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WIR SCHAFFEN WISSEN – HEUTE FÜR MORGEN

Composition of ship-engine PM emissions for 3 fuels: black carbon, light absorption, trace metals

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Background

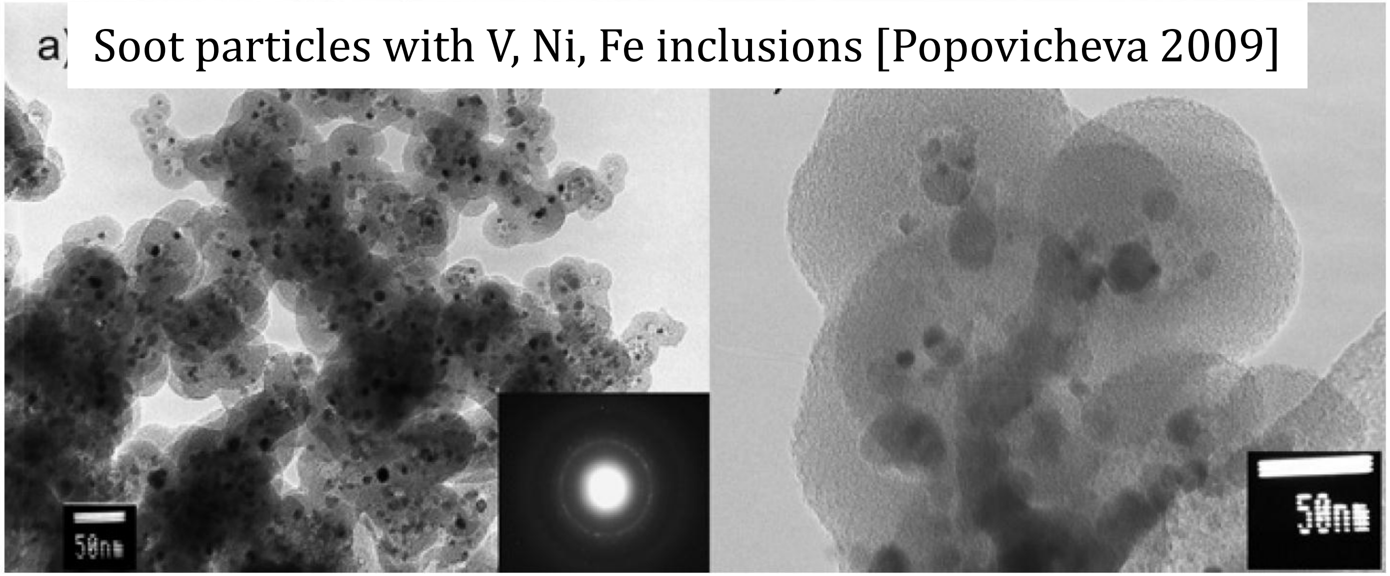
➢ Ship-engine fuels

- "Heavy Fuel Oil" **HFO**, used in open ocean:
  - Cheap, residual fuel
  - High S content *(23,000 ppm)*
  - High heavy metal content
- "Distillate fuels" fuels, used near shore:
  - Low S
  - Diesel *(**DF**, 7 ppm S)*
  - Marine Gas Oil *(**MGO**, 780 ppm S)*

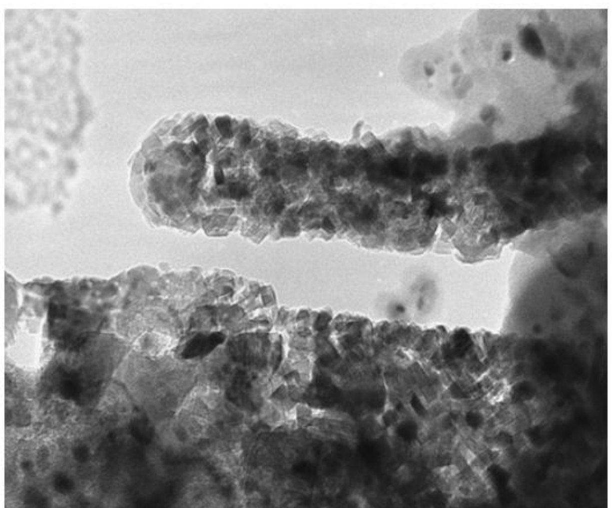
- Different fuels, different PM emissions, different…
  - Climate effects
  - Health effects for HFO and DF [1]
  - Heavy metals

[1] Oeder et al., PLoS One 2015 [2] Jonson et al., ACP 2015

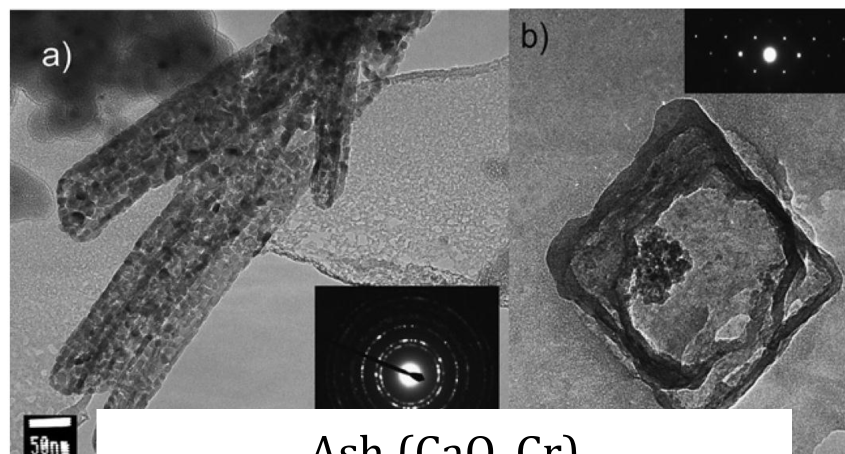
Heavy metals in soot from Heavy Fuel Oil combustion



Soot particles with V, Ni, Fe inclusions [Popovicheva 2009]



Ash (Ca, Ni, V, Fe)



Ash (CaO, Cr)

Popovicheva et al.

J. Environ. Monit. 2009

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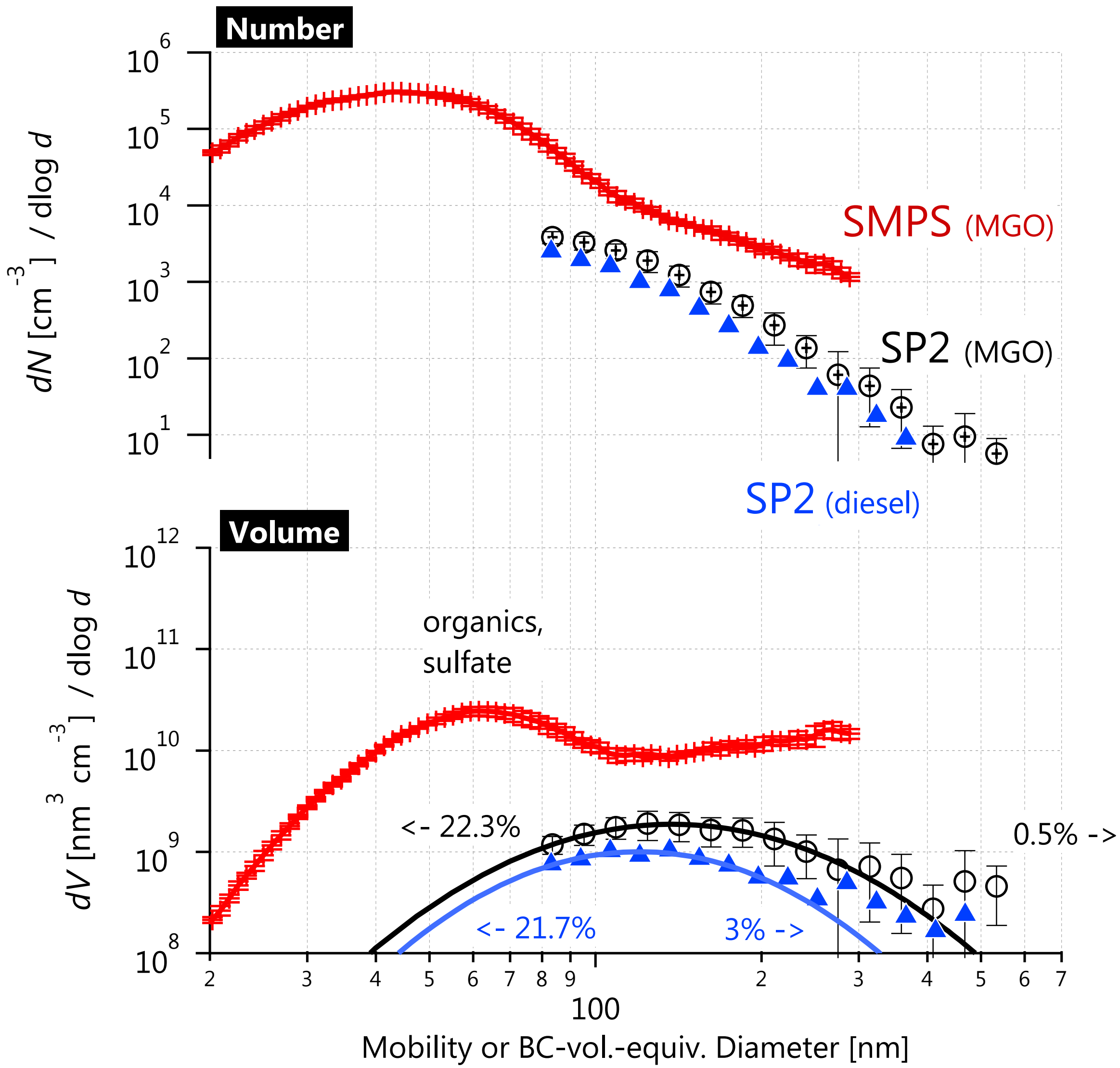
Talk outline

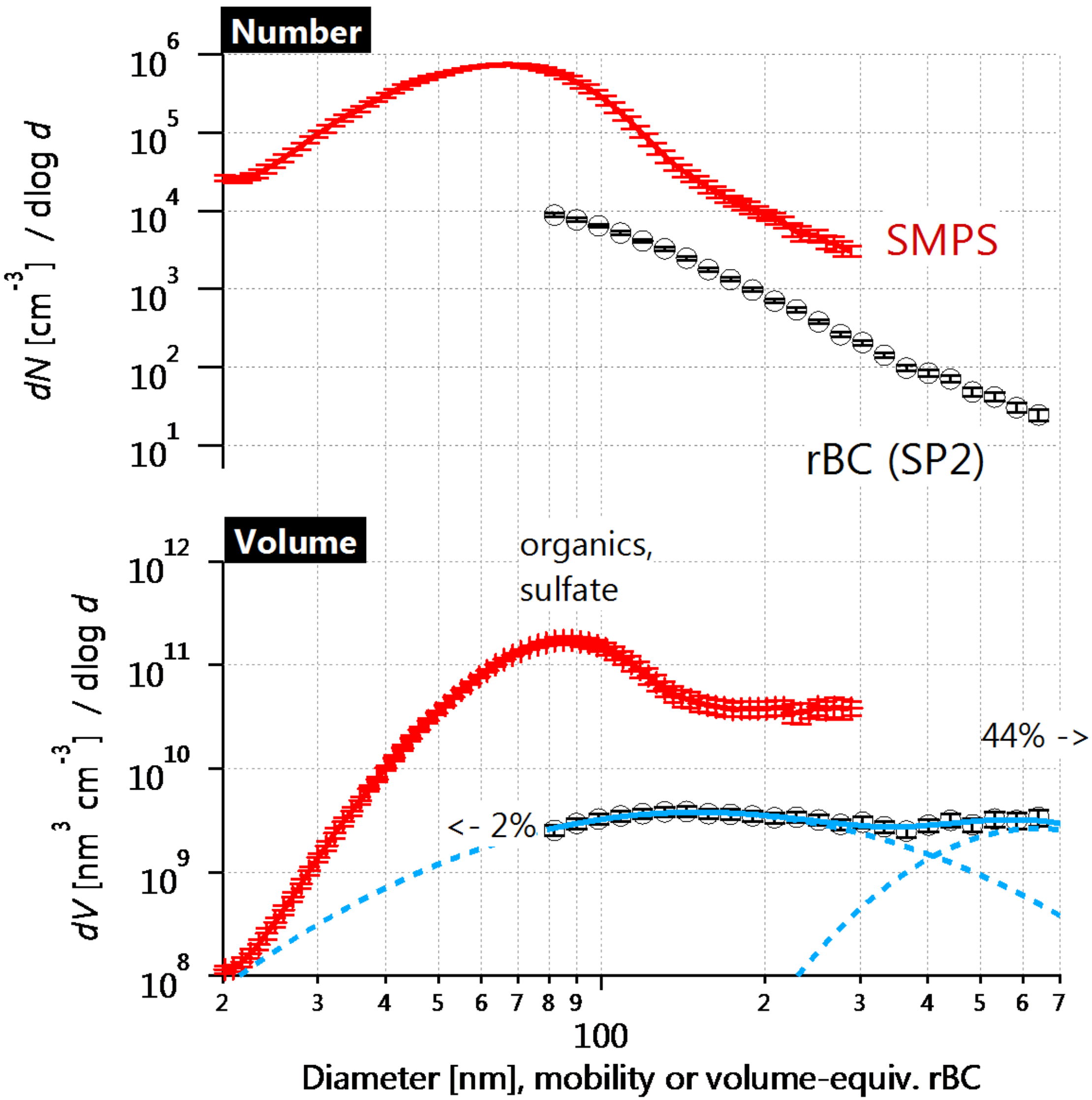
1. Background
2. **Black carbon**
   – Fundamental measurements
3. **Optical properties**
   – Climate-relevant
4. **Trace metals**
   – Health, source identification
5. Summary

Marine gas oil (MGO) and diesel (DF) size distributions



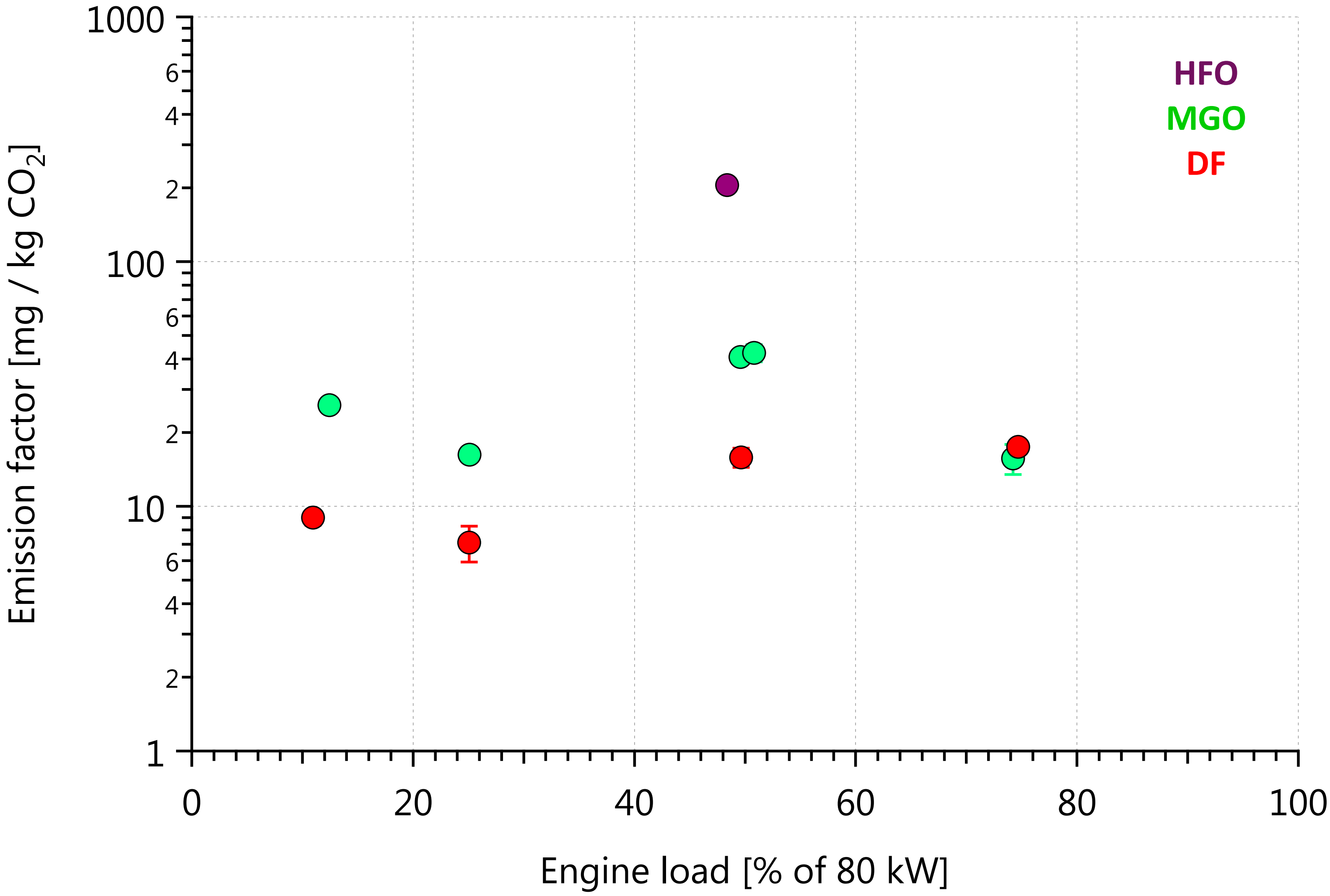
- BC particles larger than bulk nucleation mode
- rBC GSD~2.1
- MGO BC mass outside of detection range:
  - 23% below
  - 3% above

Heavy Fuel Oil: very large BC distribution



- BC core size ***much*** larger than normal
  - Modes at 150, 630 nm $d_{\mathrm{mass-equiv}}$
- Size effects corrected below:
  - HFO scaling factor 1.46
  - MGO factor 1.26
  - DF factor 1.22

rBC emissions highest for HFO, lowest for DF

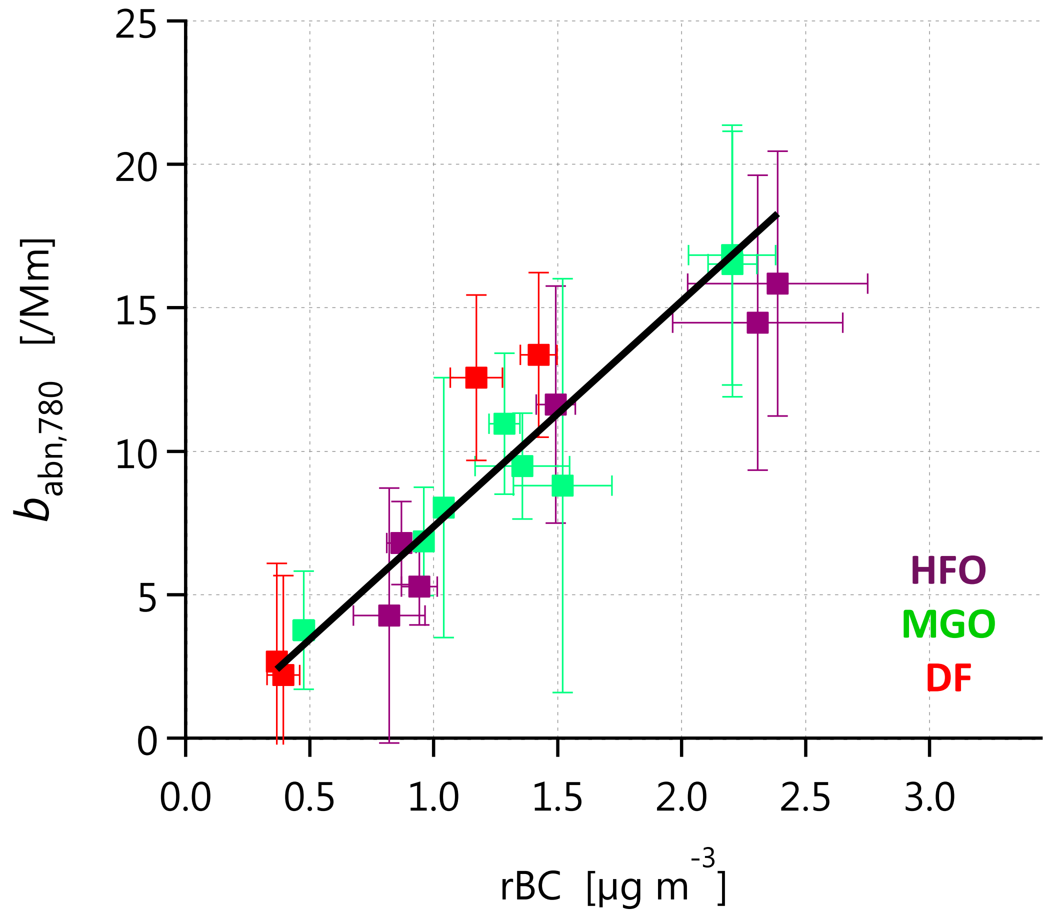


2/3) Optical properties

BC and organic ("brown carbon") absorption

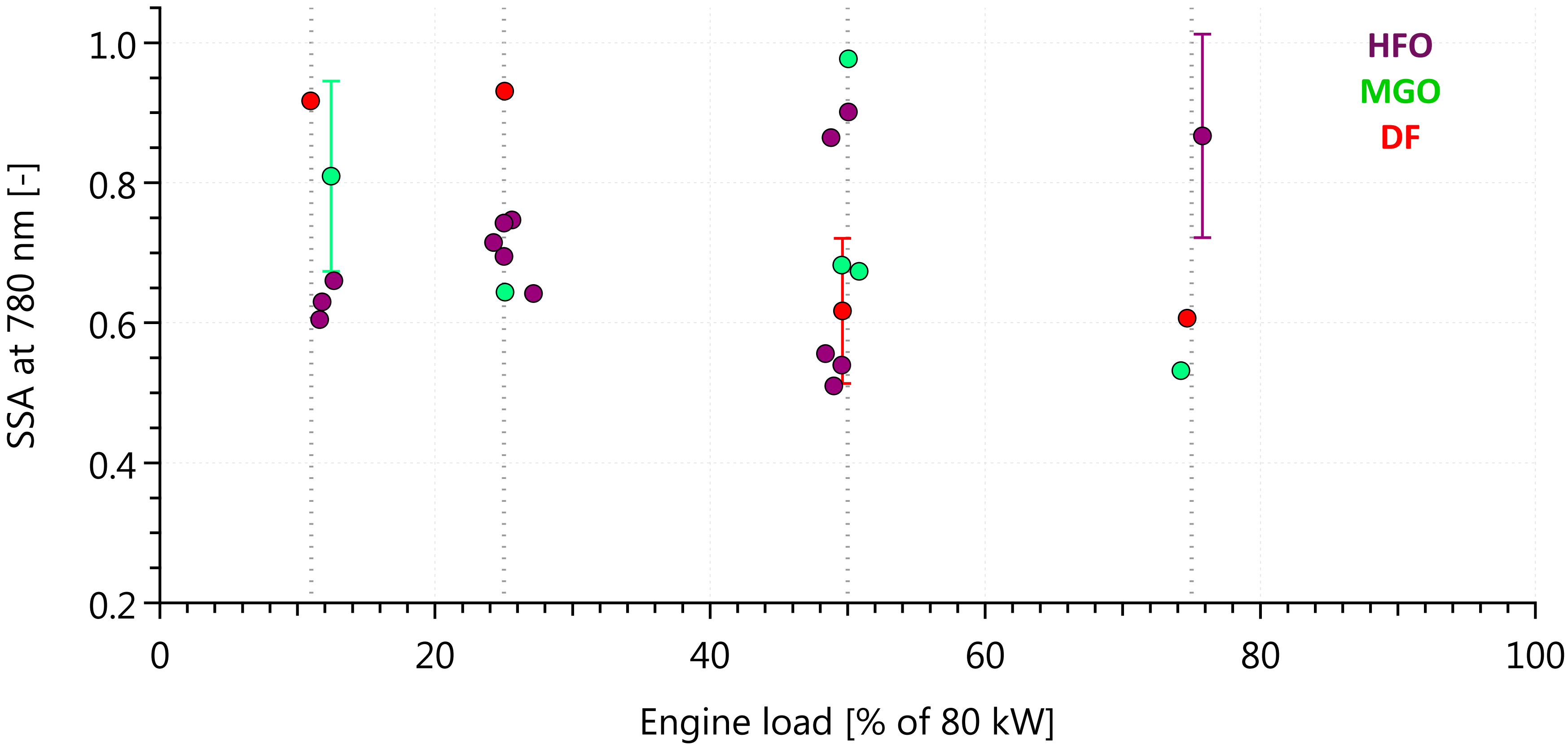
BC mass absorption cross-section: similar for all fuels

- Similar for 3 fuels
- In-situ $MAC_{780} = 7.9\ m^2/g$
- consistent[1] with literature, considering reference value[1] of 5.29 m^2/g, and mixing enhancement[2] ("lens effect") of 1.49x



[1] Bond, Habib and Bergstrom (2006); [2] Mikhailov et al., 2006; Cappa et al., 2012

Single-Scattering Albedo no dependence on load



$$\mathrm{SSA} = \frac{b_{\mathrm{scattering}}}{b_{\mathrm{extinction}}}$$

- Measured in-situ by CAPS-PMssa
- Wide range of SSA ←→ wide range of BC%

Aethalometer (AE33) Evaluation

- Aethalometer absorption estimation:

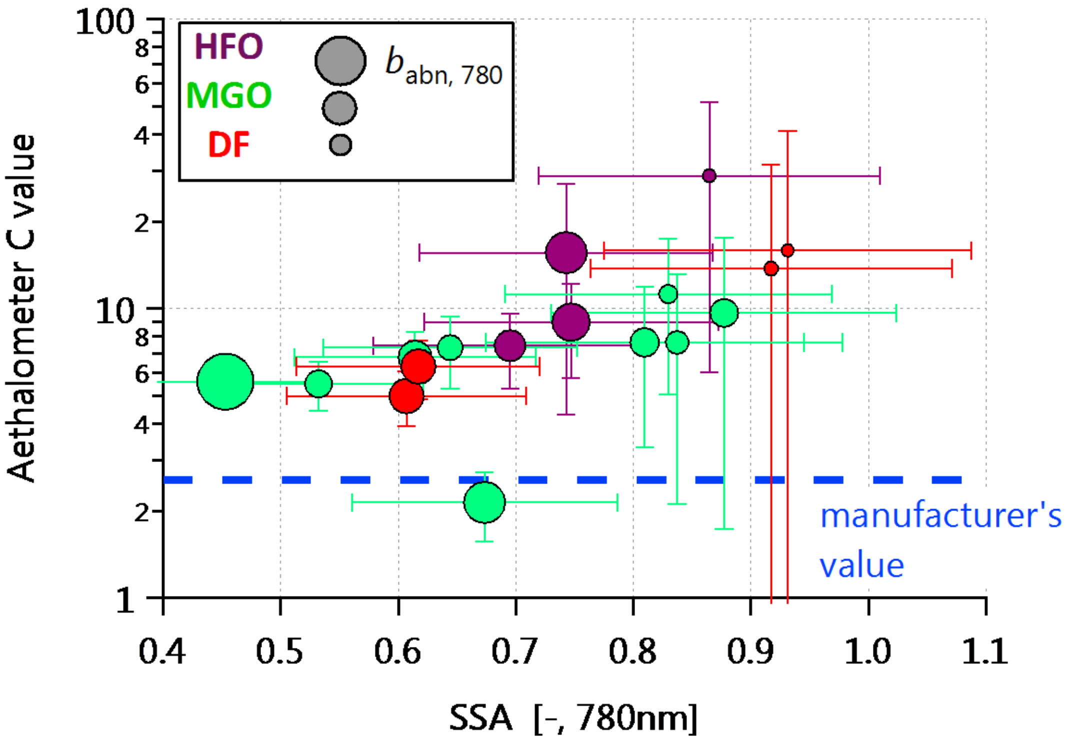
$$b_{\mathrm{abn,AE}} = \frac{b_{\mathrm{ATN,corr}}}{C}$$

- "C": empirical, f(aerosol type)

$C_{\mathrm{default}} = 2.57$ *[ref 3]*

$1.6 < C_{\mathrm{atmos}} < 4.0$ *[ref 1,2]*

- With default treatment, <u>aethalometer would overestimate BC by a factor of 2.3—6 !</u>



[1] Collaud Coen et al., 2015
[2] Müller et al., ACTRIS report, 2015
[3] Calculated with correct MAC (Bond, AST 2006), not "apparent" MAC of 1.57 (Drinovec et al. AMT 2015).

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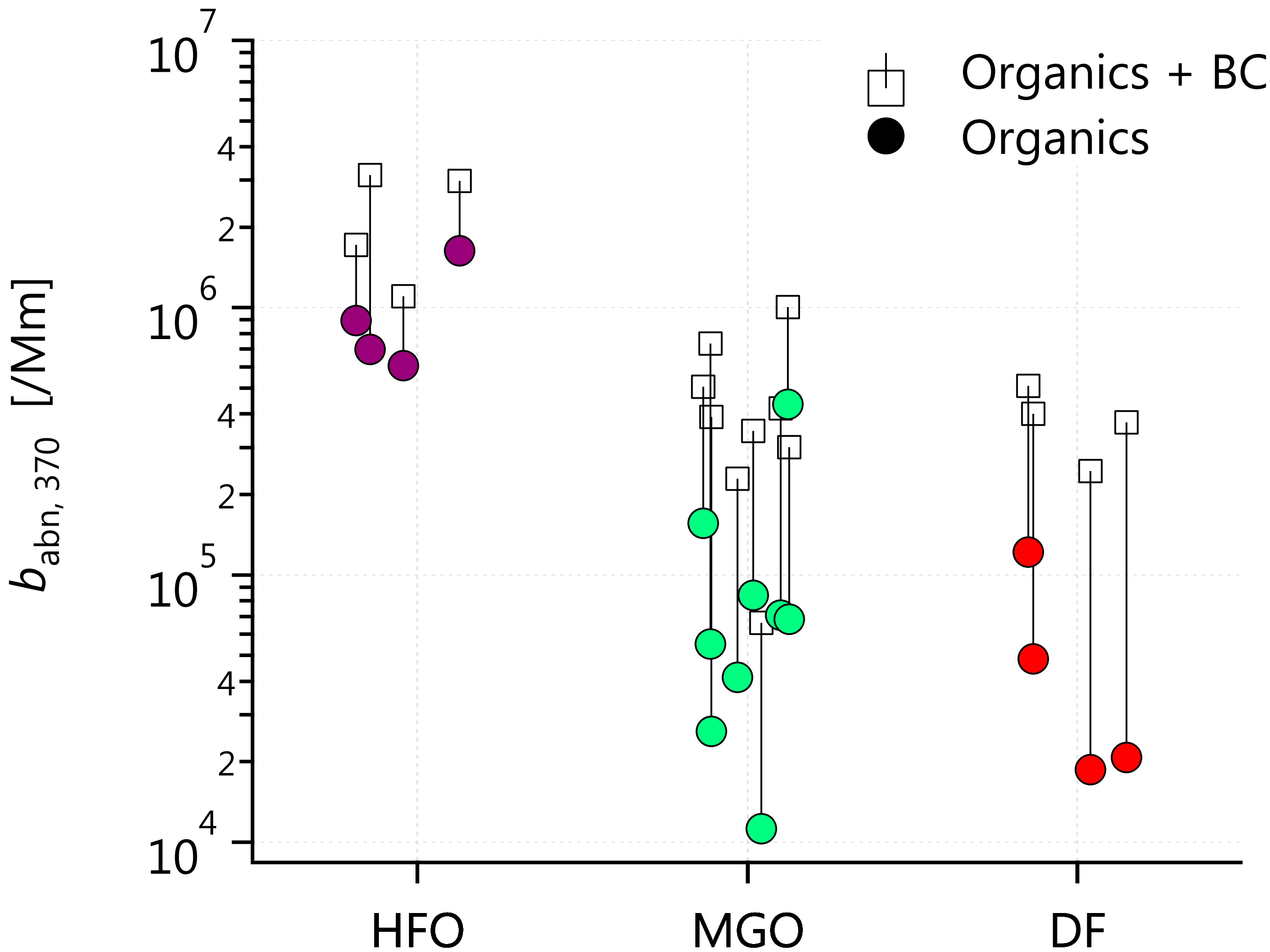
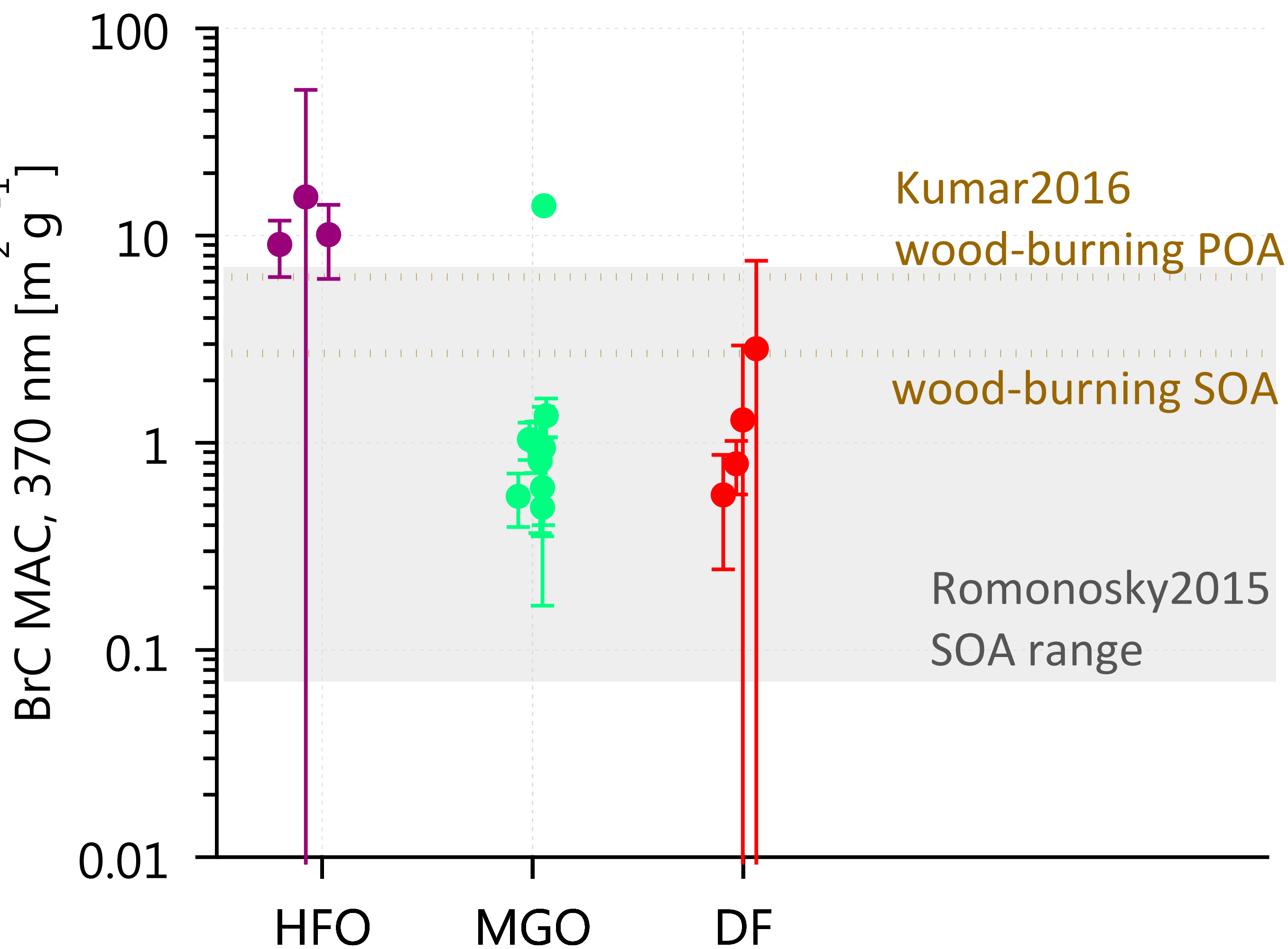
Brown carbon absorption dominates HFO total at 370



- Wavelength dependence from aethalometer; absorption from CAPS PMssa

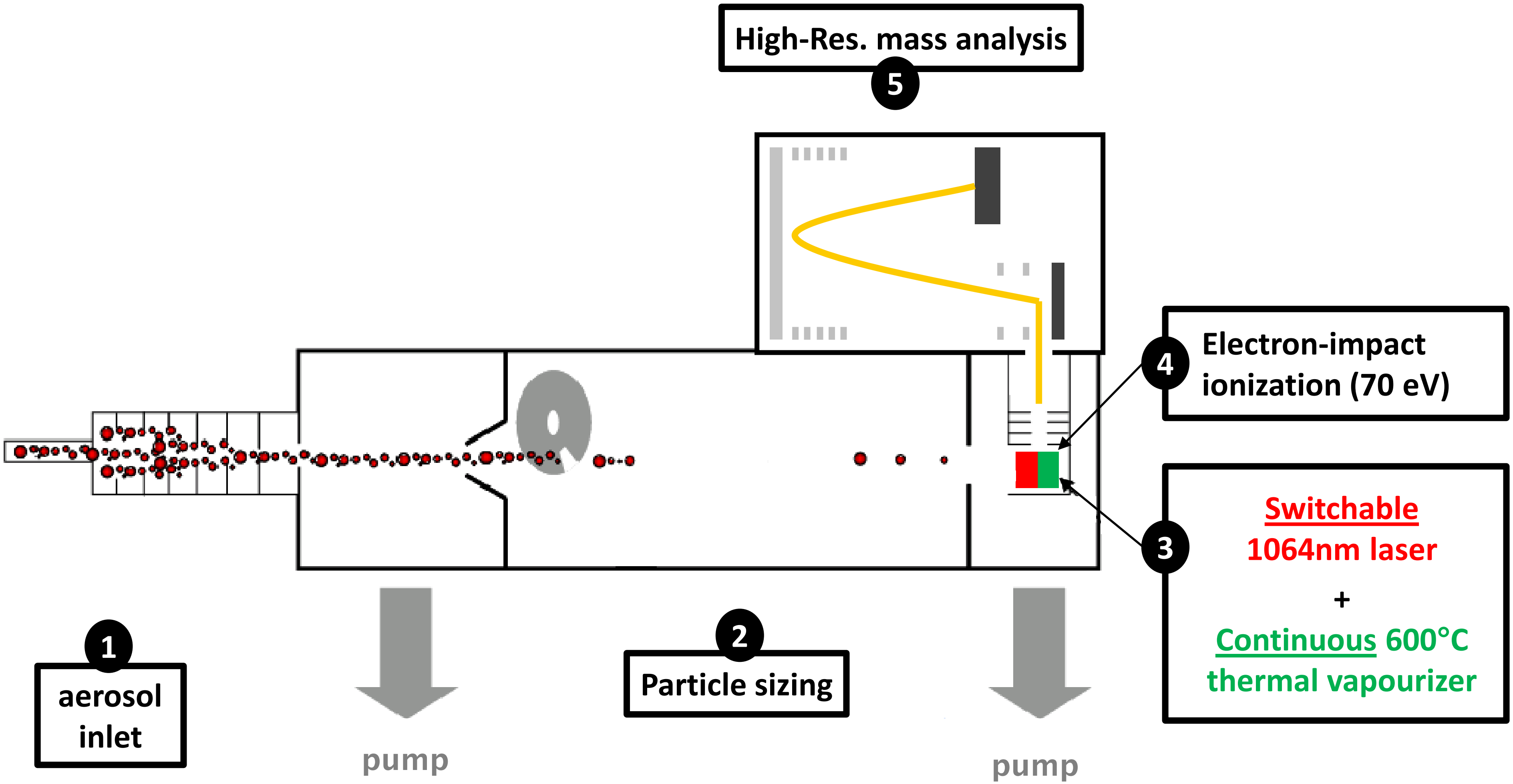
Brown carbon MAC very high for HFO only



- MAC = Mass Absorption Cross-section

3/3) Heavy metals

Soot-Particle Aerosol Mass Spectrometer: SP-AMS



Onasch et al. AS&T 2012

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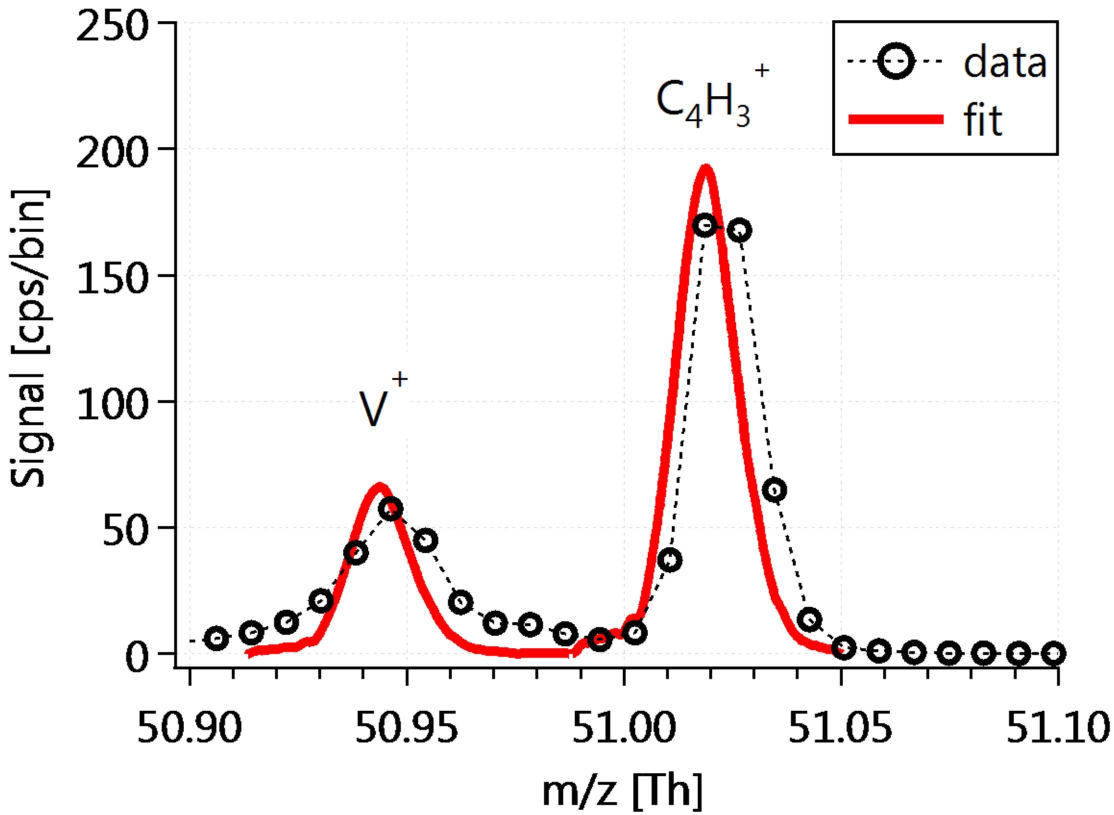
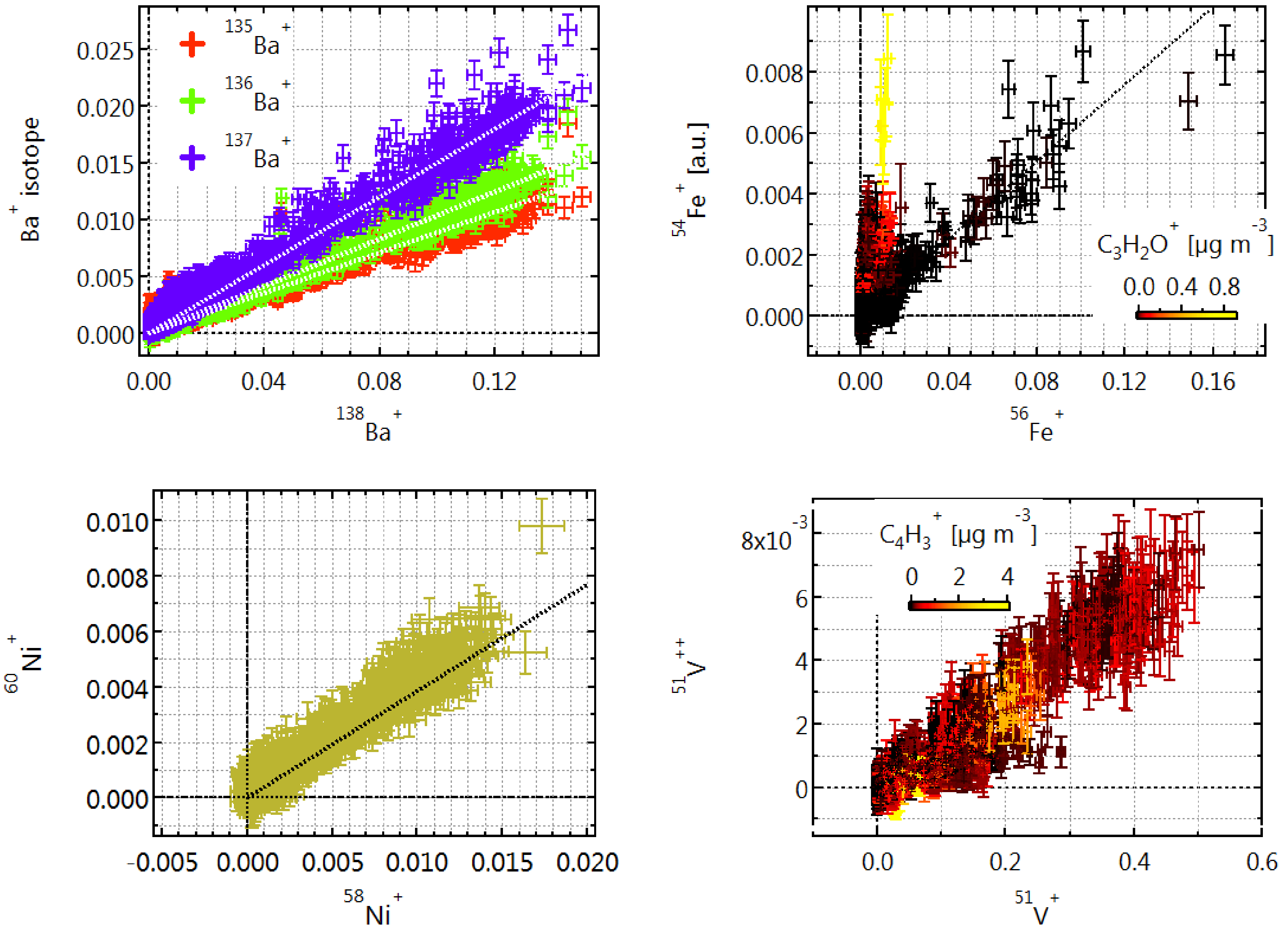
Vanadium-ion signals



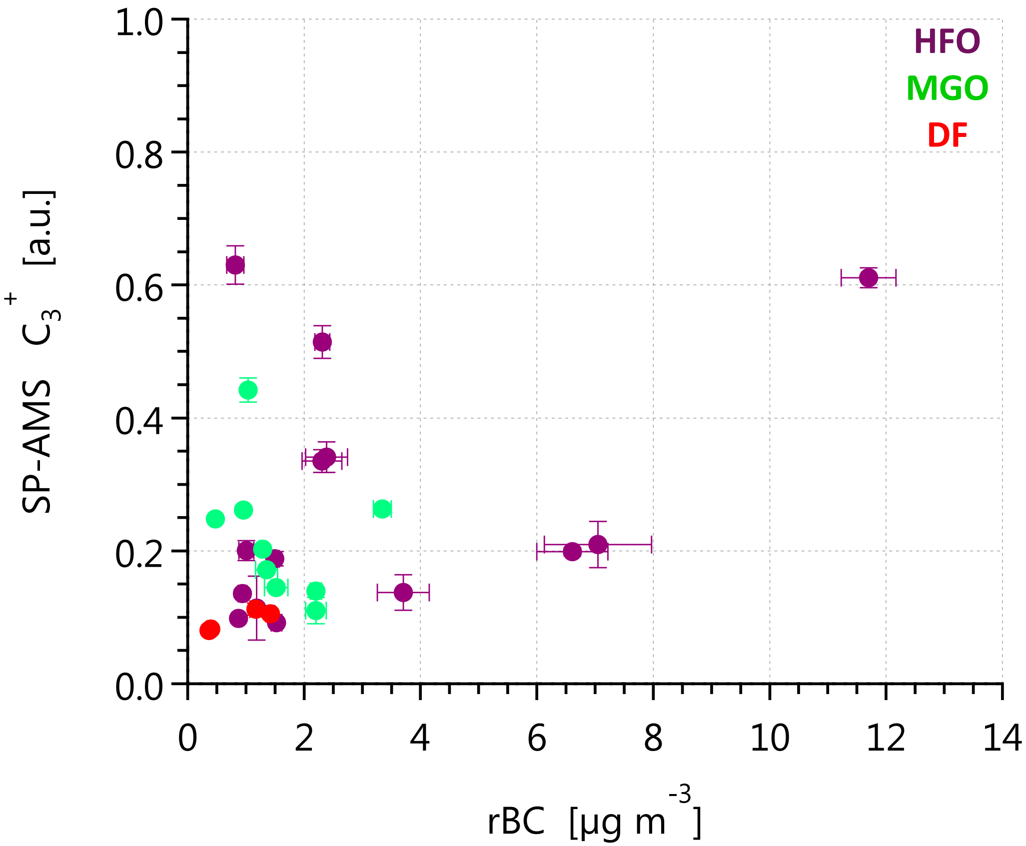
Validation of SP-AMS metal ions



Dashed lines: expected slopes (IUPAC, 2003)

Failed validation of SP-AMS BC concentrations

- Very poor correlation with rBC
- Size range measured by SP-AMS is significantly narrower than rBC size
  - Particles too small to be focused into BC laser
- BC quantification by SP-AMS needs reference

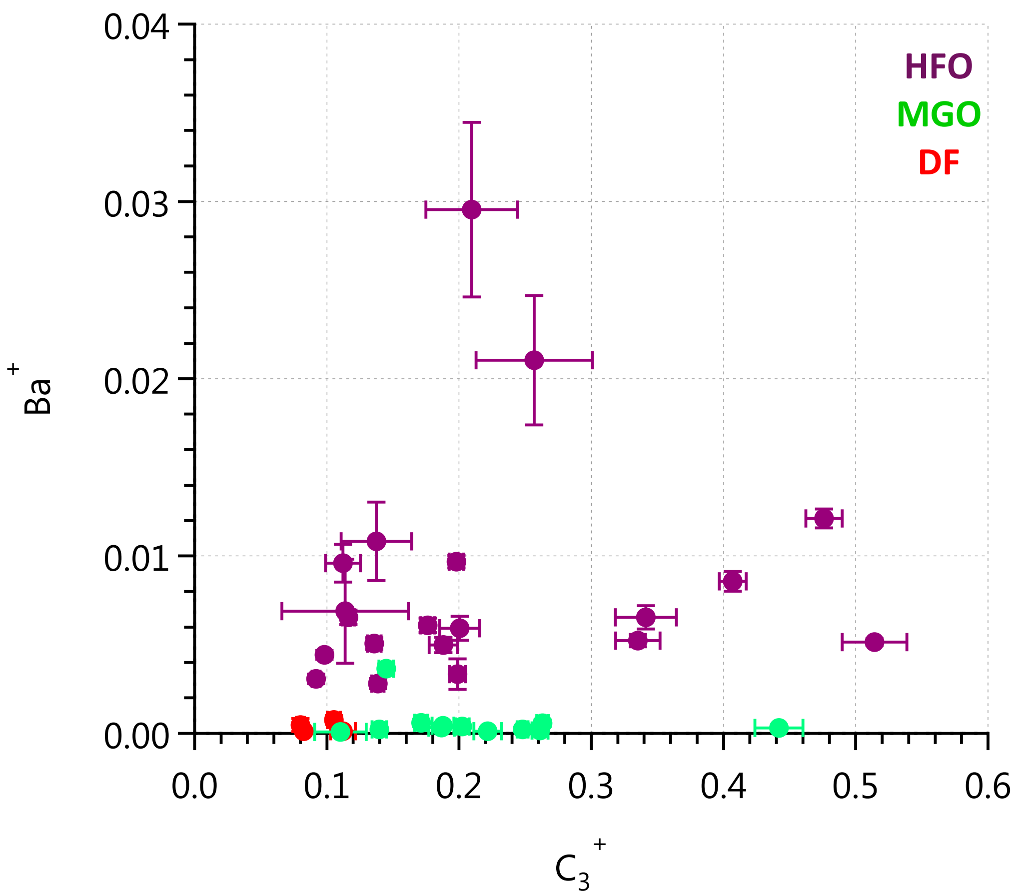


Corbin [2014]

SP-AMS metal vs rBC signals: no correlation

- Both pure metal[1] and rBC particles vaporized in SP-AMS
  - Metal oxides/salts should vaporize via conduction if on rBC

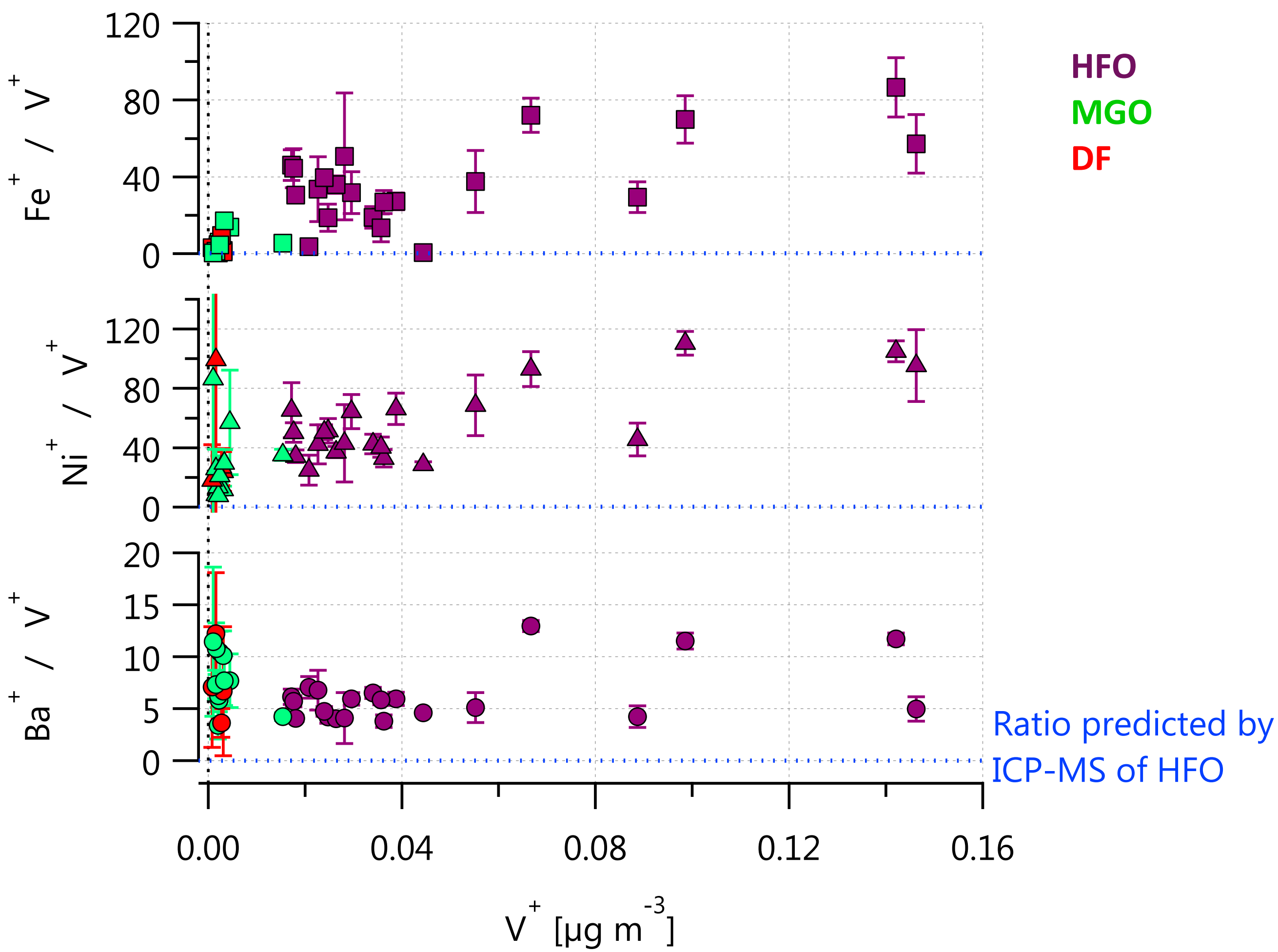
- No clear relationship
  - Implies externally-mixed ash, in contrast with previous studies[2]



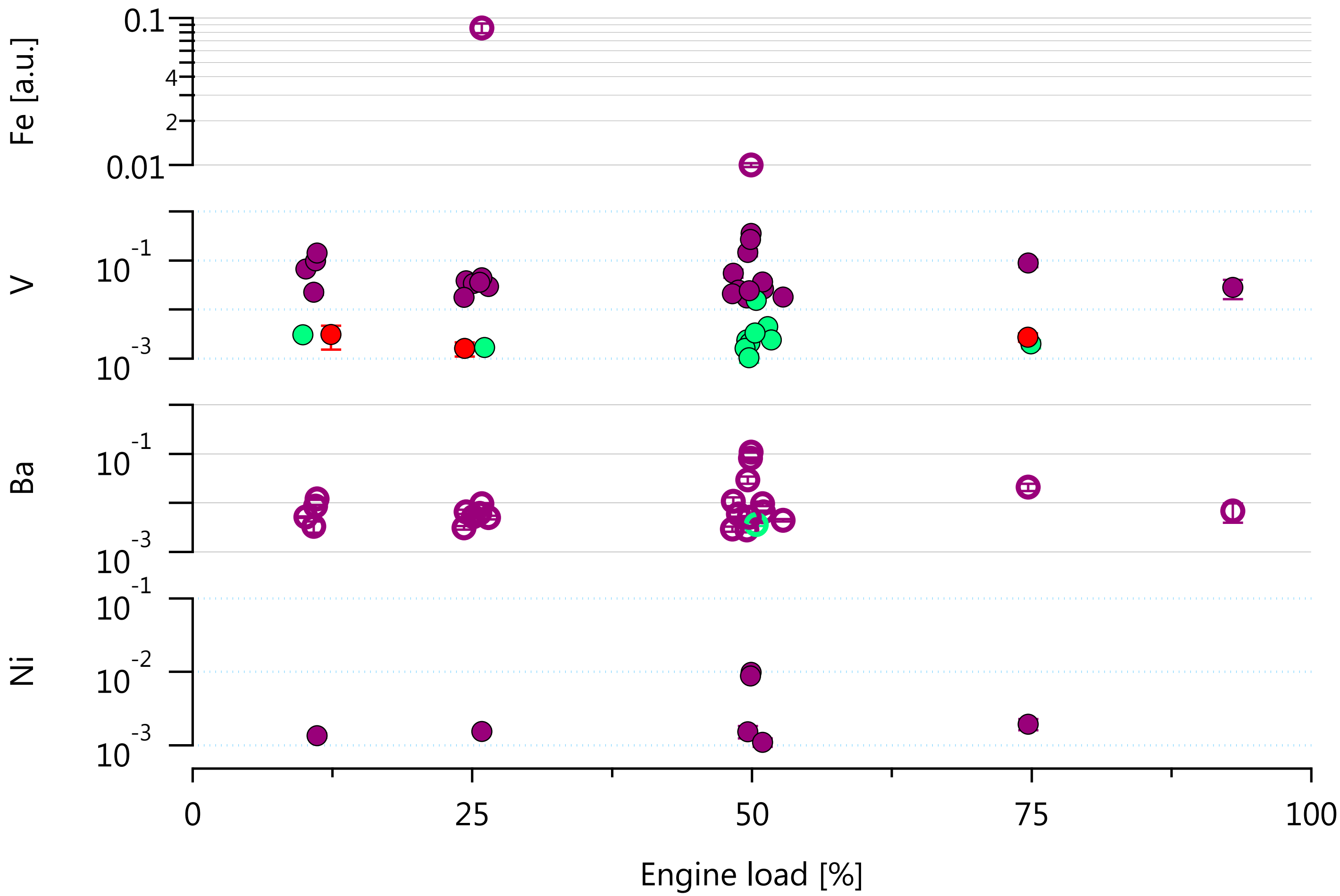
[1] Nilsson, 2015 [2] Carbone et al., 2015

Constant ratio of different metals for HFO

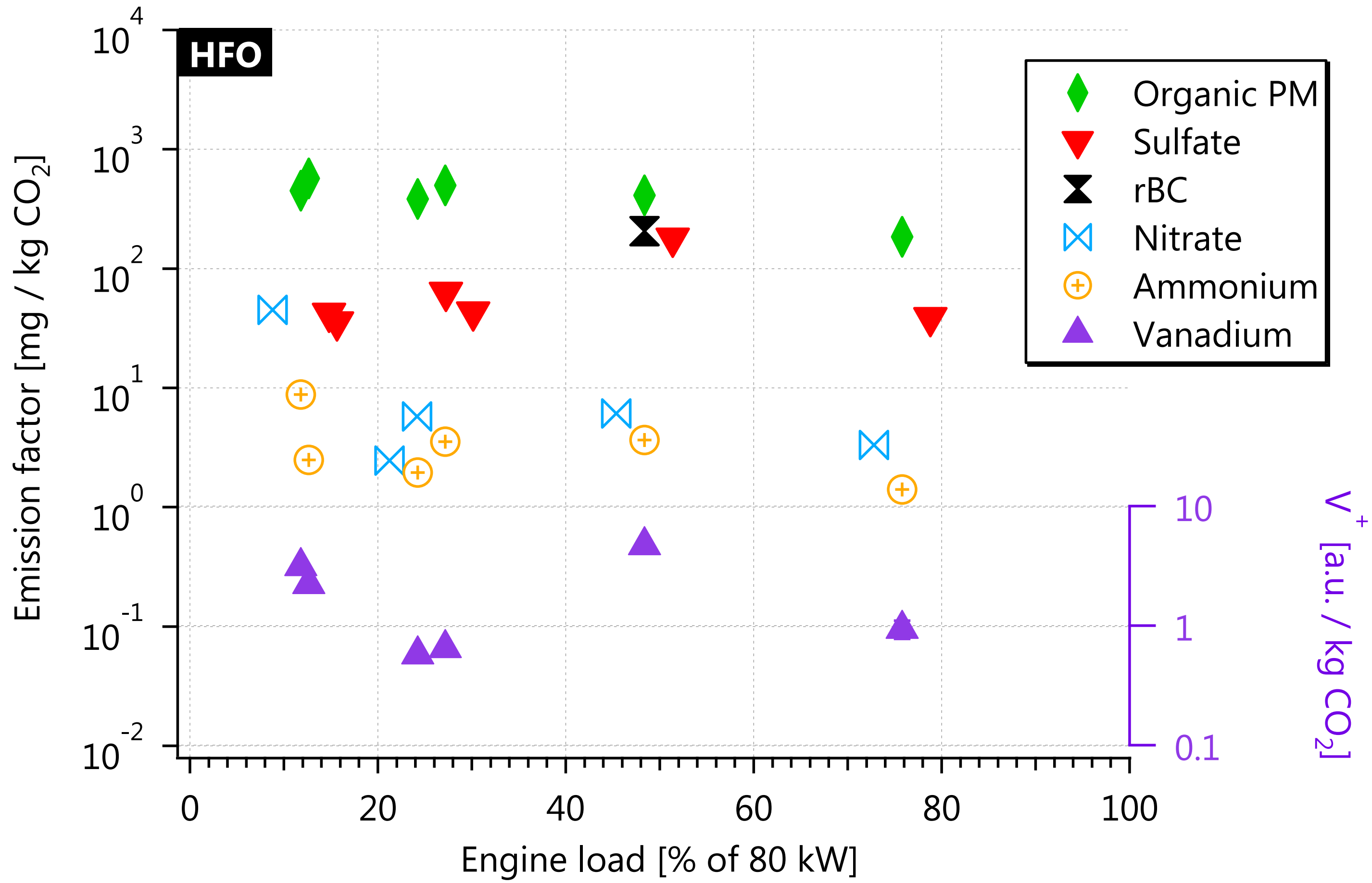
- M/V⁺ ratios inconsistent with ICP-MS of fuel
  - Either not measurable ($M_xZ_y^+$) or different sensitivity
  - Planned direct comparison



Metal-ion signals do not change with engine load

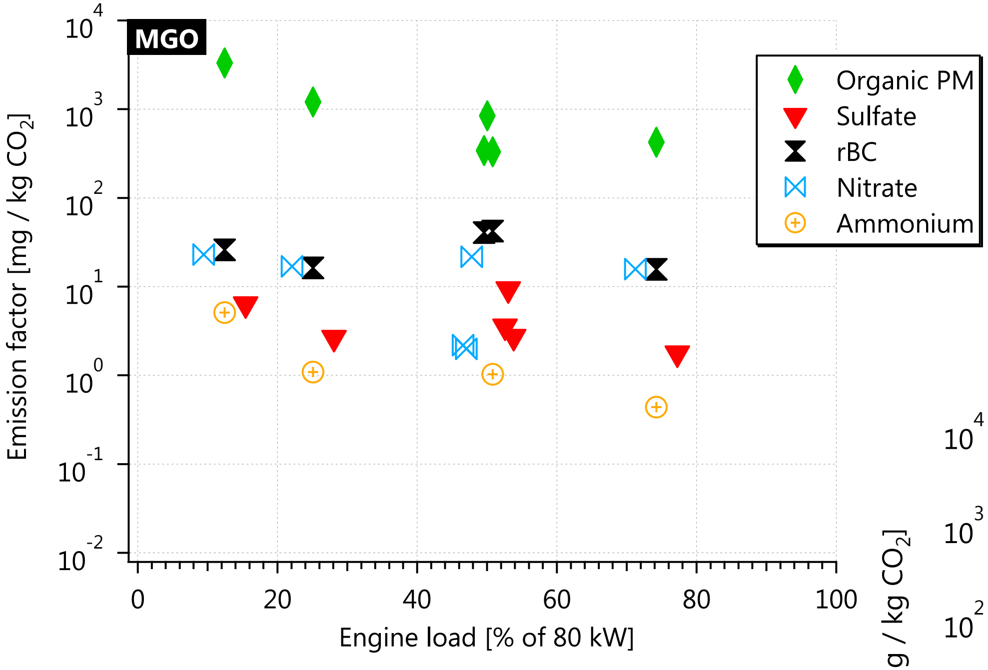


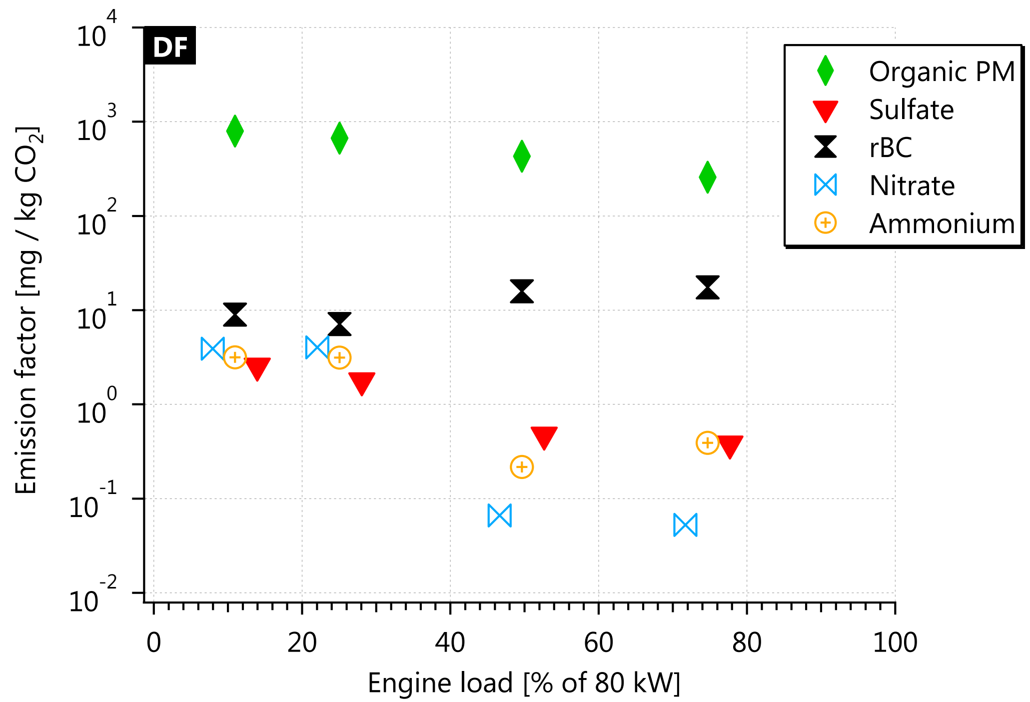
HF O emission factors approx. constant with load



- ➢ Organics, sulfate, BC, heavy metals

MGO and DF emission factors





- Main component organics

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Conclusions

- BC
  - particles from HFO *much larger than* other sources
  - absorption from all fuels *similar to* other sources, MAC_{780} = 7.9 m^2/g

- Organic absorption (370 nm)
  - HFO absorption very high, 10 m^2/g
  - MGO and DF typical, 1 m^2/g

- Heavy metals (V, Ni, Ba, Fe) from SP-AMS
  - Not internally-mixed with rBC
  - Not a function of load%

Implications

- Mass absorption cross-sections of BC and BrC ➔ radiative modelling
  - Brown carbon of HFO must be modelled

- Ratio of SP-AMS heavy metals (V, Ni, Ba, Fe) to co-pollutants insensitive to engine load
  - Allows V/Ni etc to identify ship pM in mixed atmospheric aerosols
  - Will be compared to ICP-MS of filter samples

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Thanks

Marco Zanatta[1] (SP2)

Amewu A. Mensah[2] (SP-AMS)

Simone Pieber[1] (experiment)

Gert Jakobi[3] (aethalometer)

Jürgen Orasche[3] (filters), J. G. Slowik[1], N. K. Kumar[1], I. El Haddad[1], F. Klein[1],

Benjamin Stengel (engine), R. Zimmermann[3], A. S. H. Prévôt[1], U. Baltensperger[1],

Martin Gysel[1] (group leader)

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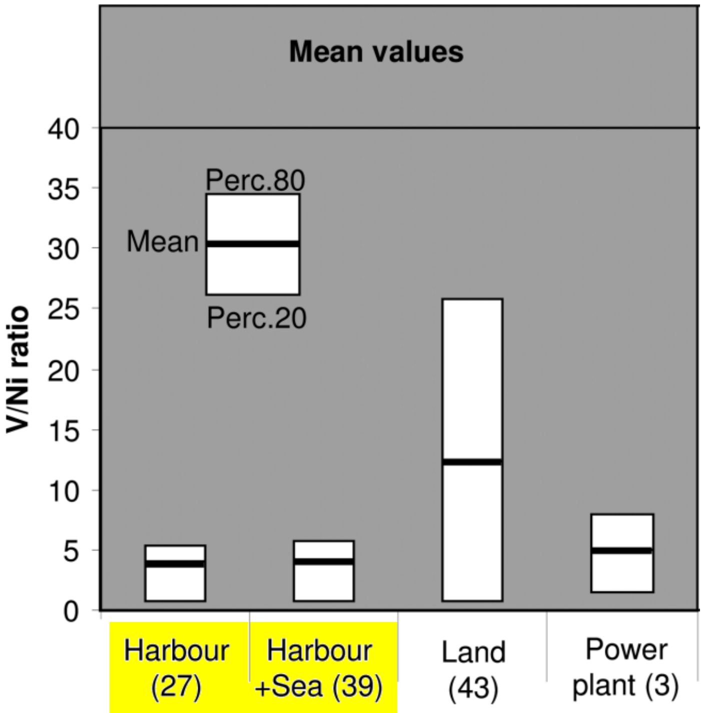
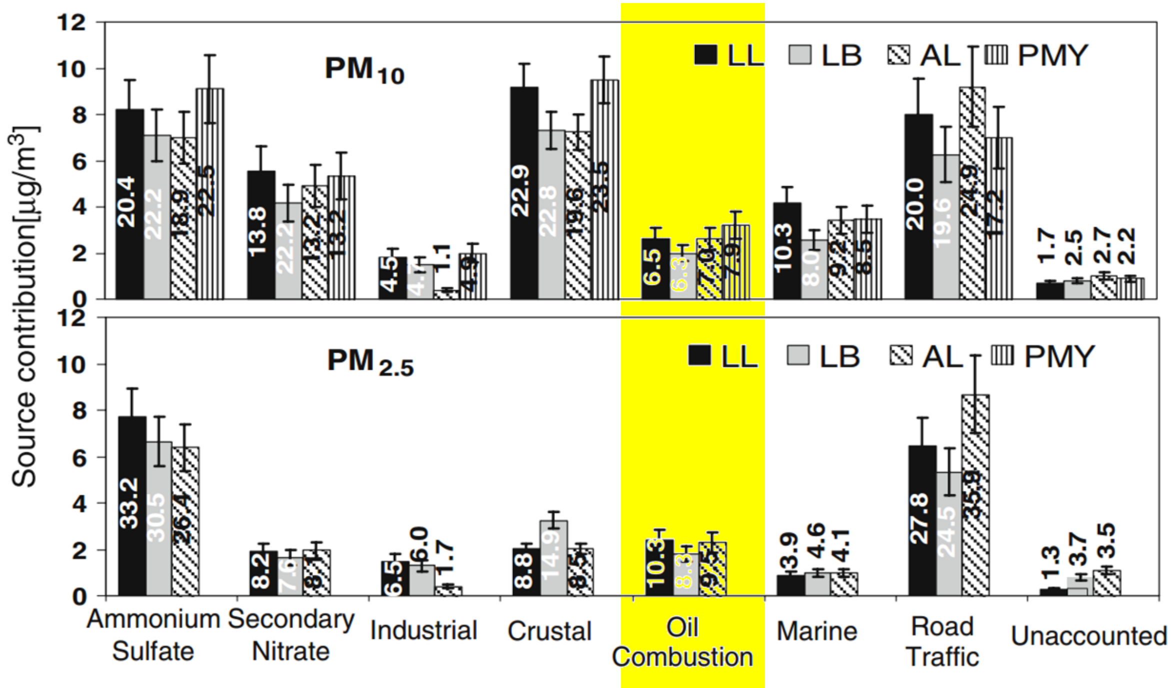
Identifying atmospheric ship PM

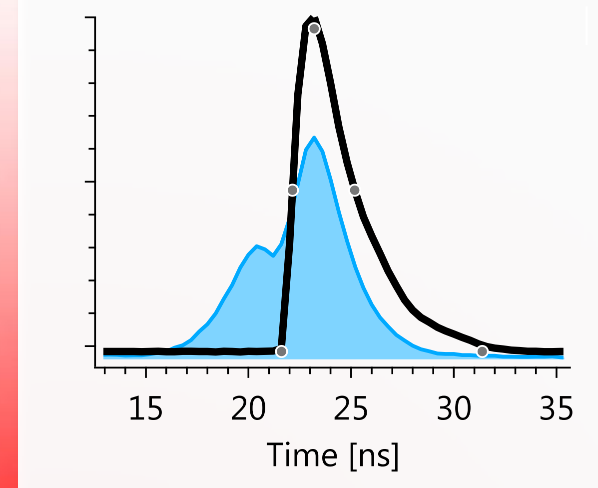




- HFO PM identified by V/Ni
- Co-pollutants by statistical analysis ("PMF")

[1] Pandolfi et al., Environ Sci Pollut Res 2011

SP2 principle of operation



4000 K

4000 K

possibly coated rBC-containing particle

uncoated, incandescing rBC-p

evaporated particle

non-absorbing particle

Gaussian, 1064 nm, CW laser

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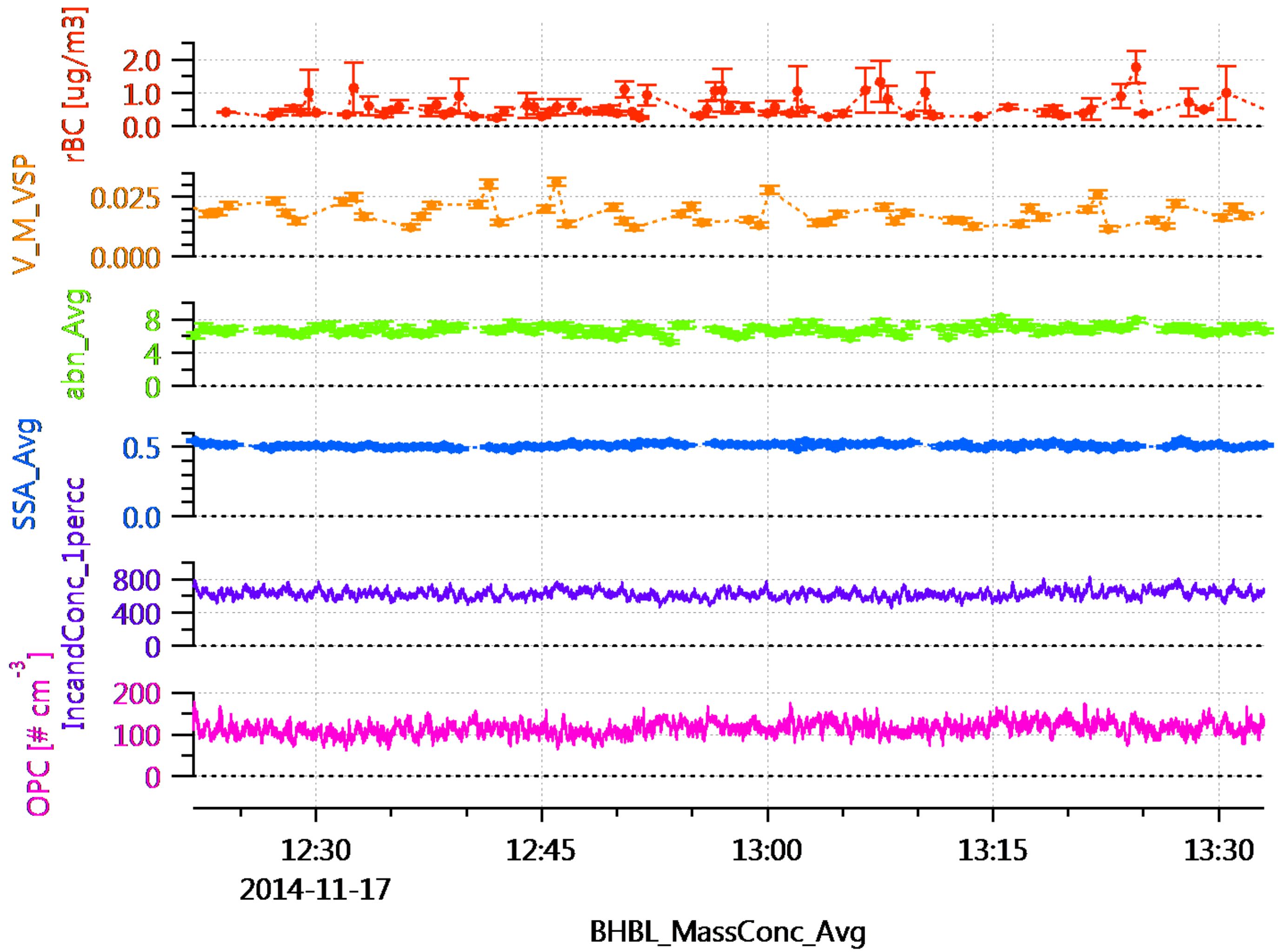
Fuel composition

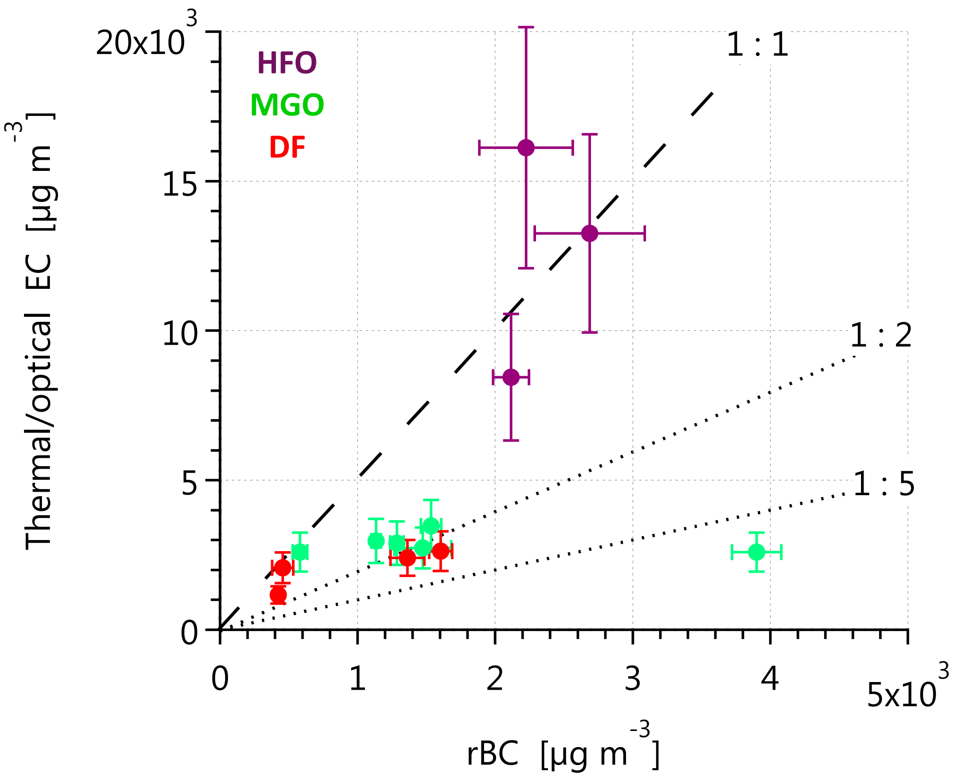
- MGO: diesel + sulfur
- HFO: crude-oil residue

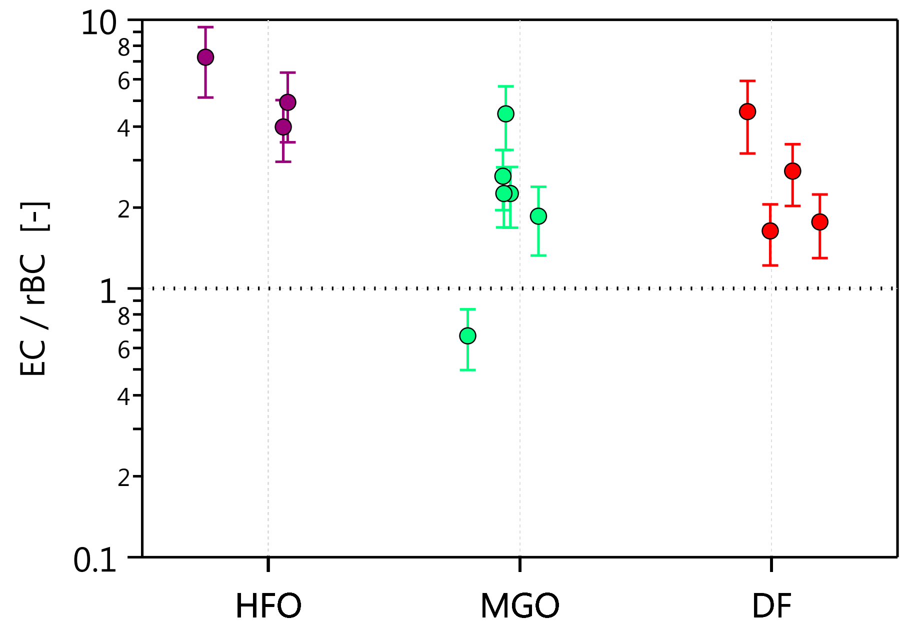
Parameter	Unit	HFO	DF	MGO
Density	kg/m3	989.5	833.8	833.9
Viscosity	mm2/s	341.9	2.68	2.83
Heating value	kJ/kg	39871	42708	42675
C	%	85.91	85.3	85.12
H	%	11.23	13.91	13.89
O	%	0.56	<0.01	<0.01
S	ppm	23306	7	783
V	ppm	138	<0.1	<0.1
Ni	ppm	31.3	<0.1	<0.1
Na	ppm	29.2	<0.1	<0.1
Ca	ppm	24.8	<0.1	0.1
Fe	ppm	14.3	<0.1	<0.1
Si	ppm	2.6	<0.1	<0.1
Al	ppm	1.6	<0.1	<0.1
Zn	ppm	1.4	<0.1	<0.1
P	ppm	1.3	<0.1	<0.1
Cr	ppm	1	<0.1	<0.1
K	ppm	0.7	<0.1	<0.1
Ba	ppm	0.6	<0.1	<0.1
Mo	ppm	0.5	<0.1	<0.1
Ash	%	0.03	<0.01	<0.01

Detailed time series



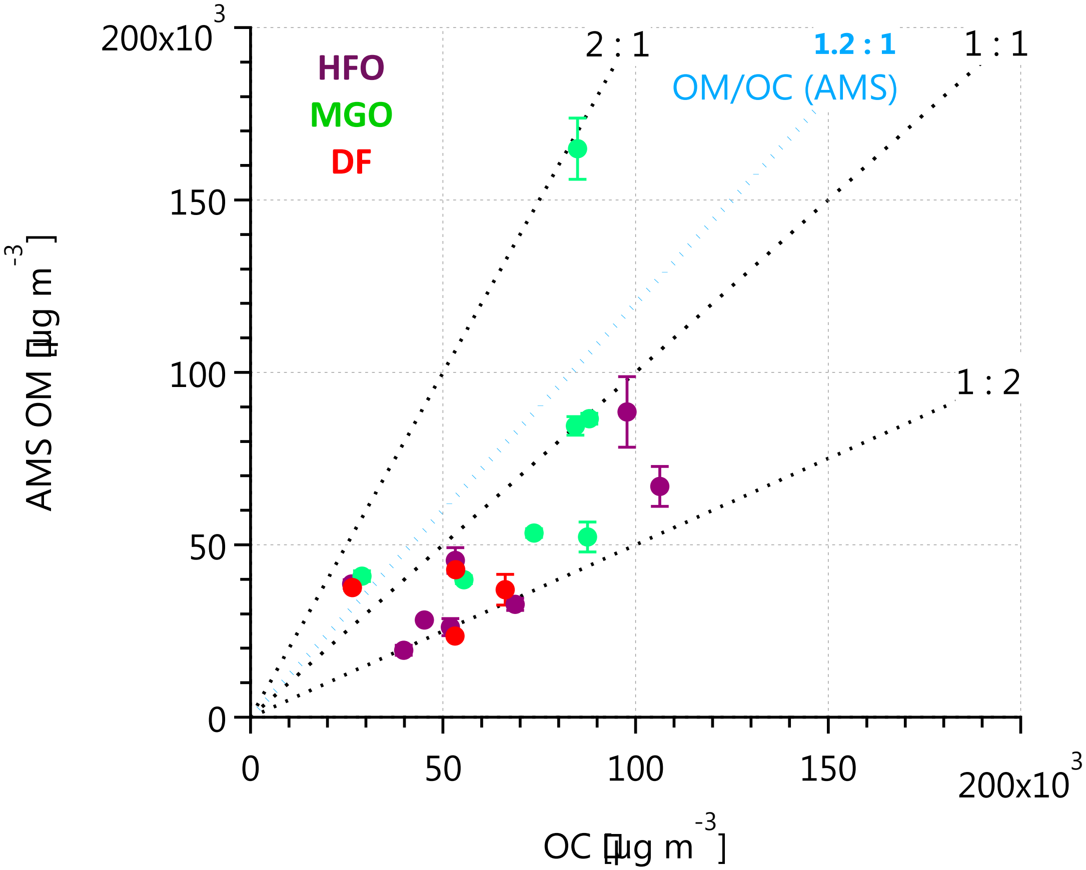
"Elemental carbon" vs. "refractory BC"





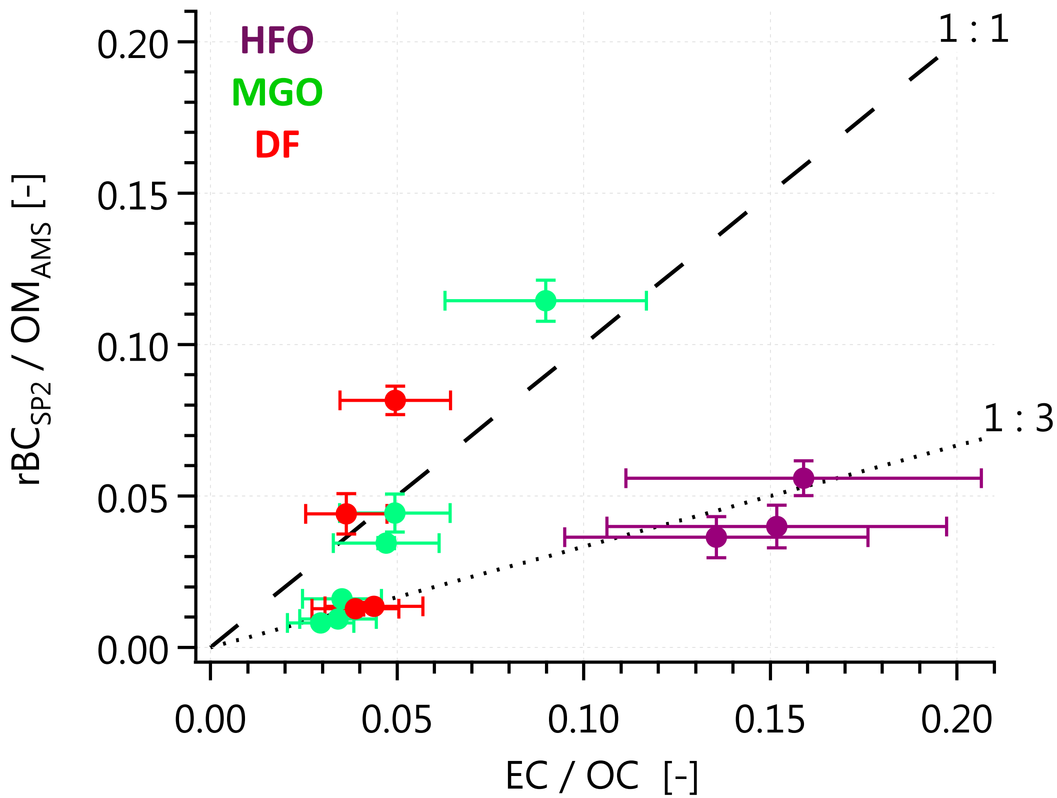
- ➢ "EC" by IMPROVE-A protocol
- ➢ EC on a separate sampling line

“Organic carbon” vs. “AMS organic”



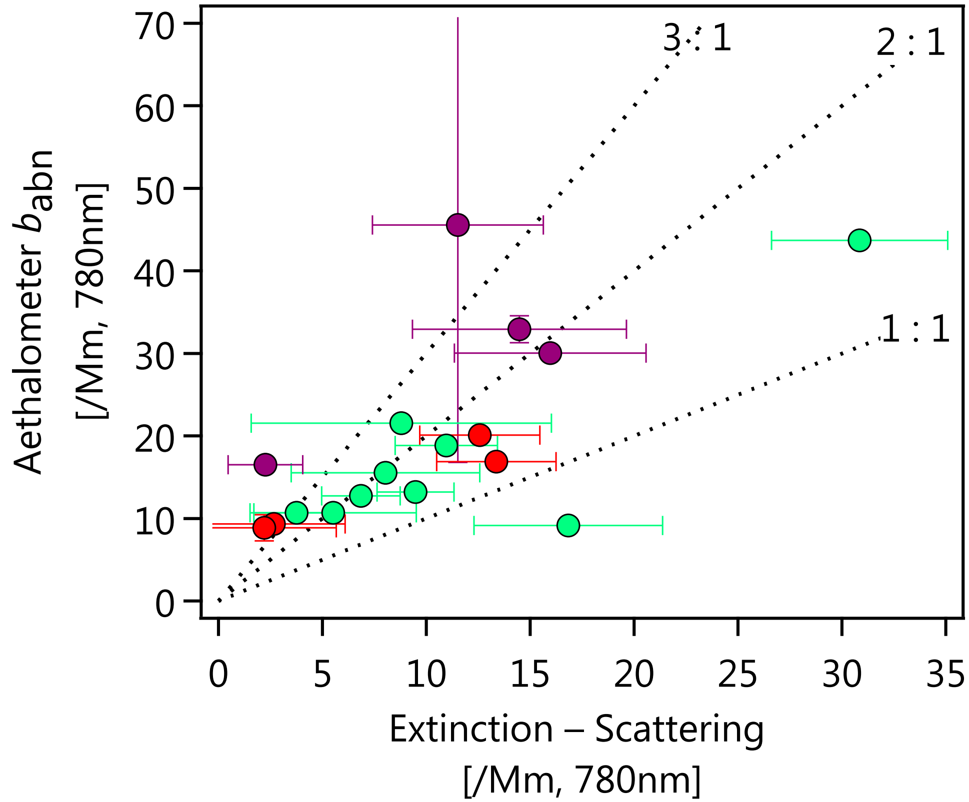
- “OC” by IMPROVE-A *(C evolved in He with pyrolysis correction)*
- “OM” by AMS (organic ions measured after evaporation at 600°C)
  - Some underestimation expected considering small nucleation mode (~100 nm $d_{\text{aero,vacuum}}$, lower D50 is ~80 nm $d_{\text{aero,vacuum}}$)

Thermal OC/EC vs. online OC/EC



- IMPROVE-A EC/OC > online EC/OC
  - Online EC by SP2 (rBC, by LII)
    plus AMS (organics volatile at 600 °C, by mass spec.)
- Possible positive bias of EC, due to pyrolysis
- Aethalometer performs much worse

Aethalometer (AE33) Evaluation

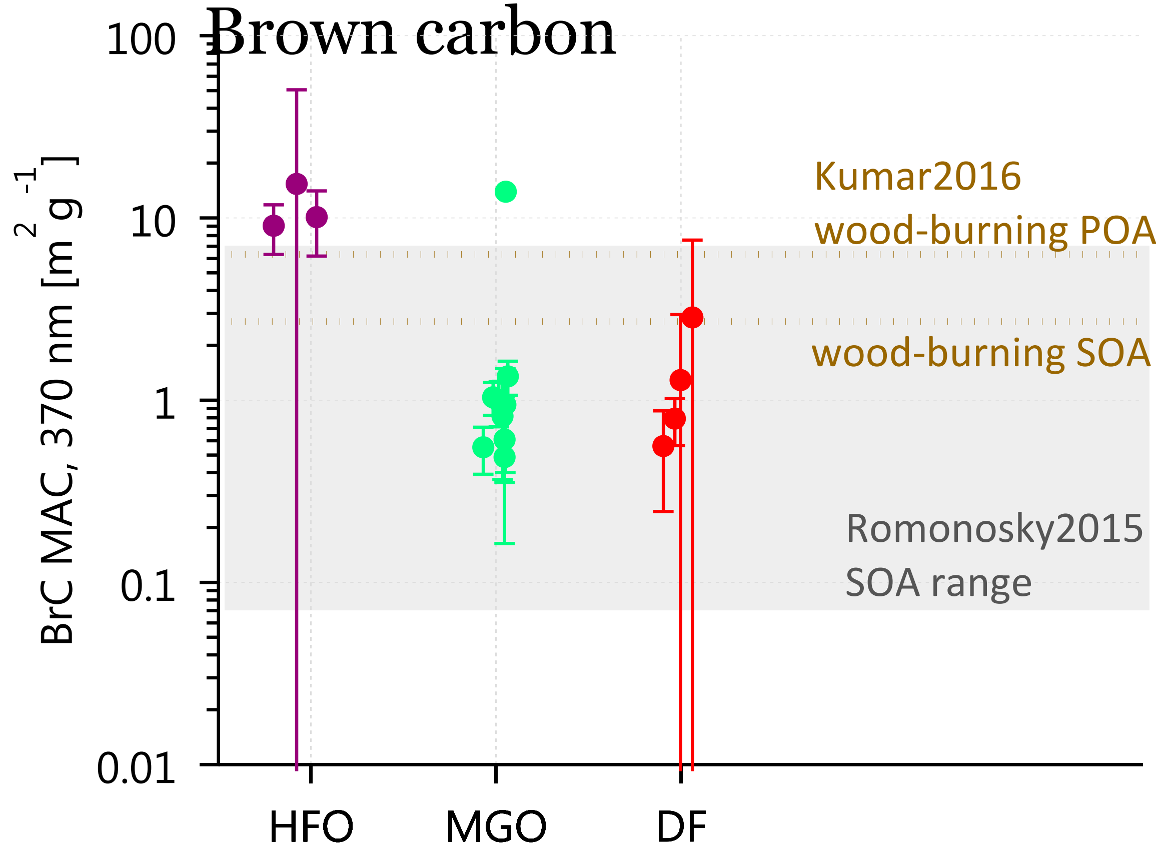


[1] Collaud Coen et al., 2015

[2] Müller et al., ACTRIS report, 2015

[3] Bond, Habib, and Bergstrom, AST 2006

Brown carbon



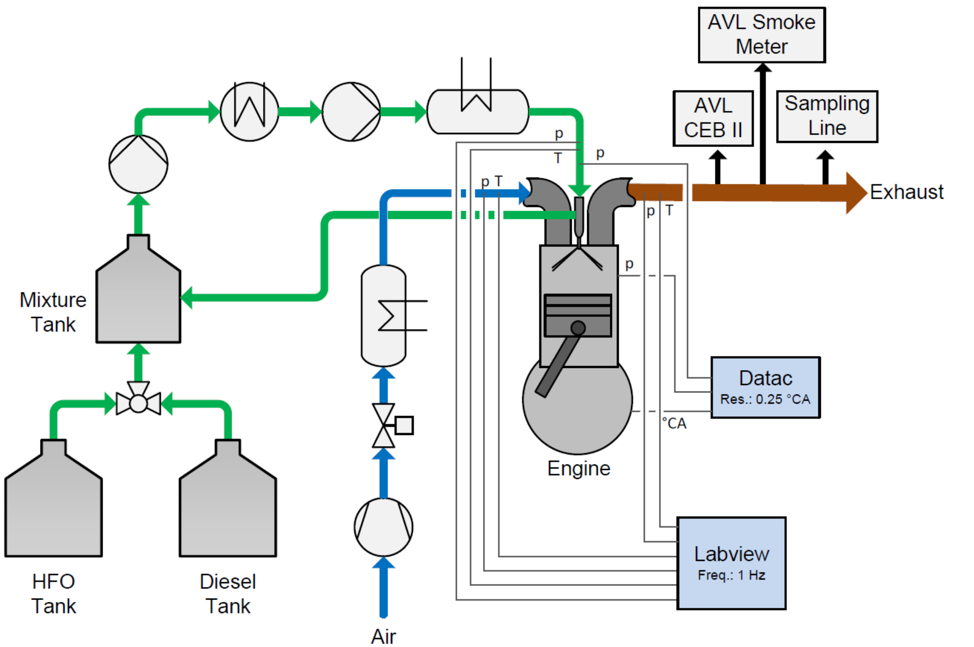
$$\boldsymbol{b}_{\mathbf{abn,BrC}} = \boldsymbol{b}_{\mathbf{abn,total}} - \boldsymbol{b}_{\mathbf{abn,BC}}$$

$$\boldsymbol{b}_{\mathbf{abn,BC,370}} = b_{\mathrm{abn,BC,880}} \left(\frac{370\ \mathrm{nm}}{880\ \mathrm{nm}}\right)^{-1}$$

$$MAC = \frac{\boldsymbol{b}_{\mathbf{abn,BrC}}}{M_{\mathrm{OM},AMS}}$$

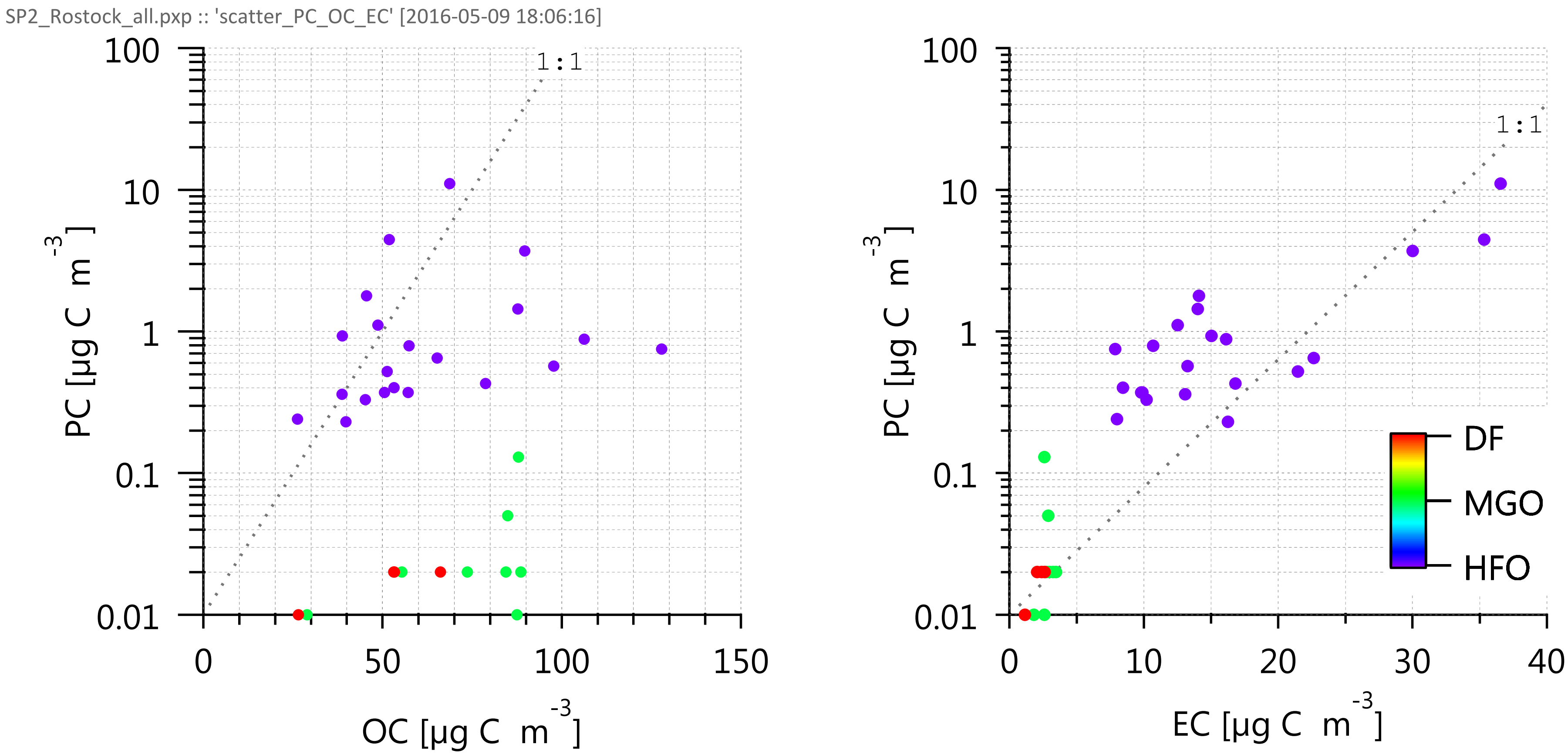
Engine details

Engine model	1 VDS 18/15
Method of operation	Four stroke diesel, direct injected, compressor charged
Amount of cylinders	1
Valves	4
Stroke	180 mm
Bore	150 mm
Length of connecting rod	332 mm
Nominal speed	1,500 min^{-1}
Compression ratio	13
Maximum power	80 kW
Nominal power	60 kW



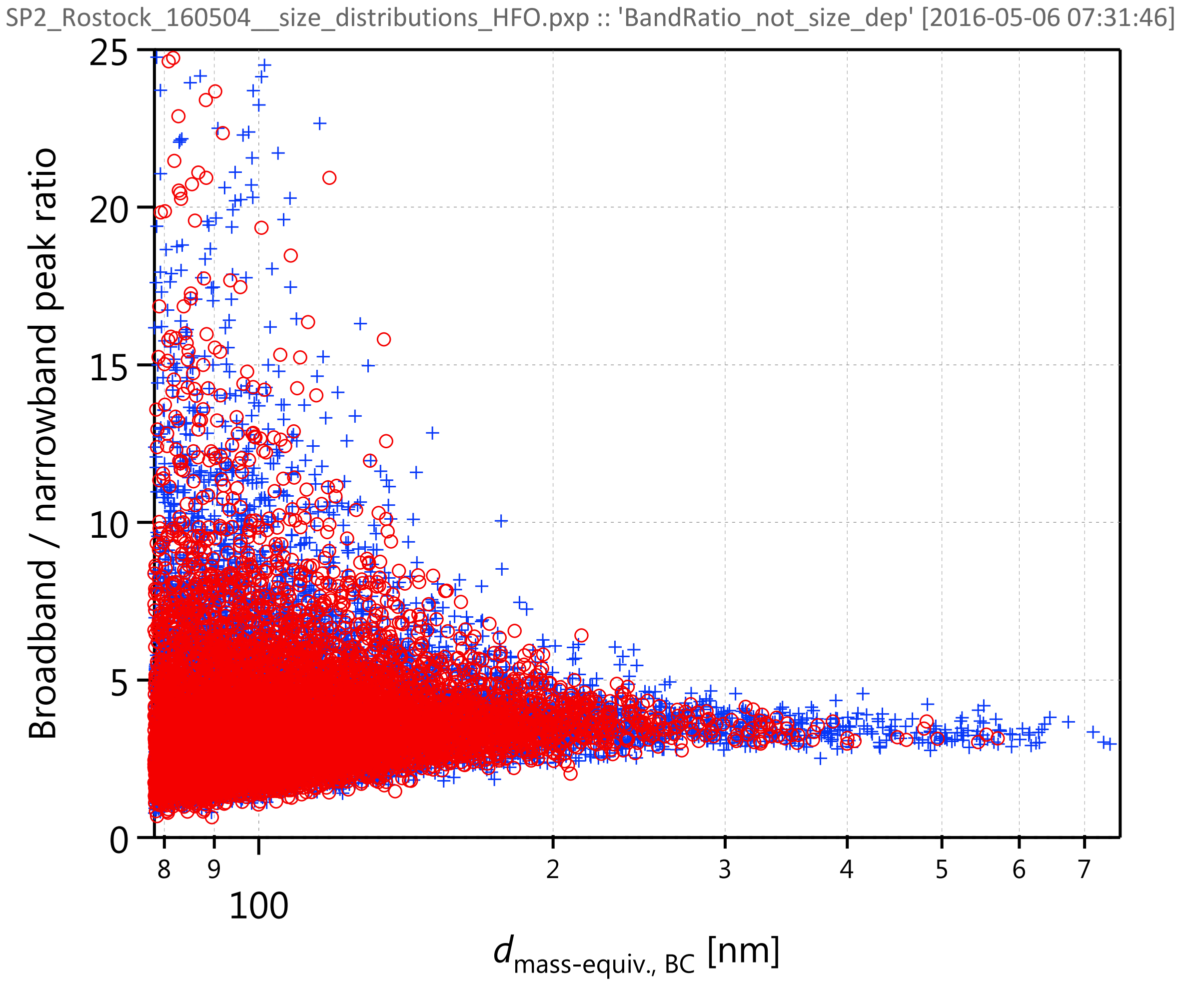
Oeder et al. (PloS One, 2015)

Thermal-optical carbon: HFO pyrolysis



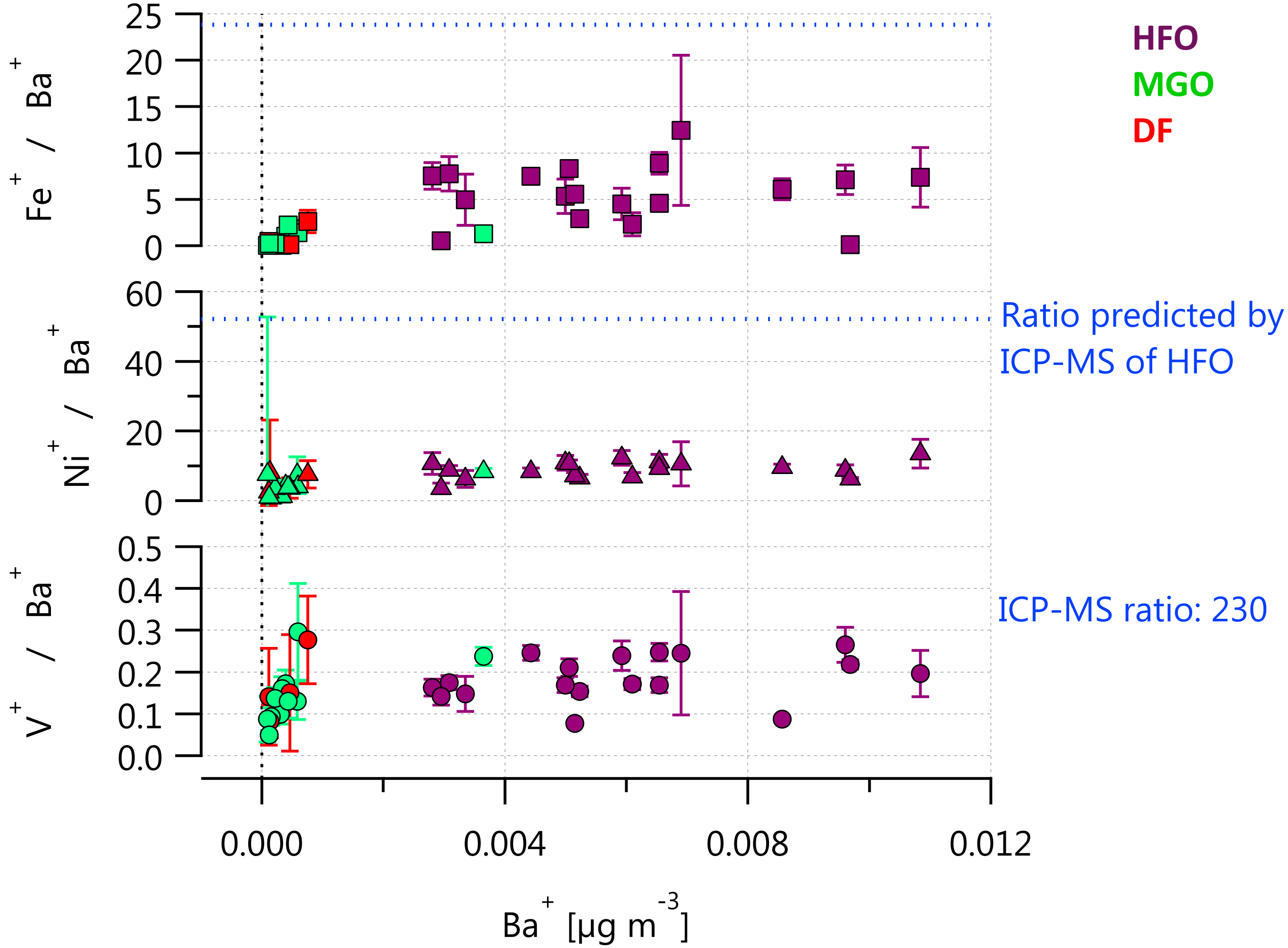
➢

SP2: No evidence of a second incandescent material → negligible pure-metal particles



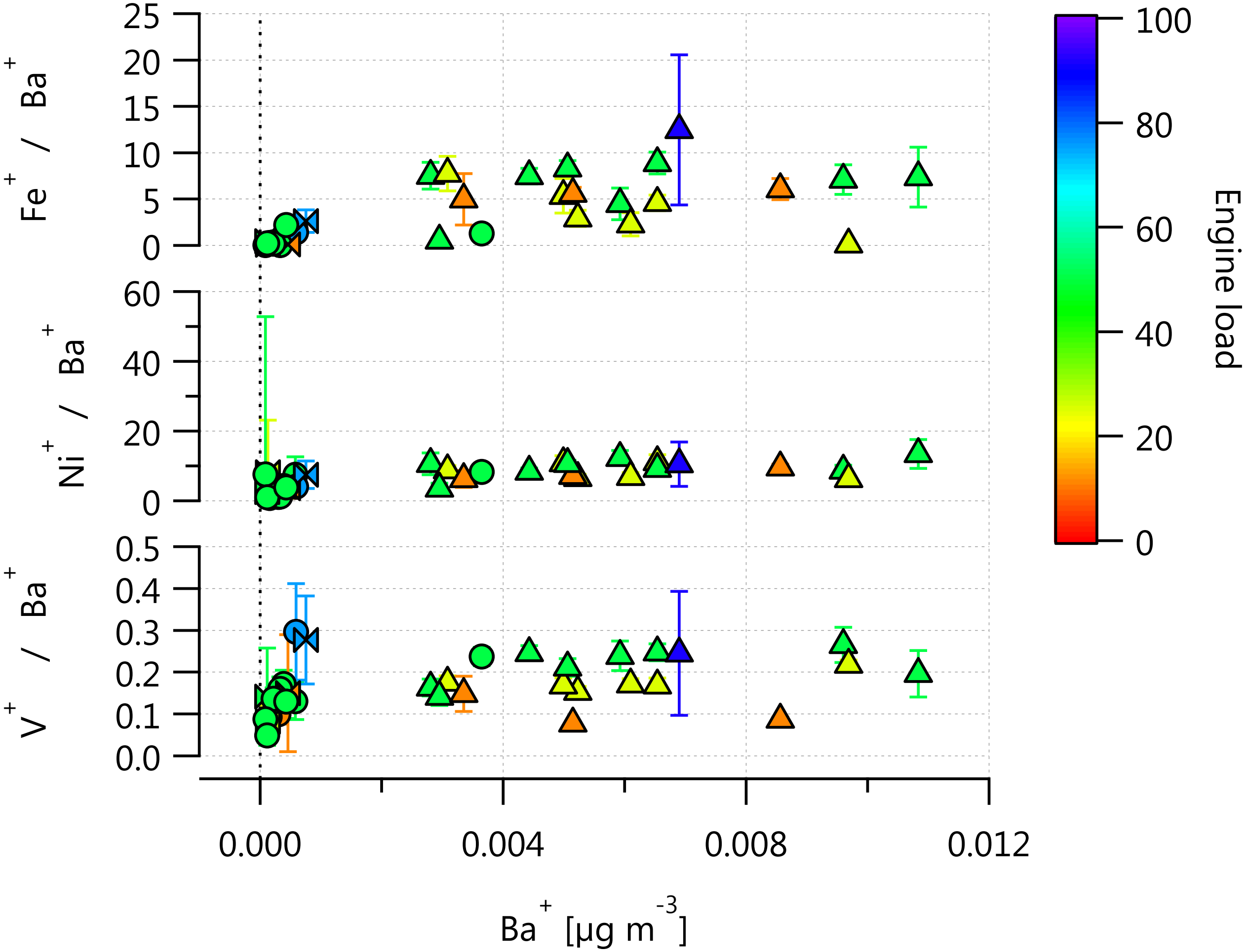
Metal-ion abundance in different fuel samples, vs Ba

- Relative to Barium

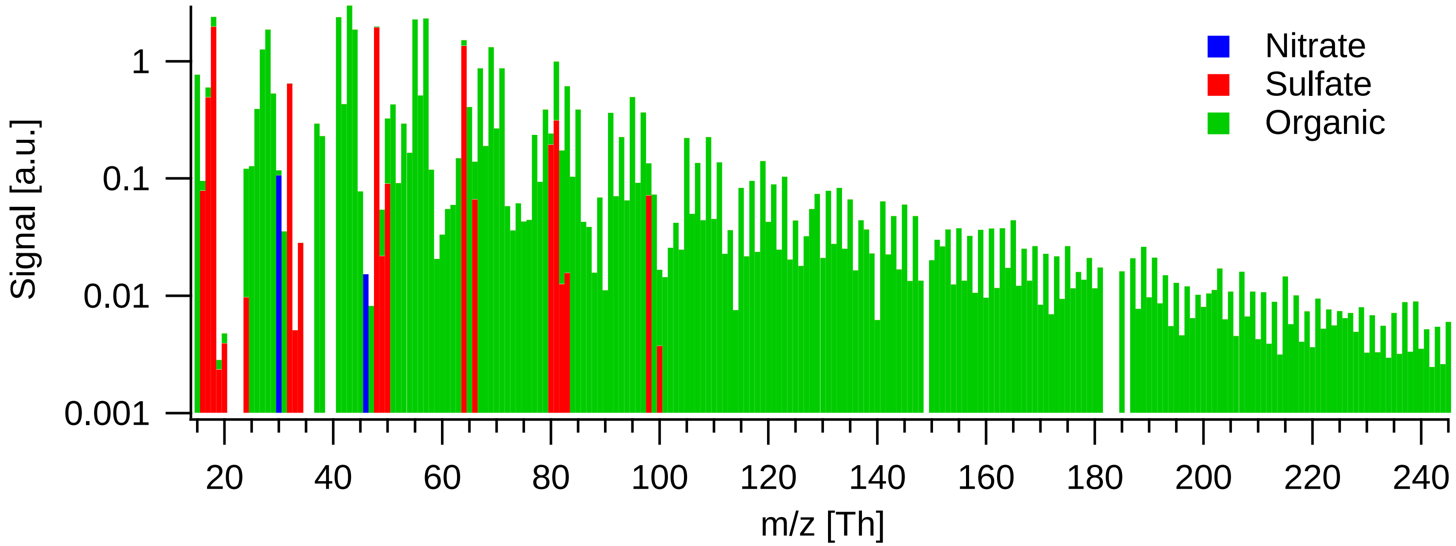


Metal-ion abundance in different fuel samples, vs Ba

- M/Ba⁺ similar to M/V⁺
- Weak response to engine load



Not just metals



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Study

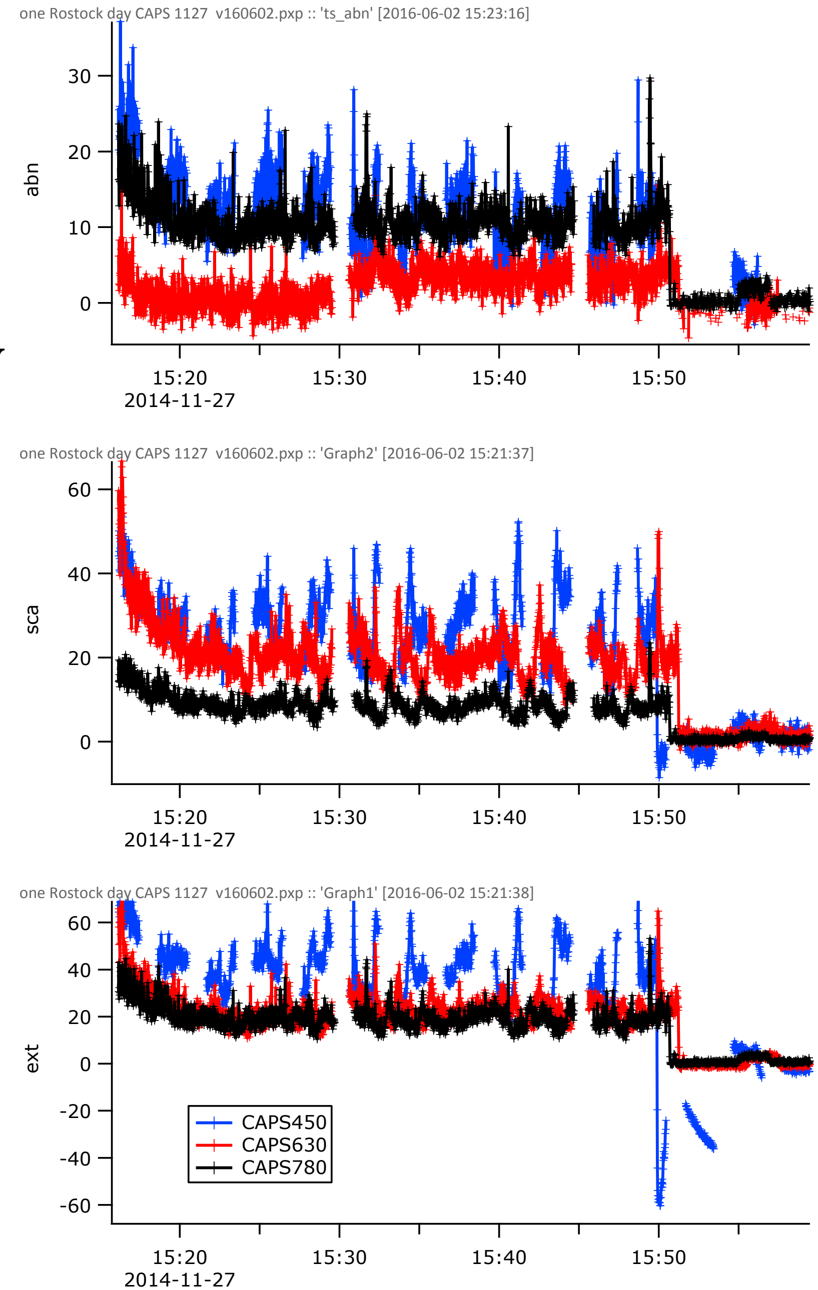
Ship engine (80 kW, 1-cylinder, 4-stroke, 150-mm bore[1]) → Porous tube dilutor → Ejector dilutors → Instruments

Goal: understand physico-chemical properties of ship-exhaust emissions with 3 fuels

[1] Oeder et al., PloS One, 2015.

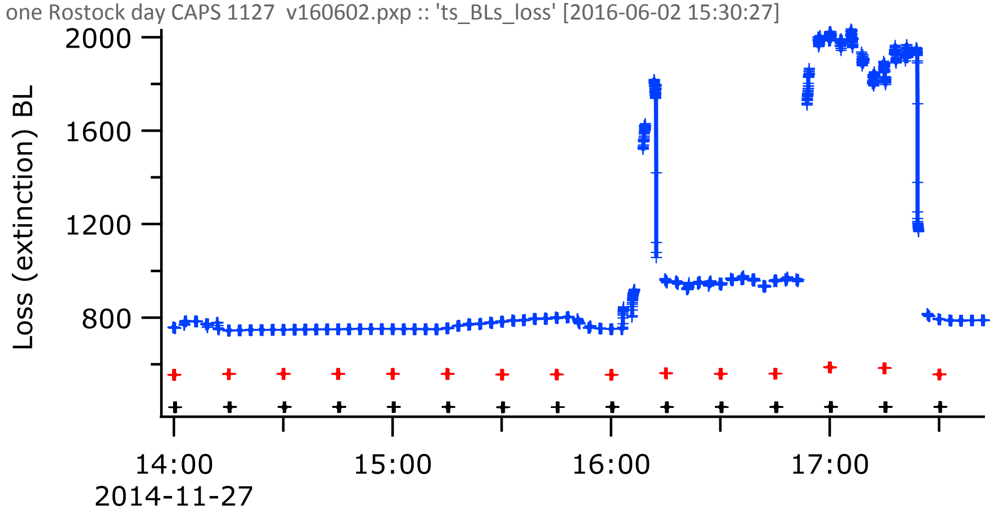
CAPS PMssa comparison

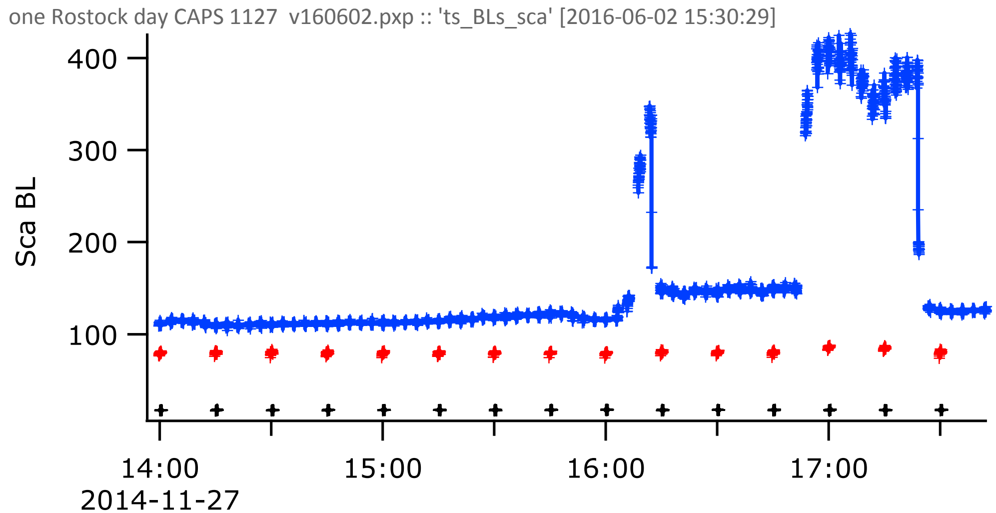
- Reasonable comparison for scattering
- CAPS 630 extinction too low (or 780 too high)



CAPS PMssa baselines

- Clear gaseous interference in blue
- No spikes in red -> probably not the issue
- Melpitz-like high-baseline issue proposed but cannot be tested





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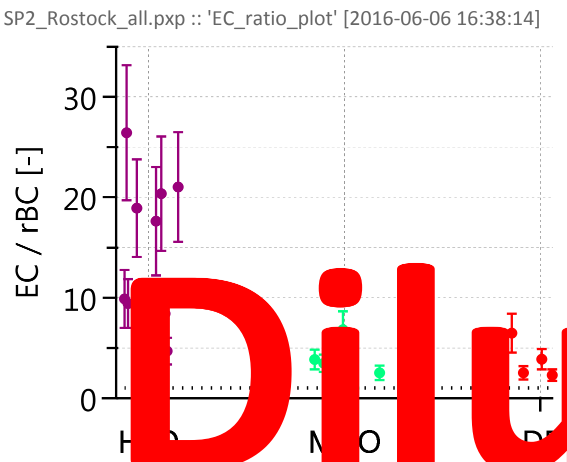
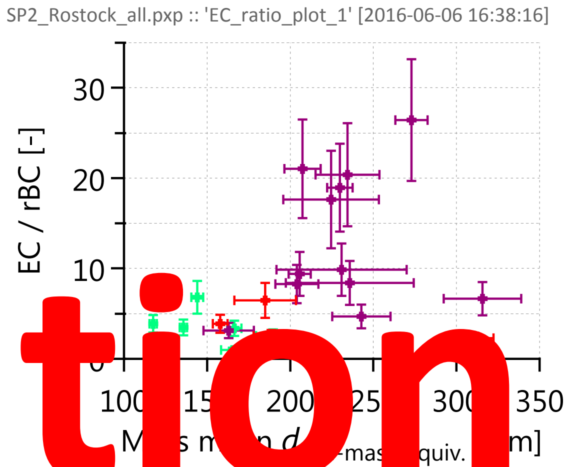
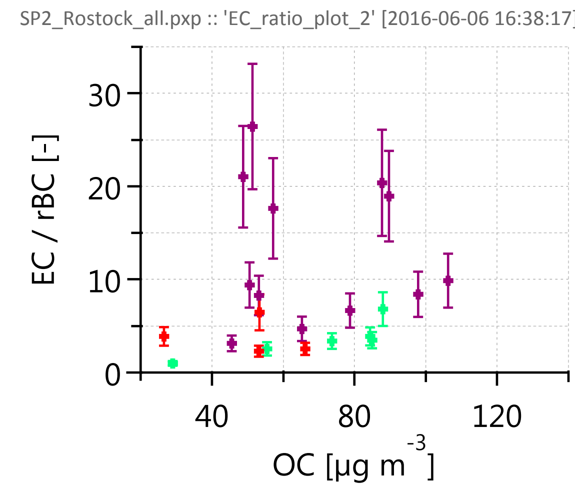
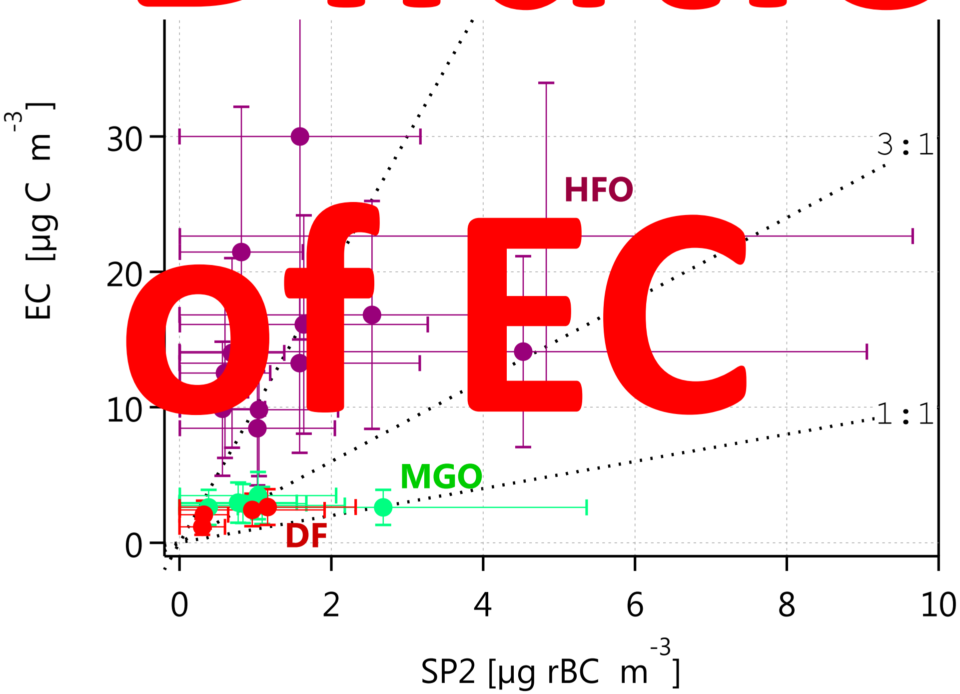
EC (thermal-optical) vs **BC** (SP2)







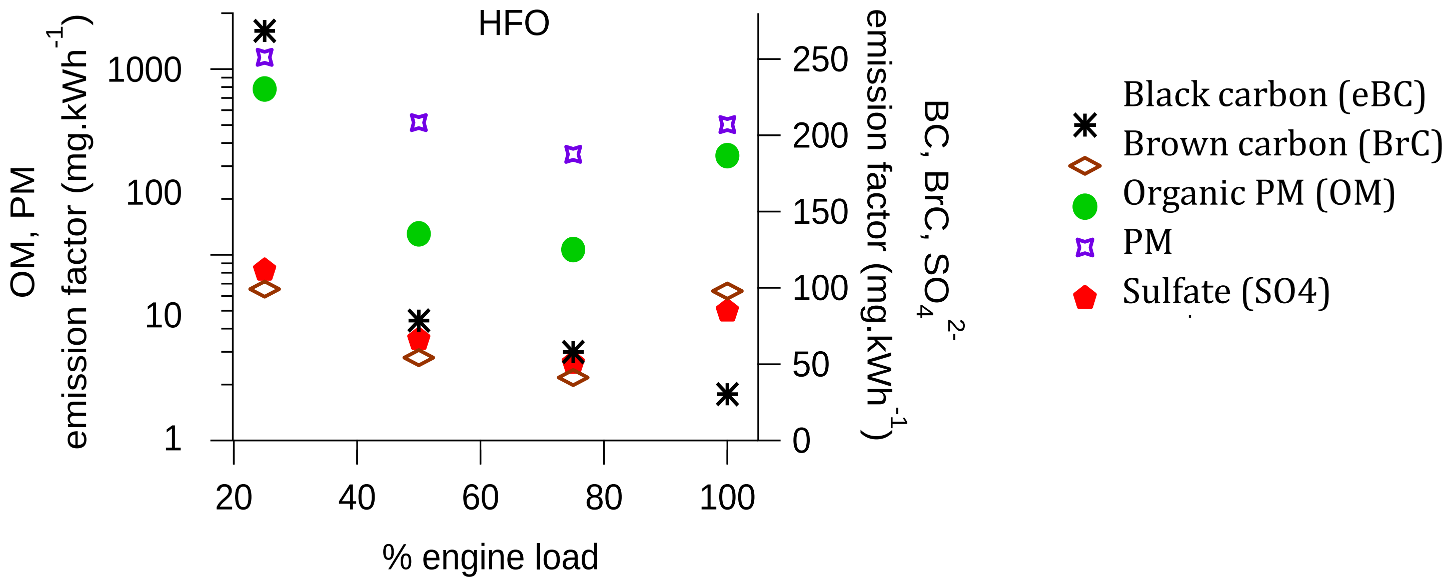
Dilution of EC



- EC >> rBC (SP2) for HFO
  - The 5 particles on previous slide would need to be 7—10 μm in diameter
  - EC was sampled at a higher flow rate, closer to source => different losses
  - EC / rBC correlated with rBC size
- Unknown if pyrolysis bias of EC is significant

[1] EC error bars ±25% (Emblico et al., 2012)

Other studies showing emission factors changing with engine load

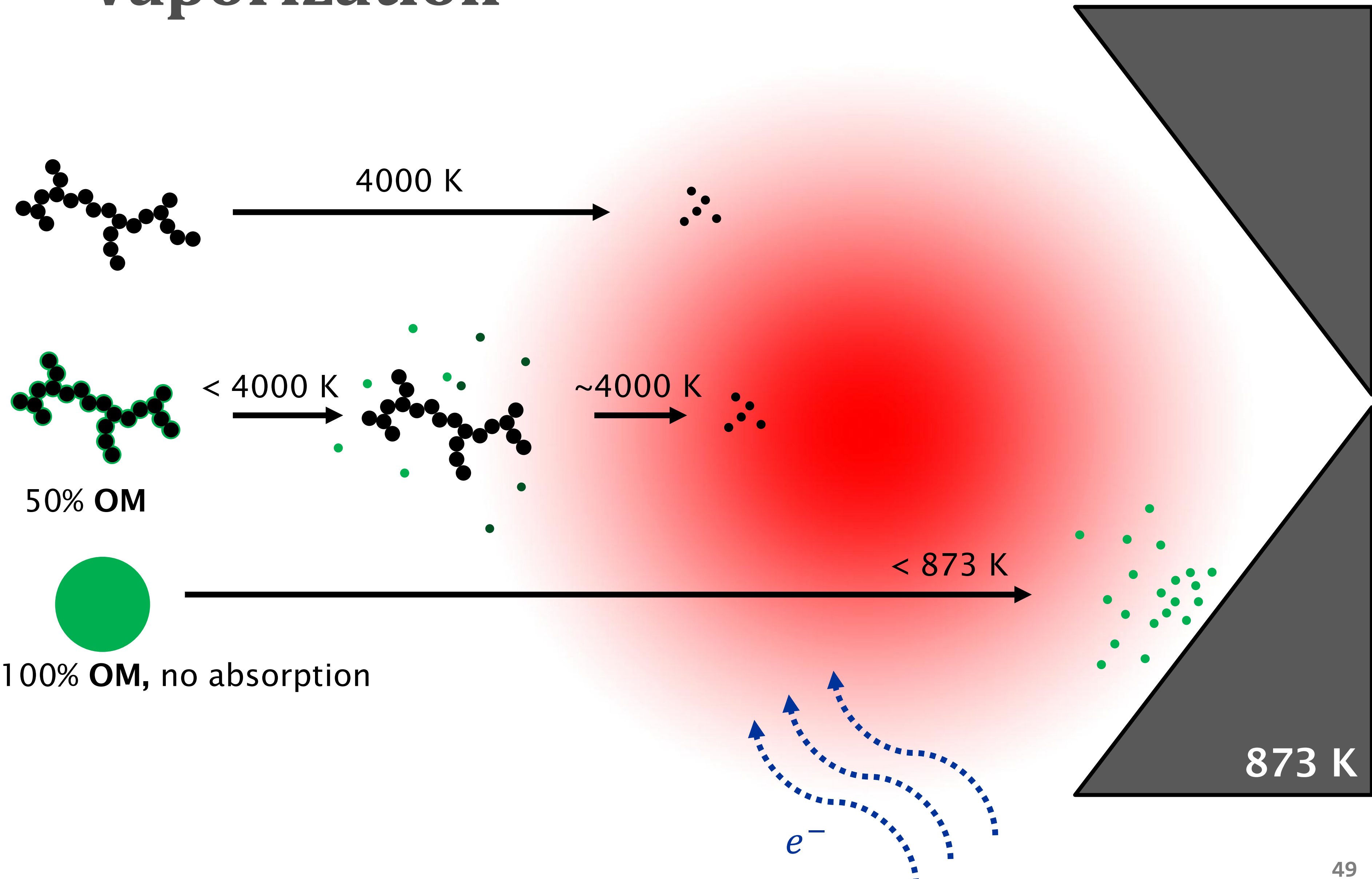


- Changing emission factors with engine load *(Mueller et al., 2016)*
- ➔ metal-based source identification will not capture these variations

Müller et al., 2016, in prep

SP-AMS Vaporization

refractory Black Carbon (4000 K) = **rBC**
Organic particulate matter = **OM**



AMS Vaporization

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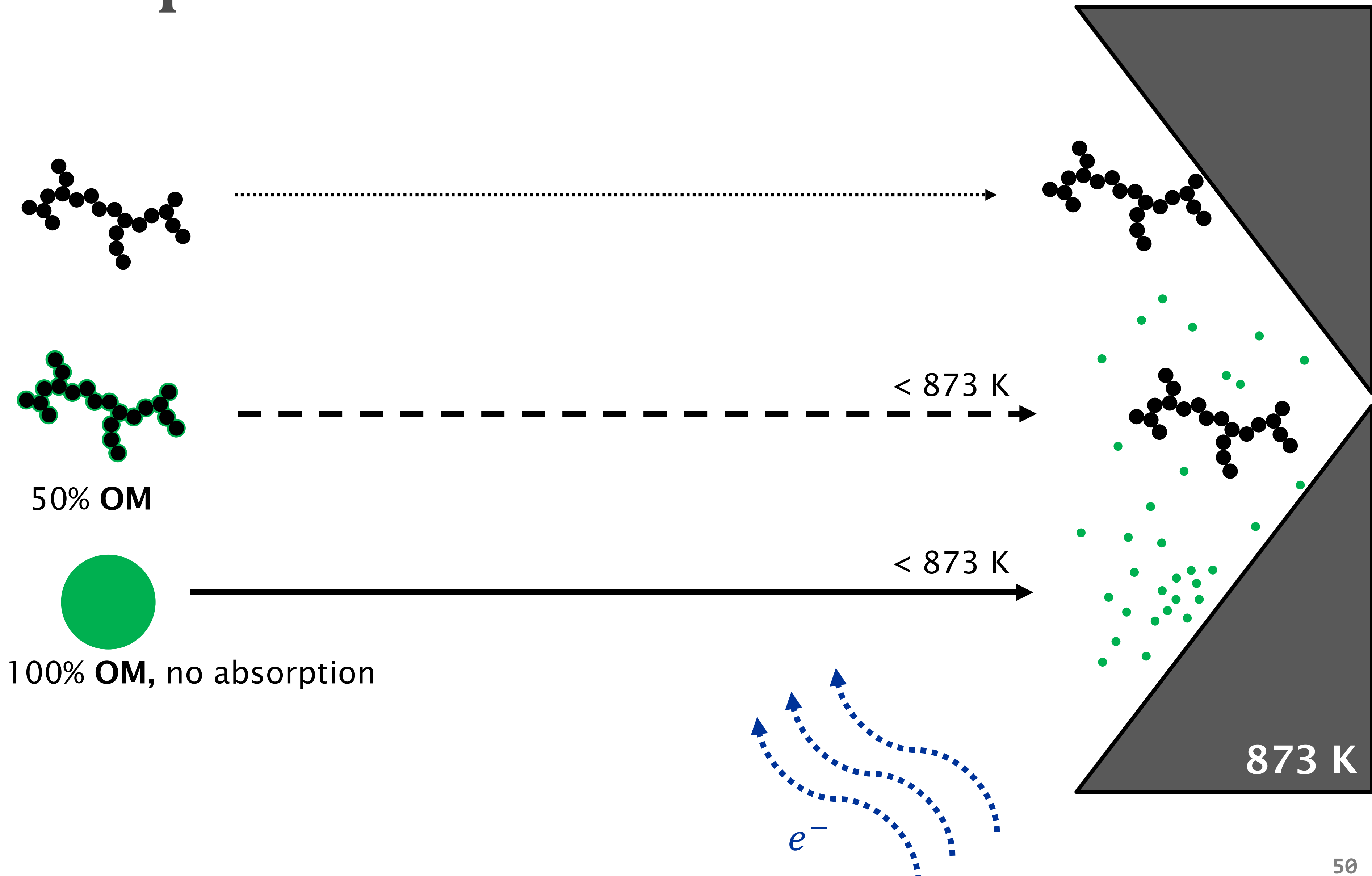
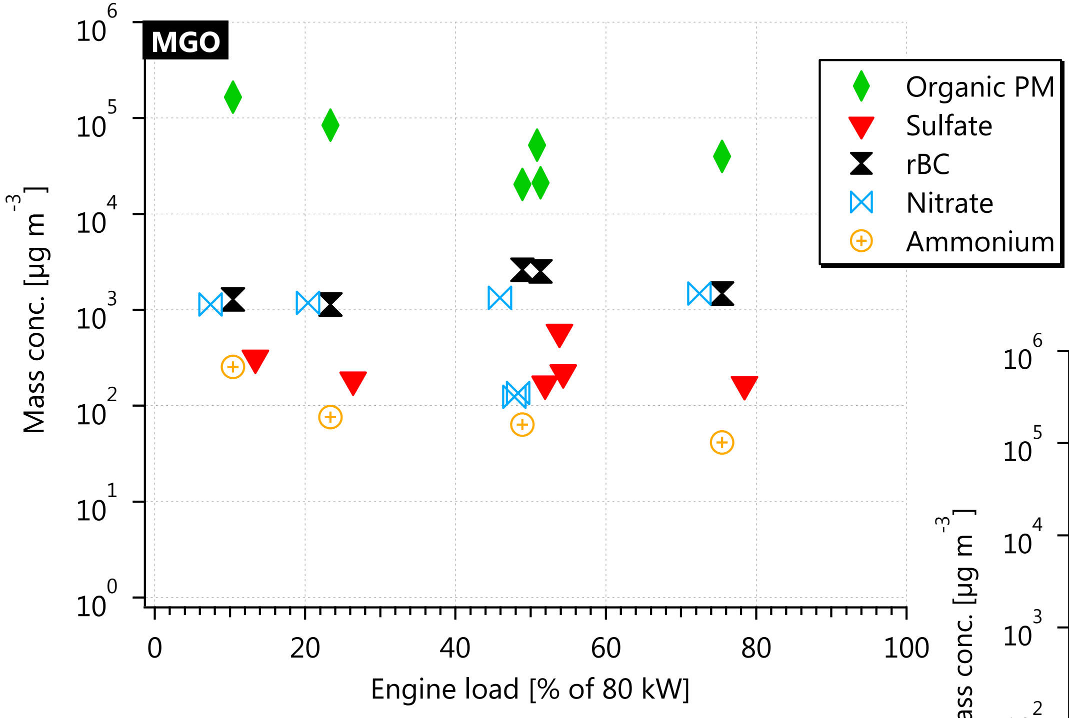
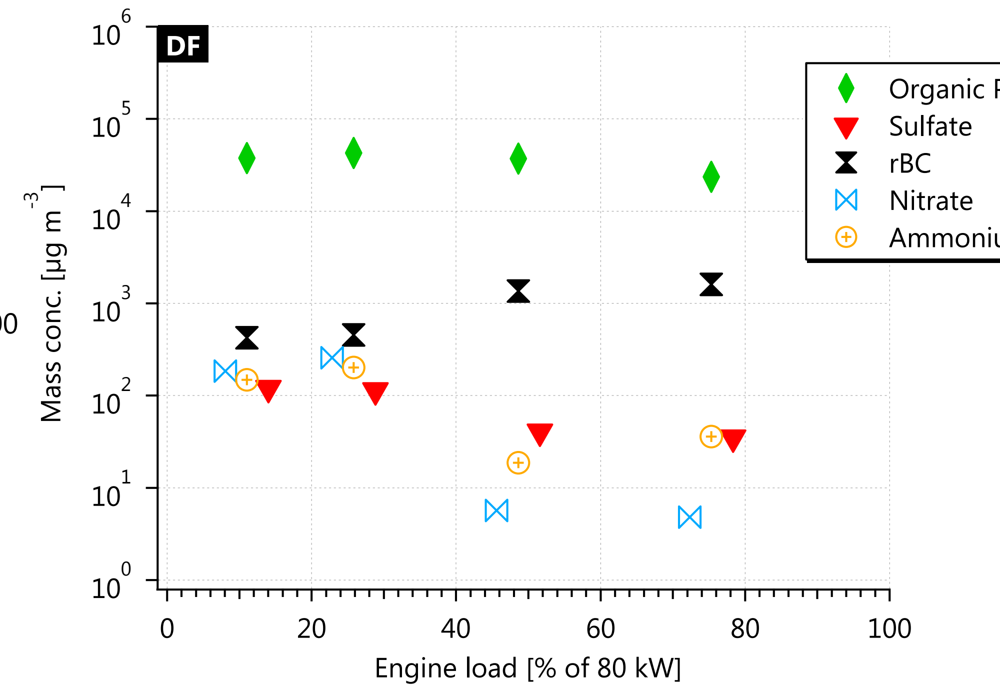


Before CO2 normalization MGO and DF emission factors





- Main component organics