. "
- …

Emissions Composition (Small Combustion Installations)



Metrics based on **mass, surface or number fail to capture the diversity of emissions.** Soluble non carbonaceous material can be cleared fast from the lungs compared tot, e.g., insoluble soot.

Graphic adapted from: Lamberg et al. / Atm. Env. 45 (2011) 7635-7643

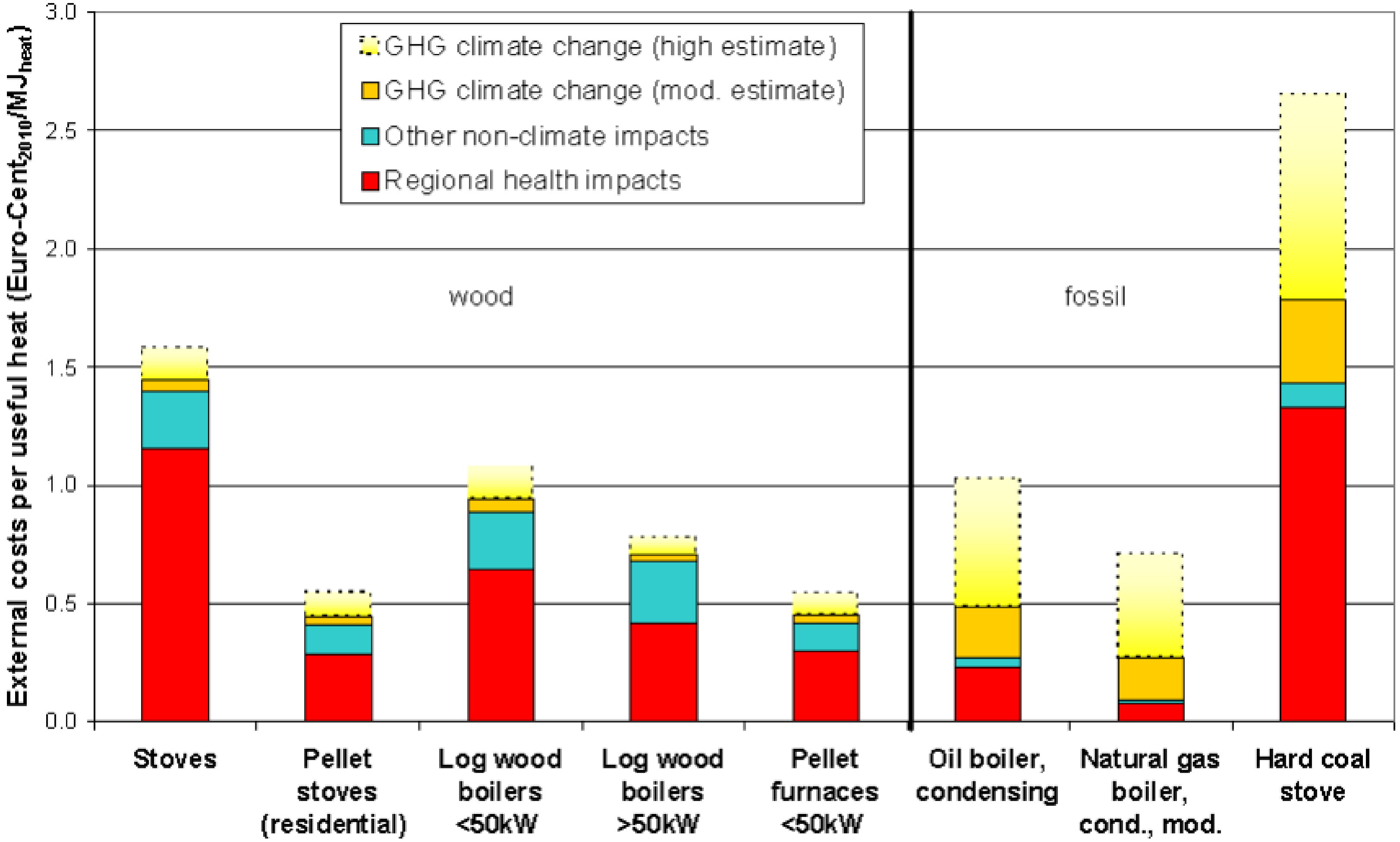
IMBALANCE Project (2008-2012): IMpact of Biomass burning AerosoL on Air quality aNd ClimatE

GOAL: Assessment of the impact on air quality and climate. Considering also external costs.

FOCUS: Physical and chemical properties of aerosol emissions, aerosol's aging processes in the atmosphere.

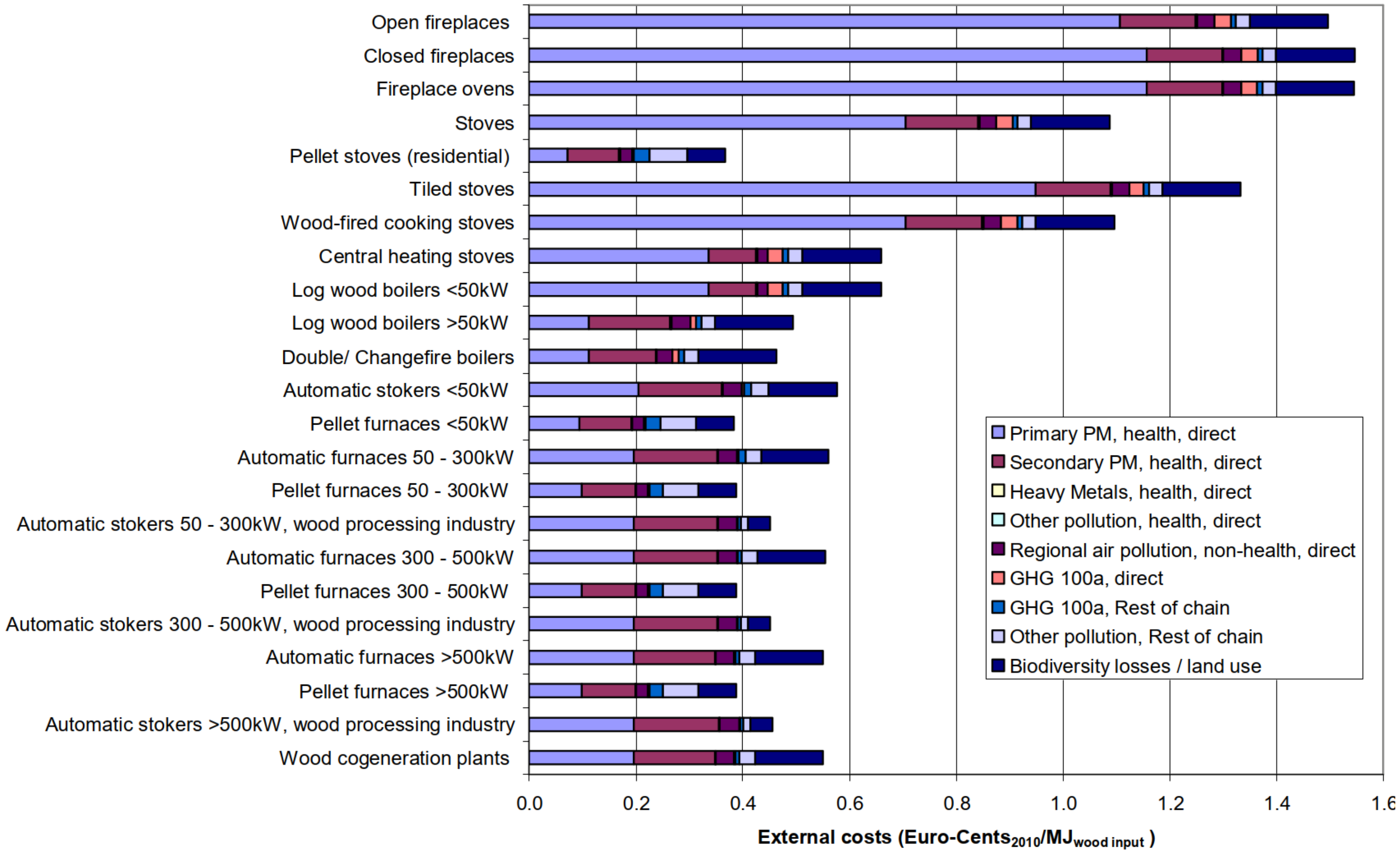
- Wood combustion and other biomass combustion represent renewable energy sources and means to reduce global CO_2 emissions.
- Biomass combustion inherently produces high emissions of particulate matter. These aerosol particles exert a climate forcing and have adverse health effects, which may lead to respiratory and cardiovascular diseases and cancer, affecting population morbidity and mortality.
- The strengths of both, climate and health effects, vary during the lifetime of the aerosol due to physicochemical aging processes in the atmosphere.

Comparison of wood and fossil heat in terms of external costs per MJ useful heat



Graphic: Heck and Meyer, 2012; DOI: 10.5071/20thEUBCE2012-5AV.1.25

External costs per MJ input wood for the major appliance classes located in Switzerland



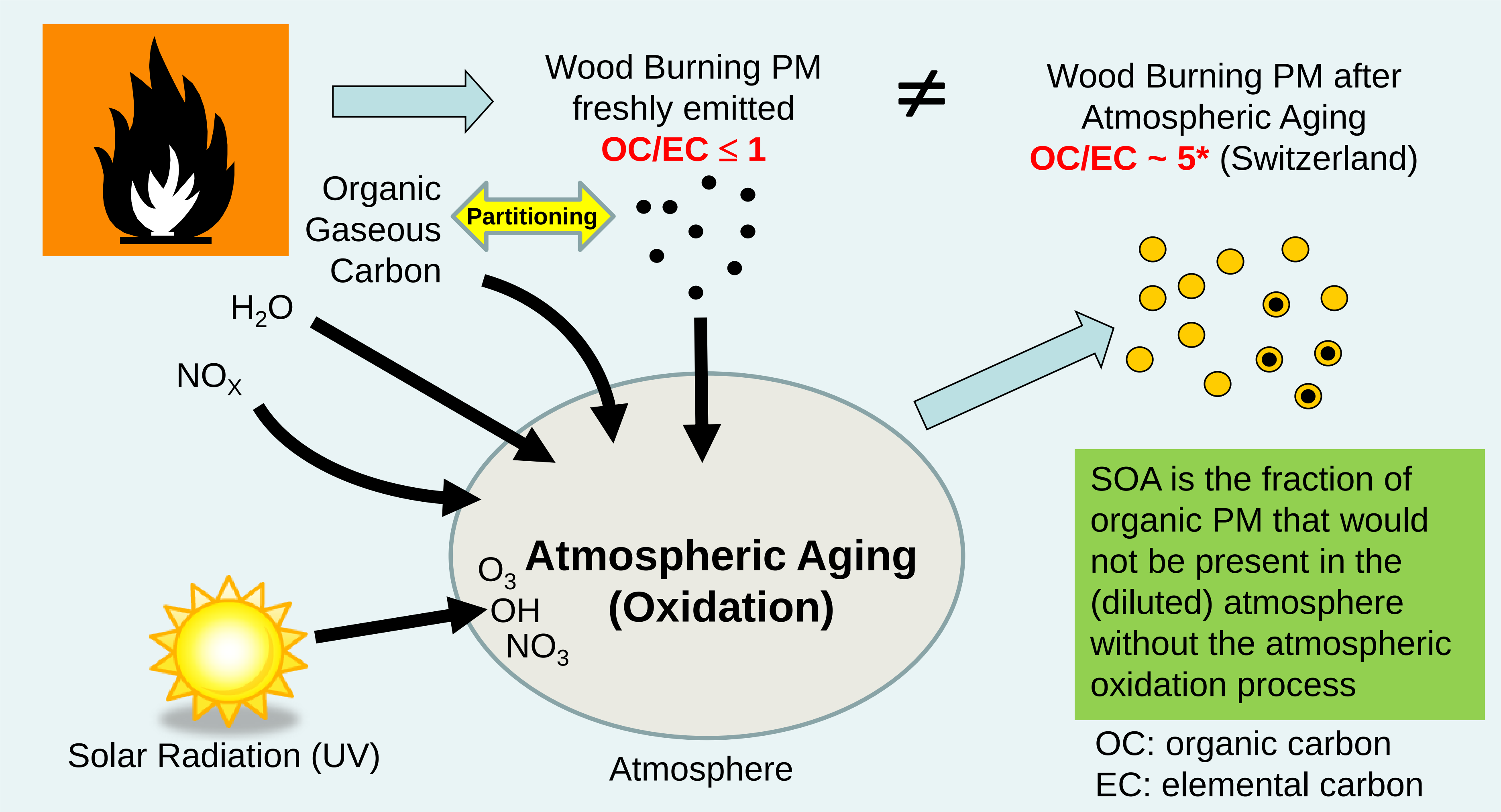
Graphic: Heck and Meyer, 2012; DOI: 10.5071/20thEUBCE2012-5AV.1.25

Some limitations:

- Wood is considered CO_2 neutral (potentially underestimation of climate effects)
- Fixed factor for the health impact of PM (composition not accounted for)
- Secondary organic aerosol formation not considered

*Secondary PM from sulfur dioxide, nitrogen oxides and ammonia emissions

Primary PM and Secondary Organic Aerosols (SOA)



*See: Gianini, 2012; https://doi.org/10.1016/j.atmosenv.2012.02.036

How important is Secondary Organic Aerosol (SOA)?

- Ambient source apportionment data suggests that the SOA fraction is larger than primary emissions from biomass burning (see, e.g., Chen 2021; doi: 10.5194/acp-21-15081-2021)
- Laboratory studies confirm that SOA may account for at least half of the emissions from wood burning appliances (Heringa, 2011; doi: 10.5194/acp-11-5945-2011; Grieshop 2009a and 2009b; doi: 10.5194/acp-9-2227-2009 and 10.5194/acp-9-1263-2009)
- Anthropogenic SOA (compared to biogenic SOA) causes higher oxidative stress, genotoxicity and inflammation in lung cell models (Offer *et al.*, 2022; doi: 10.1289/EHP9413; Leni et al. EST under review)
- The overall toxicity of emissions from wood burning appliances could be greatly increased by the additional wood burning SOA (Air-liquid interface exposure of bronchial lung cells) (Krapf 2017; doi: 10.1039/c6em00586a)

Beyond EN-PME: Long Term Method

Oxidation Flow Reactor (OFR) and Particle-Bound Total Carbon (TC) Measurement

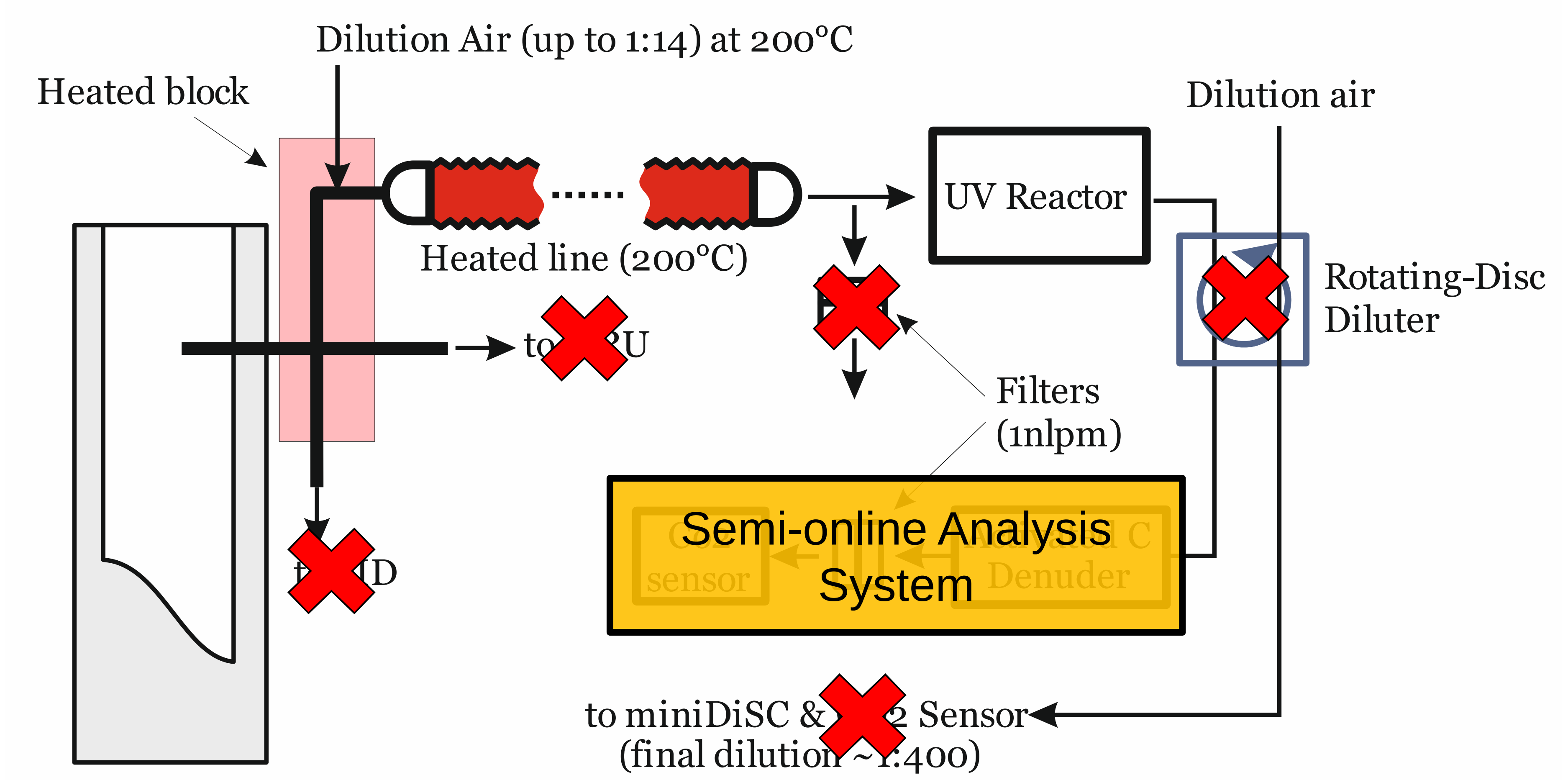
- Measuring only the particle-bound carbon atoms by means of a total carbon (TC) analysis
- Considers atmospheric processes (i.e. secondary organic aerosol, SOA, potential). The OFR simulates atmospheric processes transforming part of the organic gaseous carbon into SOA
- TC analysis is already well established for ambient pollution monitoring (good metric for comparing PM-emissions against ambient PM-measurements)
- This measurement can be combined with a standard gravimetric measurement or another metric that incorporate non-carbonaceous material

Detailed description under:

Keller & Burtscher: *Characterizing particulate emissions from wood burning appliances including secondary organic aerosol formation potential*, J. Aerosol Science 114, pp. 21-30, 2017.

https://doi.org/10.1016/j.jaerosci.2017.08.014

Setup for the Long-Term method during the EN-PME-TEST project



- On a first step, [particle bound] organic carbon (OC) and elemental carbon (EC) measurements by means of thermal-optical analysis (EUSAAR 2 protocol). Total Carbon, TC = OC + EC
- Analysis may be substituted by a relatively simpler thermal analysis for TC.

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Technological advances since the end of EN-PME-TEST

Based on the limit of detection, our systems will be able to detect Total Carbon concentrations as low as TC=70 µg-C/m^3_{STP} *

- The TCA-8 from Aerosol d.o.o. measures total carbon semi-online.
- Two sampling heads to avoid measurement downtime
- Limit of detection 0.4 µg-C sampled on the filter

Dekati® Oxidation Flow Reactor DOFR™

Keller et al. 2022 (OCU)
https://doi.org/10.1080/02786826.2022.2110448

- In house development for semi-online Total Carbon measurements (FATCAT)
- Limit of detection 0.2 µg-C sampled on the filter
- Has already been tested with wood burning emissions

* Assuming sampling duration of 30 minutes, 1:10 dilution and 1 lpm sampling flow

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