Simultaneous real-time analysis of gas phase and particulate phase of heavy duty vehicle exhaust

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Introduction:
Vehicle exhaust is a complex and dynamic mixture containing a large number of compounds. It is composed of a gaseous phase and a particulate phase, and many constituents are partitioned between these two phases. In order to understand the complex formation mechanisms and correlations between both phases, it is necessary to analyse them at the same time. Moreover, exhaust composition changes continuously and can be influenced by many factors such as sampling, ageing, or chemical analysis. Therefore, the ideal way to comprehensively investigate vehicle emissions would be to analyze simultaneously, as many relevant components/properties as possible, in both phases, in real time.

Experimental Set-up:
In the framework of a joined project, sophisticated on-line instrumentation was implemented at the novel European Commission HD test facility. Regarding the particulate phase, a High-Resolution Time-of-flight Aerosol Mass Spectrometer (HR-TOF-AMS) and a Multi-Angle Absorption Photometer (MAAP) were installed. Prior identifies the non-refractory chemical composition of PM, latter the black carbon concentration. In addition, a particle counter (CPC) was applied. For the gas phase, a Fourier-Transformation Infrared Spectrometer (FTIR) and a Resonance-Enhanced Multiphoton Ionization Time-of-flight Mass Spectrometer (REMPI-TOFMS) were implemented. This enabled to analyse a great variety of volatile and semi-volatile compounds. The tested vehicle was a medium-size truck without any exhaust aftertreatment (EURO-III). Driving cycles applied were official tests for emission certification (e.g. ETC) as well as a self-developed cycle featuring different steady velocities/states (idle, 40 km/h, 60 km/h, 90 km/h, idle; 5 minutes each). Time-resolved results were directly related to on-line recorded fuel consumption and incorporated in chemometric data analysis techniques.

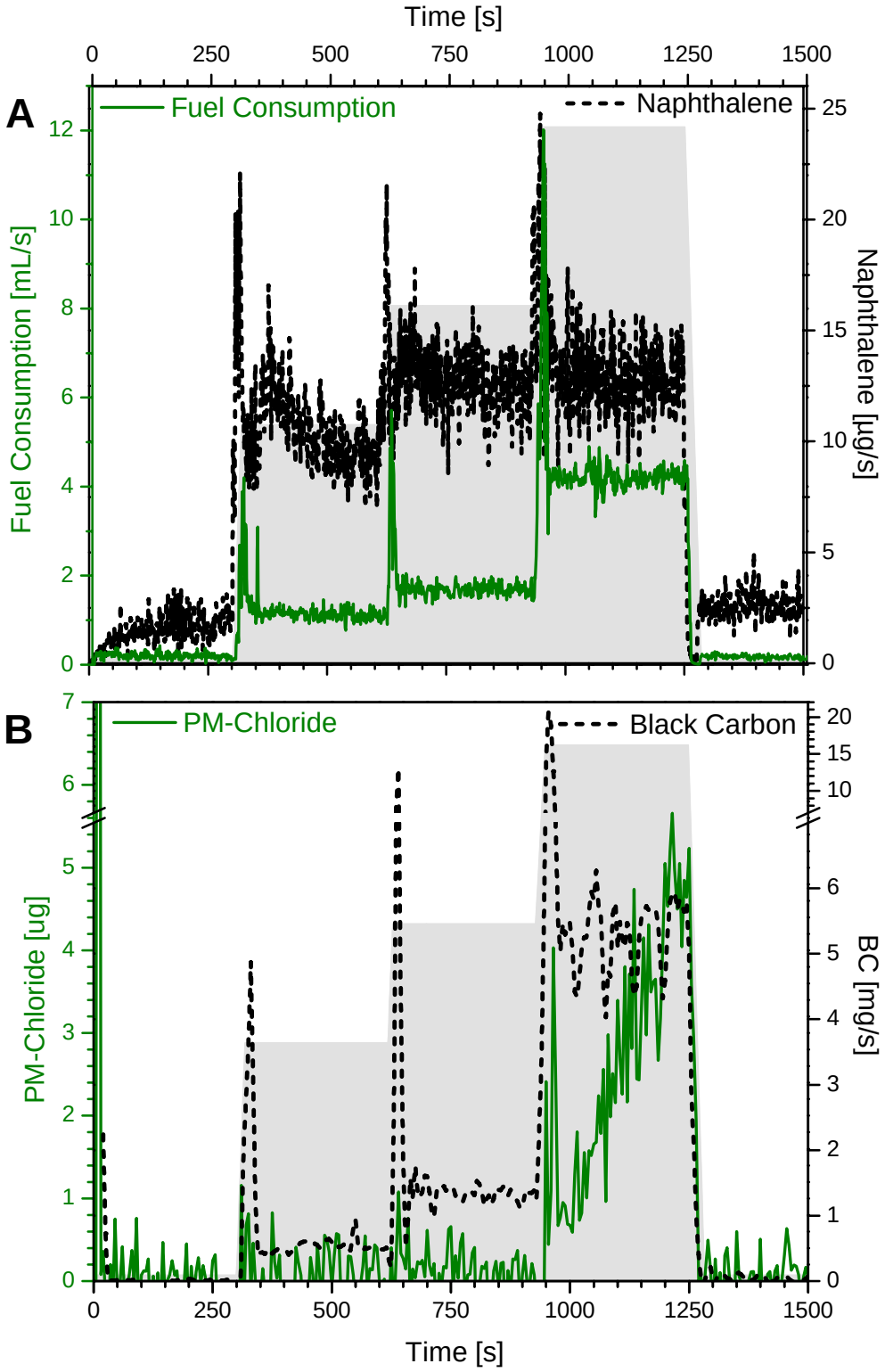

Fig A & B: Time-resolved emission results of naphthalene, black carbon, and PM-chloride as well as fuel consumption. The steady state driving cycle is indicated in gray (idle, 40 km/h, 60 km/h, 90 km/h, idle; 5 minutes each)

Results and Discussion:

Emission results of the steady state tests demonstrate that many gas phase compounds and PM properties follow the fuel consumption (Fig. A). Gas phase constituents with this behaviour were e.g. CO_2, NO, pyrene and higher homologues of benzene. Thereby, several PM properties like number, black carbon (Fig. B) and organic mass featured an even stronger pronounced increase from the moderate to the highest velocity than consumption. PM-chloride showed a unique behaviour with a steady increase during the high speed event (Fig. B). In contrast, several species resulted in elevated but rather similar values for the three velocities 40 km/h, 60 km/h, and 90 km/h. Among these were CO, NO_2, formaldehyde, and naphthalenes (Fig. A). Consequently, the more severe conditions during higher speeds in combination with more fuel and high temperatures did not lead to a further rise. In combination with statistical methods (e.g. Principal Component Analysis) a grouping of preferred conditions for individual components was carried out. Furthermore, the cold start behaviour was studied by comparing the concentration time profiles of the individual components during ETC tests with the engine hot and cold at test start.

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- Time-resolved Emission
- Correlation to Fuel Consumption

Chassis Dynamometer & Test Cell:

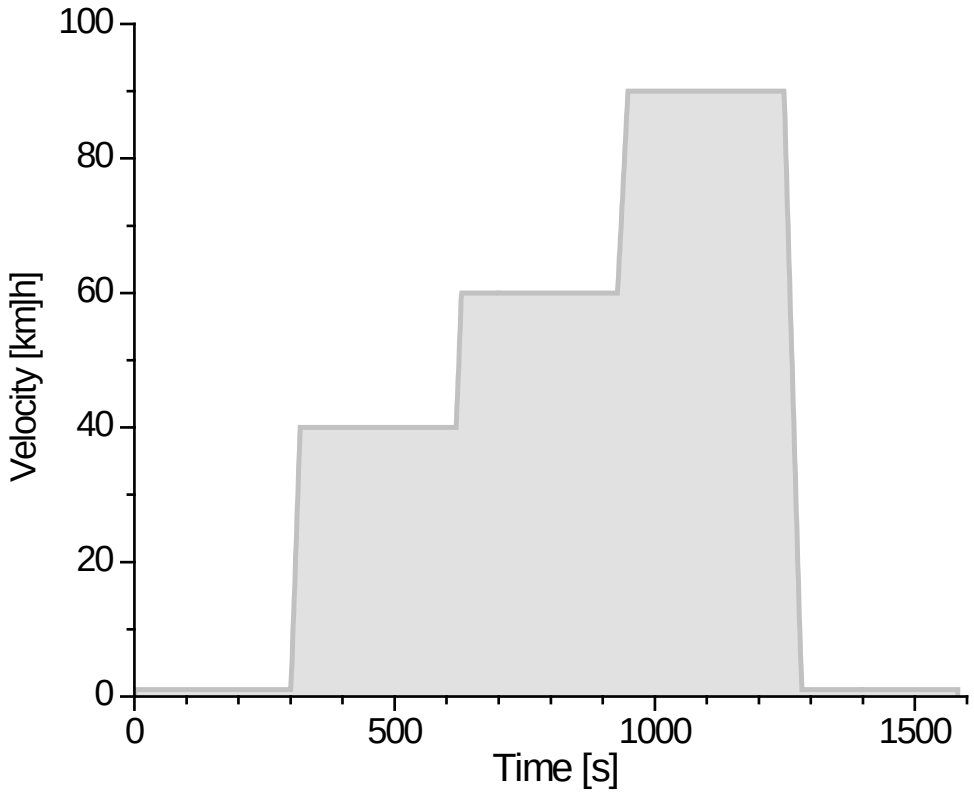
- Inaugurated in March 2009
- Bus/Trucks up to 40 tons, 12 m length, 5 m height
- Temperature range from -30 to 50°C
- Relative Humidity from 15% - 95%
- Safety Sensors for gaseous Fuels (H_2, CNG, LPG, LNG)

Heavy Duty Vehicle

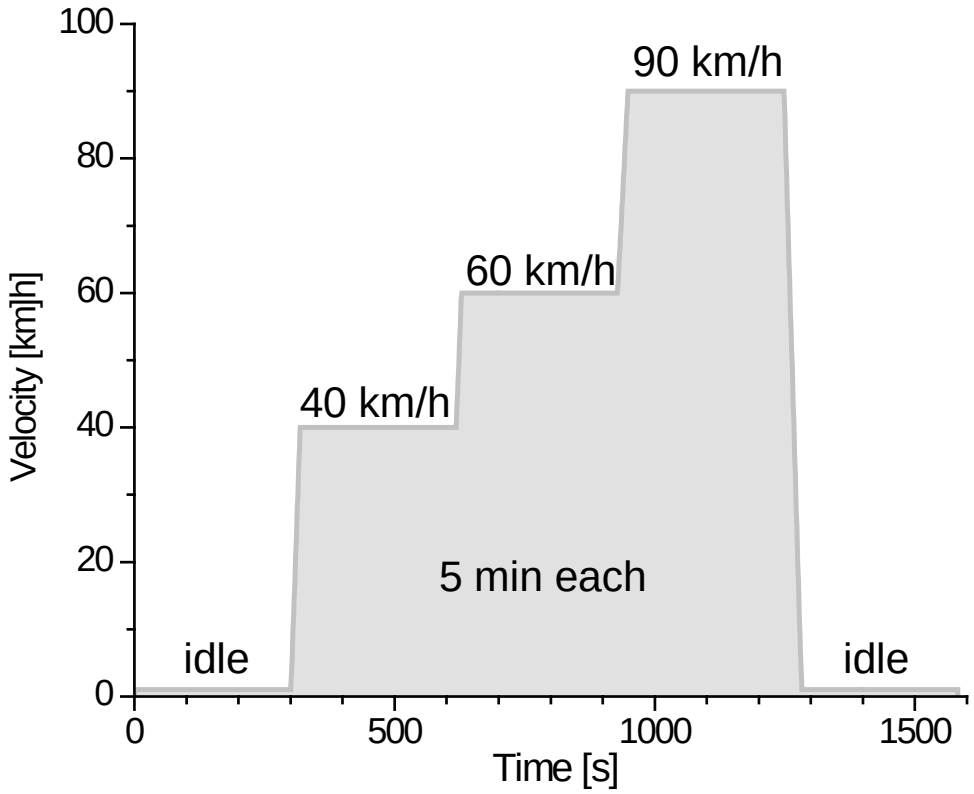
Medium size in-use Truck:

- Model: 2002
- Engine: Turbo Diesel
- Emission Level: EURO III
- Aftertreatment: none
- Power: 176 kW at 3500 rpm
- Displacement: 5880 cm^3
- Weight: 8 tons
- Odometer: 140,000 km

Steady State Test; hot start



Steady State Test; hot start



Gas Phase:

- **Conventional Sensors:** NO_x, CO, CO_2, THC etc.

- **Fourier Transformation Infrared Spectroscopy (FTIR)**
  Nitrogen-containing Species, Carbonyls, small Hydrocarbons etc.

- **Resonance Enhanced Multiphoton Ionisation Time-of-flight Mass Spectrometry (REMPI-TOFMS):**
  Monoaromatic & Polycyclic Aromatic Hydrocarbons

Particulate Phase:

- **High Resolution Time-of-flight Aerosol Mass Spectrometer (HR-TOF-AMS):**
  Organic Matter, Sulfate, Nitrate, Chloride

- **Multi-Angle Absorption Photometer (MAAP):**
  Black Carbon

- **Condensation Particle Counter (CPC):**
  Number

Exhaust Pipe: FTIR, REMPI-TOFMS

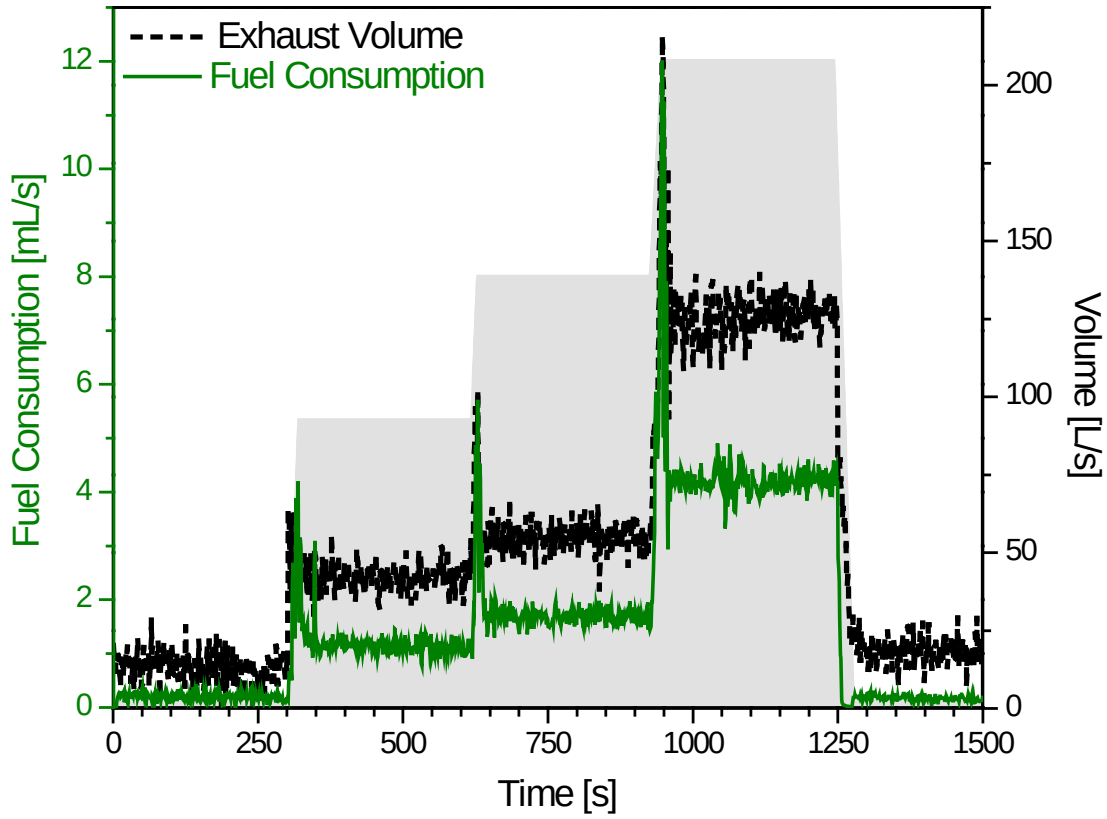
Dilution Tunnel: HR-ToF-AMS, MAAP

Time-resolved Data:

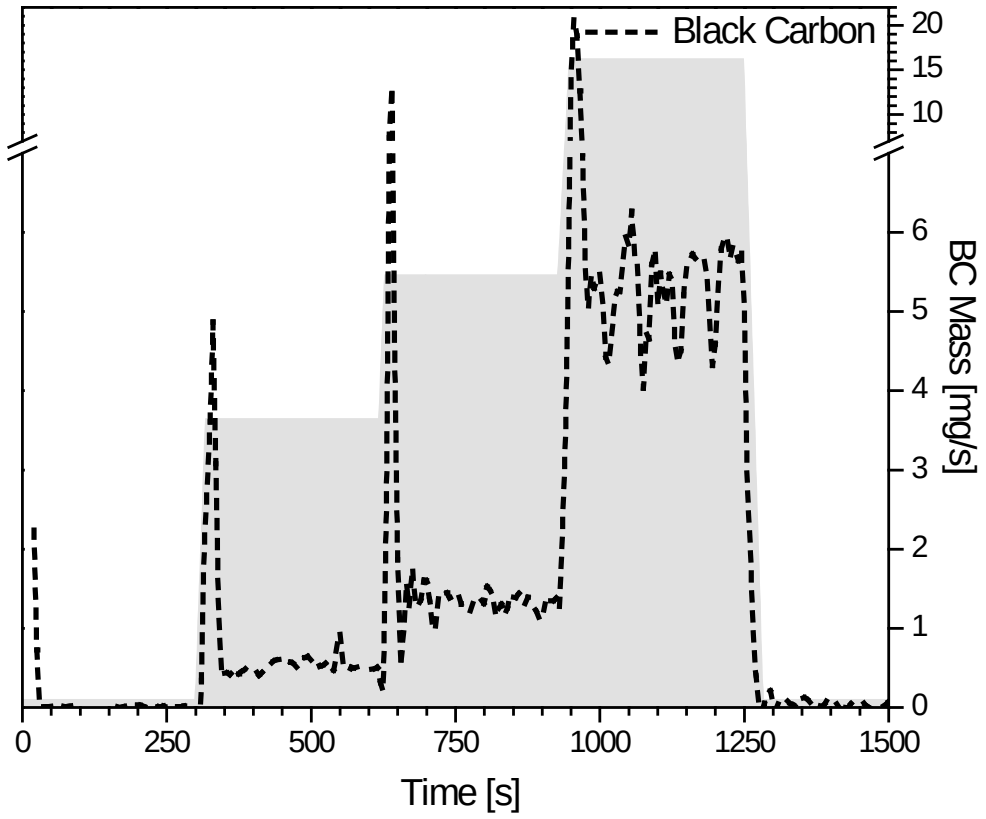
- Emission: mass/time e.g. [mg/s]

- Emission / Fuel Consumption: mass/(volume×time) [mg/s × mL^{-1}]

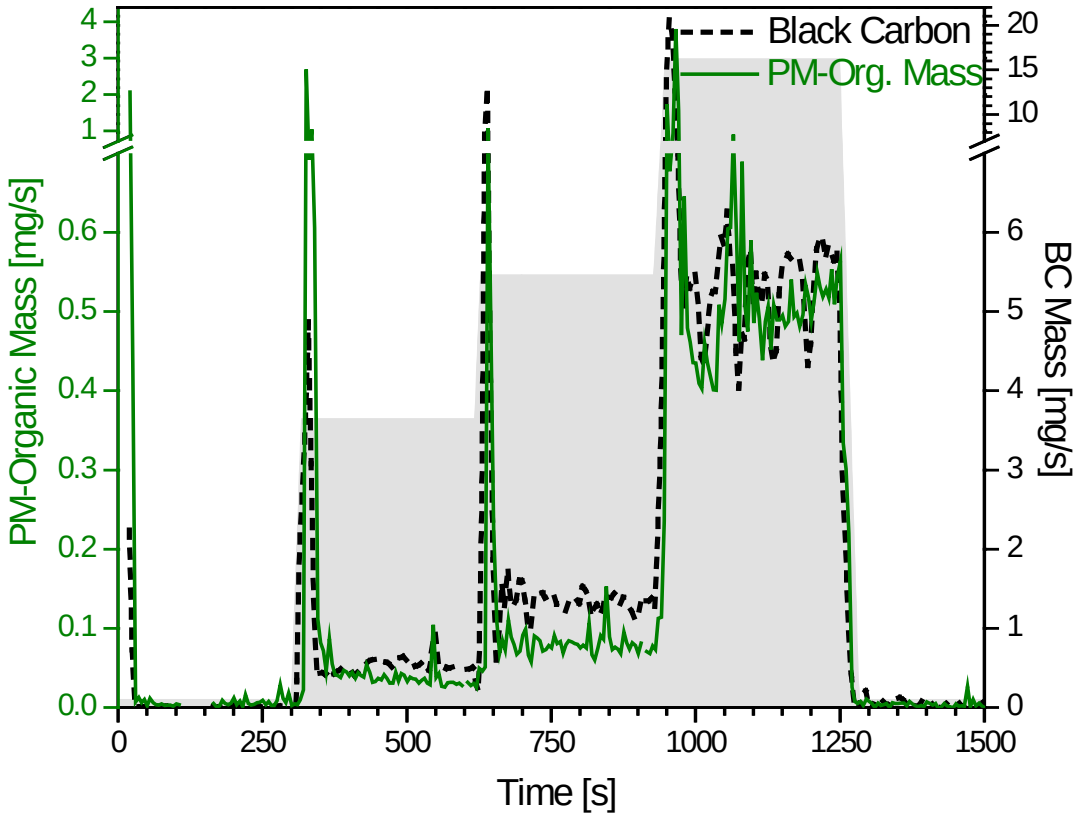
Exhaust Volume & Exhaust Temperature



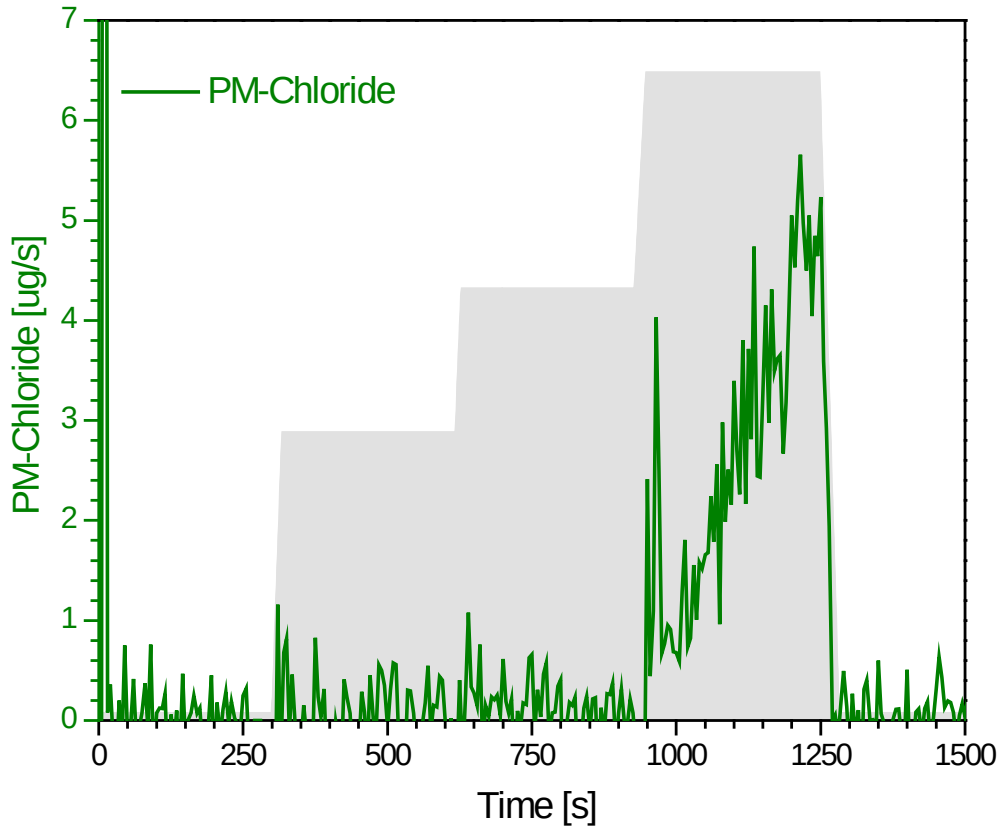
Black Carbon



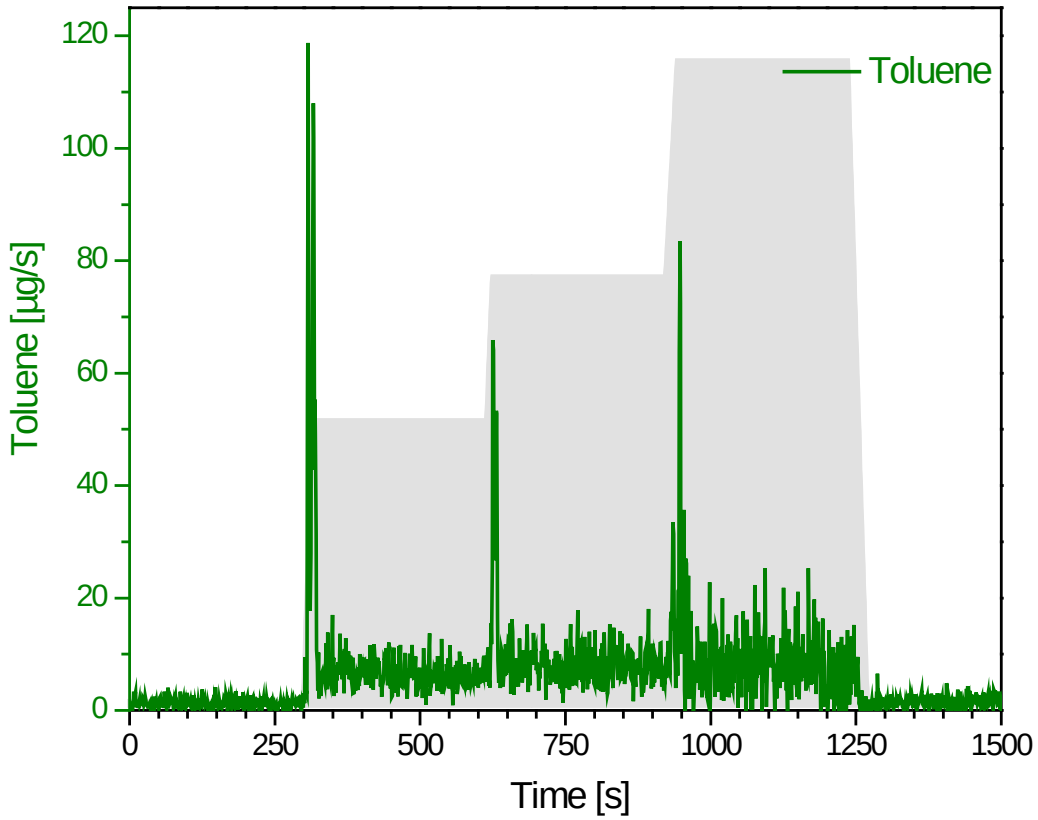
Black Carbon & PM-Organic Matter



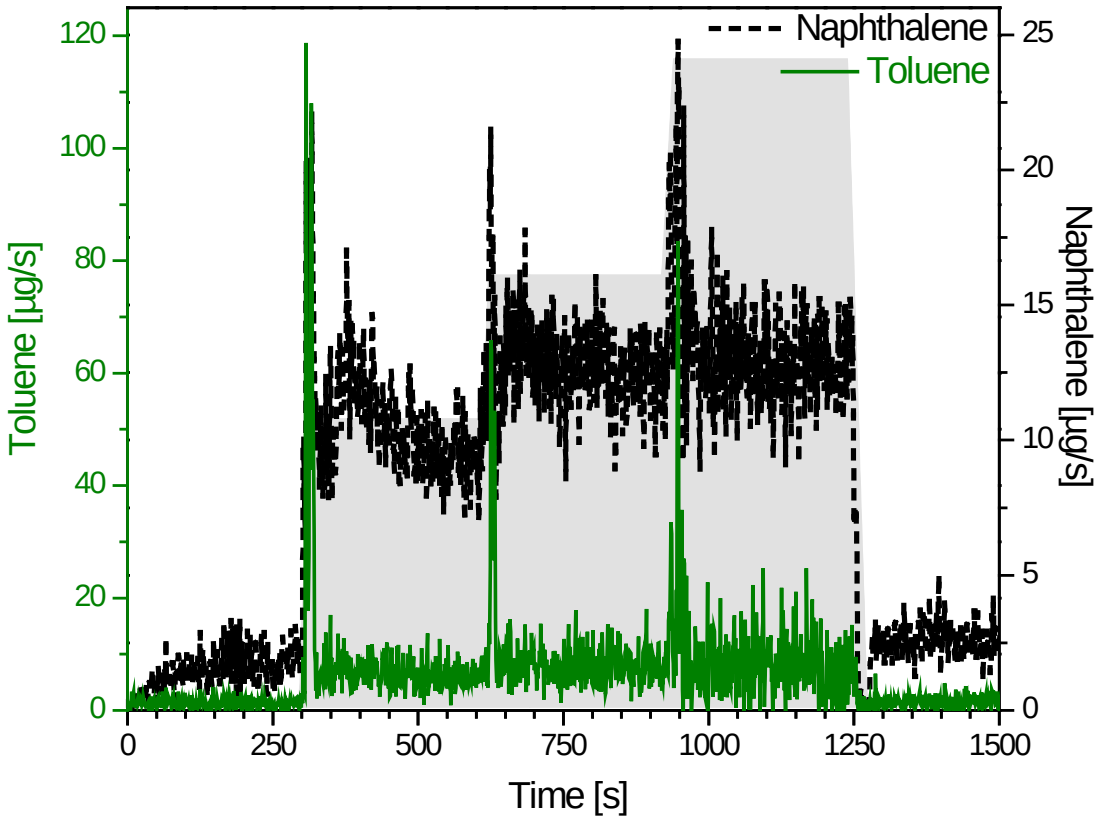
PM-Chloride


PM-Chloride
PM-Chloride [ug/s]
Time [s]
0
1
2
3
4
5
6
7
0
250
500
750
1000
1250
1500

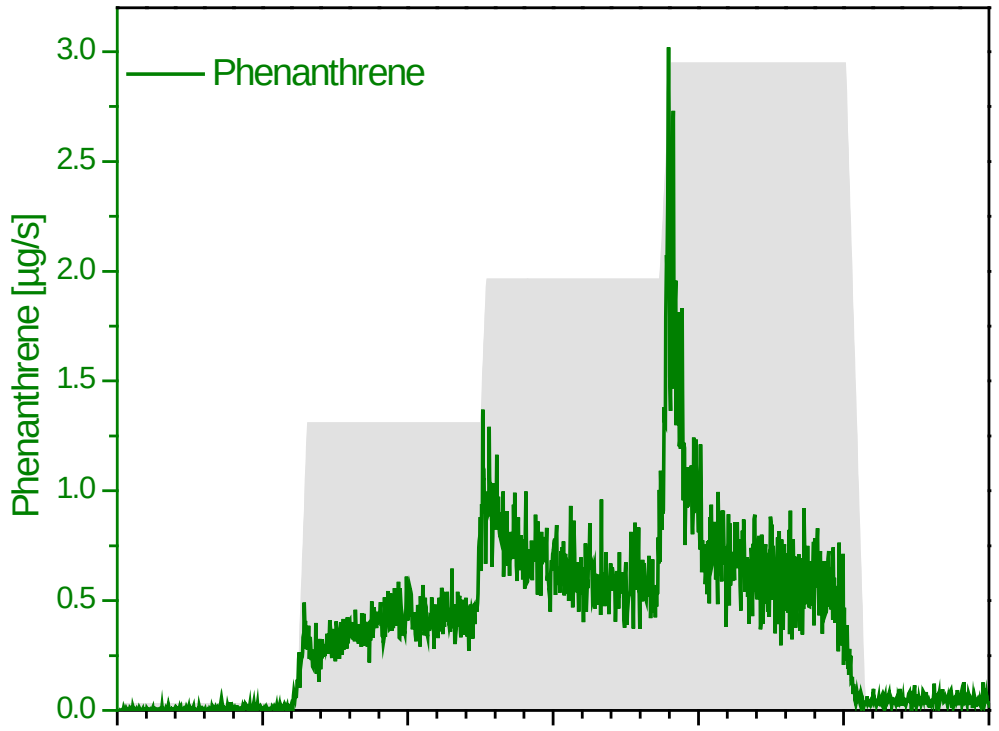
Toluene


Toluene
Toluene [µg/s]
Time [s]
0
20
40
60
80
100
120
0
250
500
750
1000
1250
1500

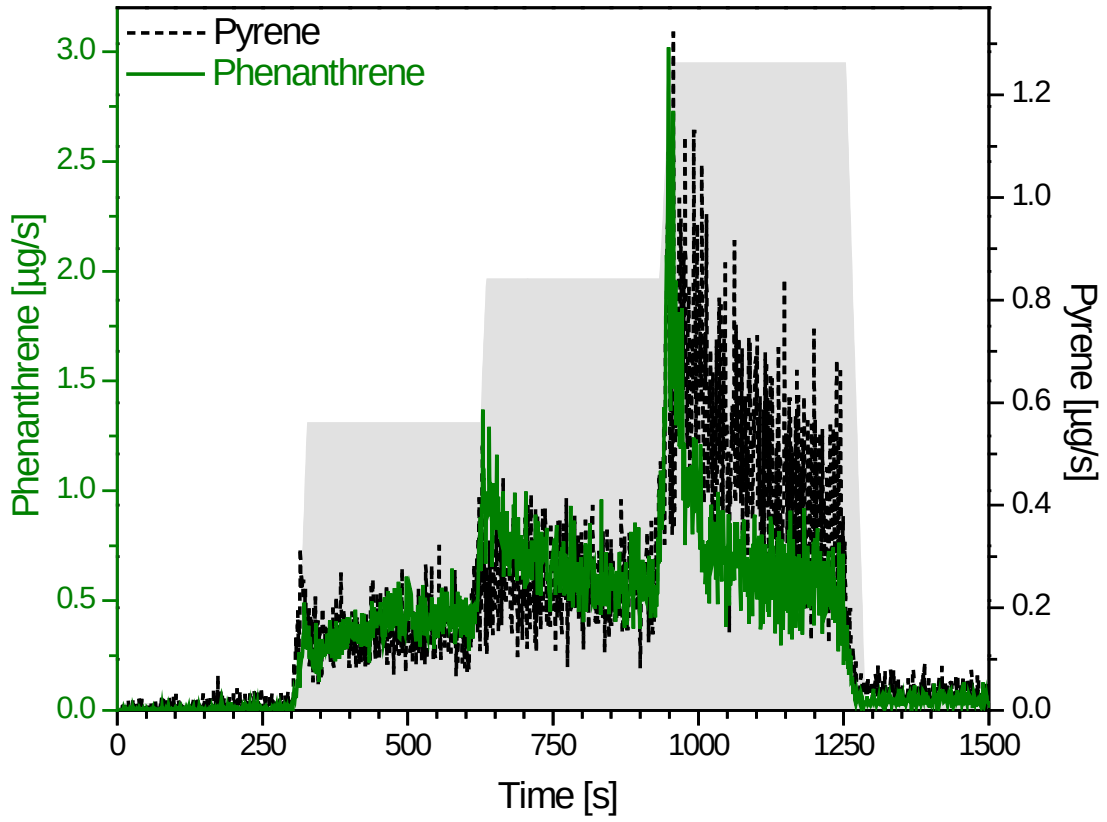
Toluene & Naphthalene



Phenanthrene



Phenanthrene & Pyrene



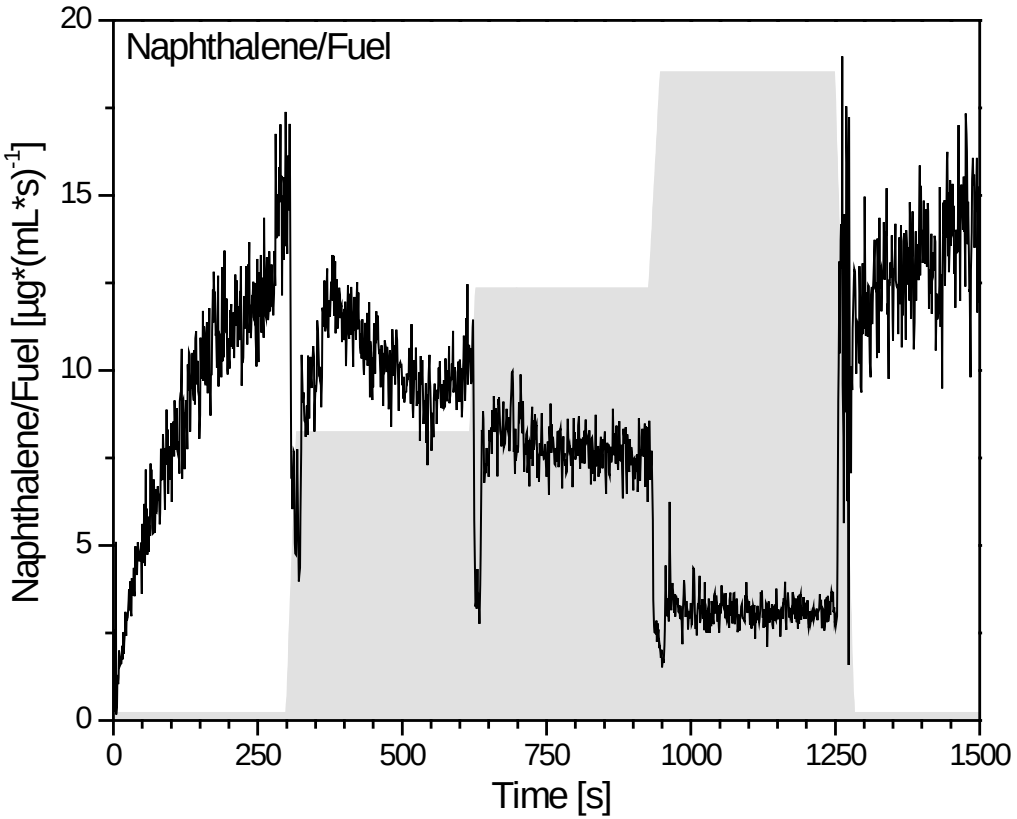
Classification of Emission:

1. CO_2, NO, N_2O, H_2O, SO_2, Black Carbon, Organic Mass, less pronounced: Acetylene, Pyrenes, C3-C6 Benzenes, Particle Number,
   ➞ Fuel Consumption, Exhaust Volume

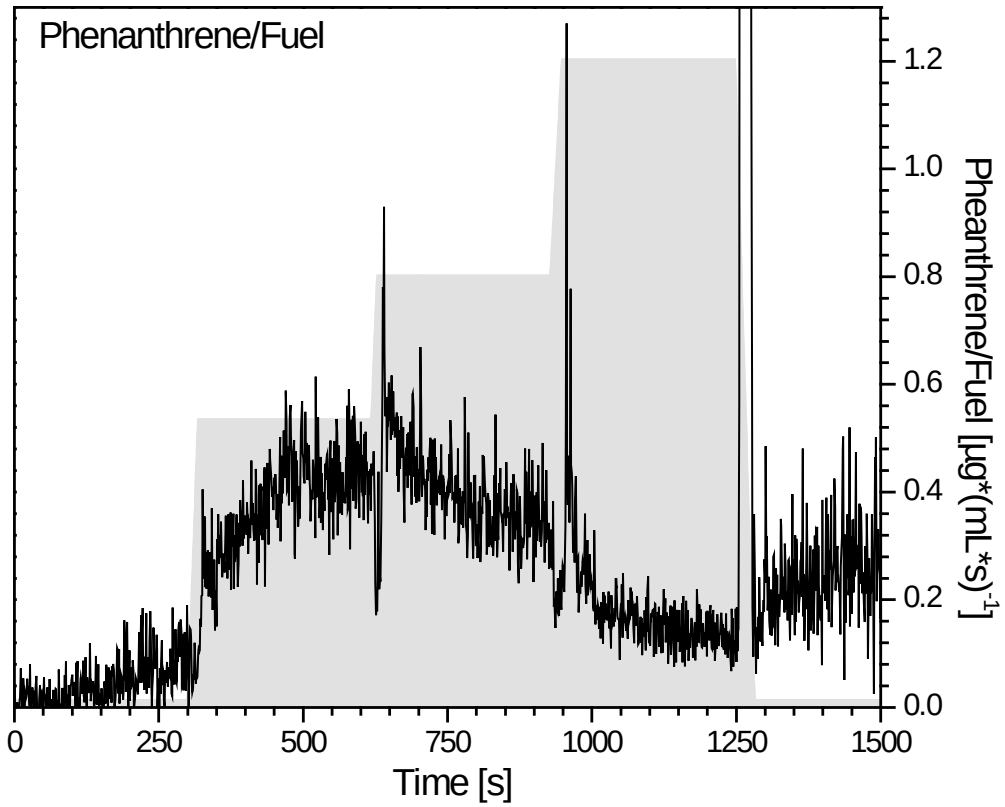
2. CO, NO_2, Formaldehyde, Formic Acid, Ethane, Benzene, C2-Benzene, Toluene, Naphthalenes, less pronounced: Phenanthrenes

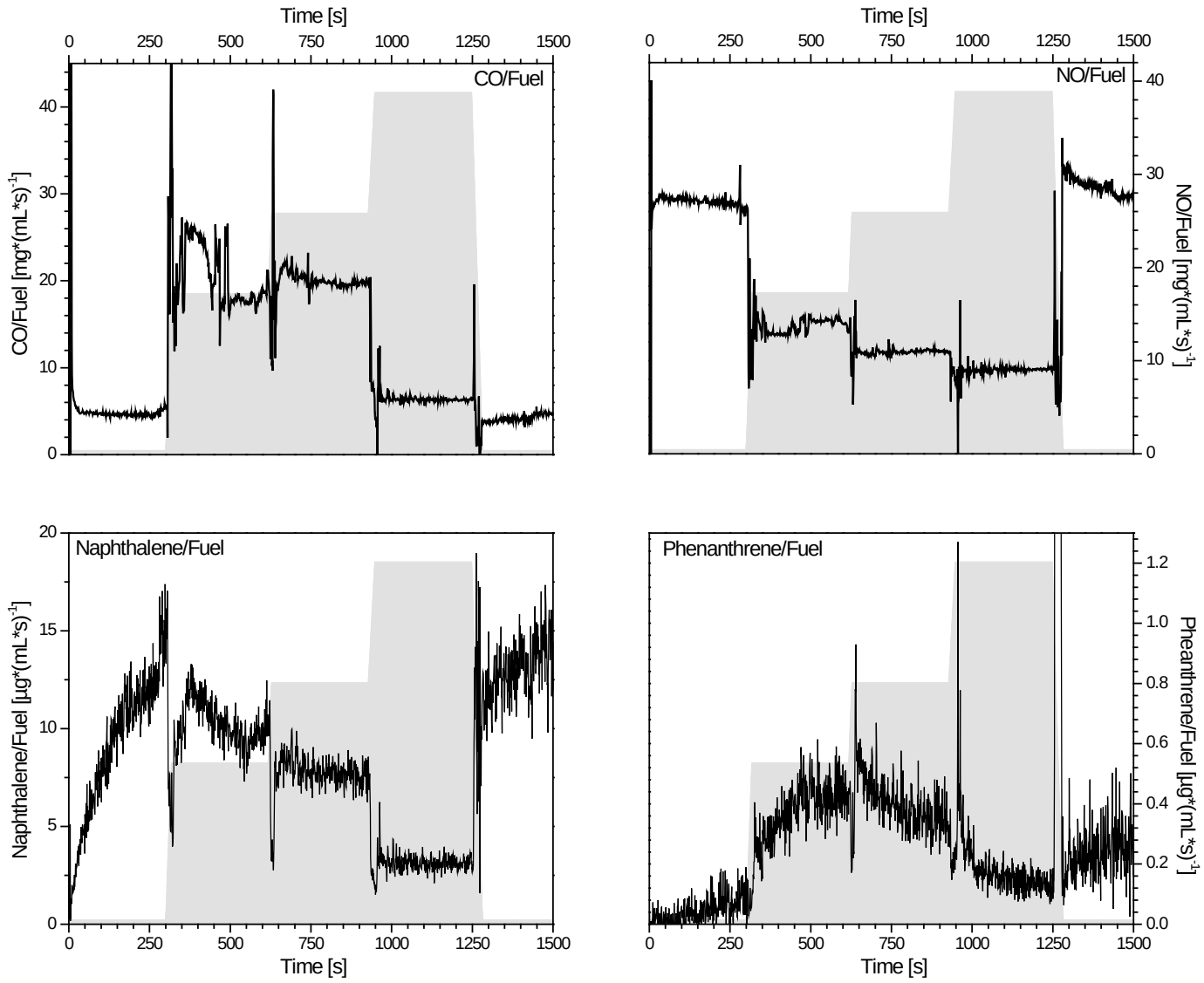
3. Some with unique Behavior e.g. PM-Chloride

Naphthalene / Fuel



Phenanthrene / Fuel




Time [s]
CO/Fuel
CO/Fuel [mg*(mL*s)-1]
Time [s]
NO/Fuel
NO/Fuel [mg*(mL*s)-1]
Naphthalene/Fuel
Naphthalene/Fuel [µg*(mL*s)-1]
Time [s]
Phenanthrene/Fuel
Pheanthrene/Fuel [µg*(mL*s)-1]
Time [s]

Selected Results show that

- Comprehensive Real-time Characterization of Emission
- Classification of Exhaust Components
- Study of preferred Formation Conditions

On-going Work:

- Incorporation of more vehicles for classification
- Comparison of Cold-Start / Hot-Start (ETC-Cycle)

Thank you for your Attention!

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Transport & Air Quality Unit
Institute for Environment & Sustainability IES
European Commission Joint Research Centre Ispra

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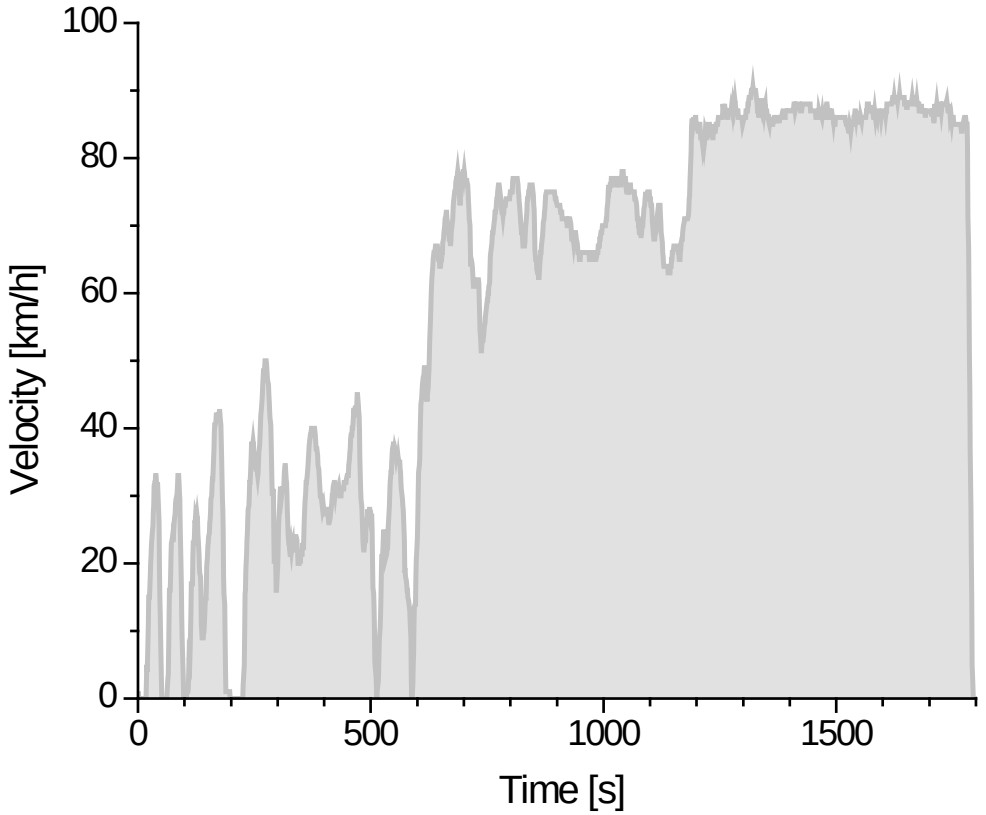
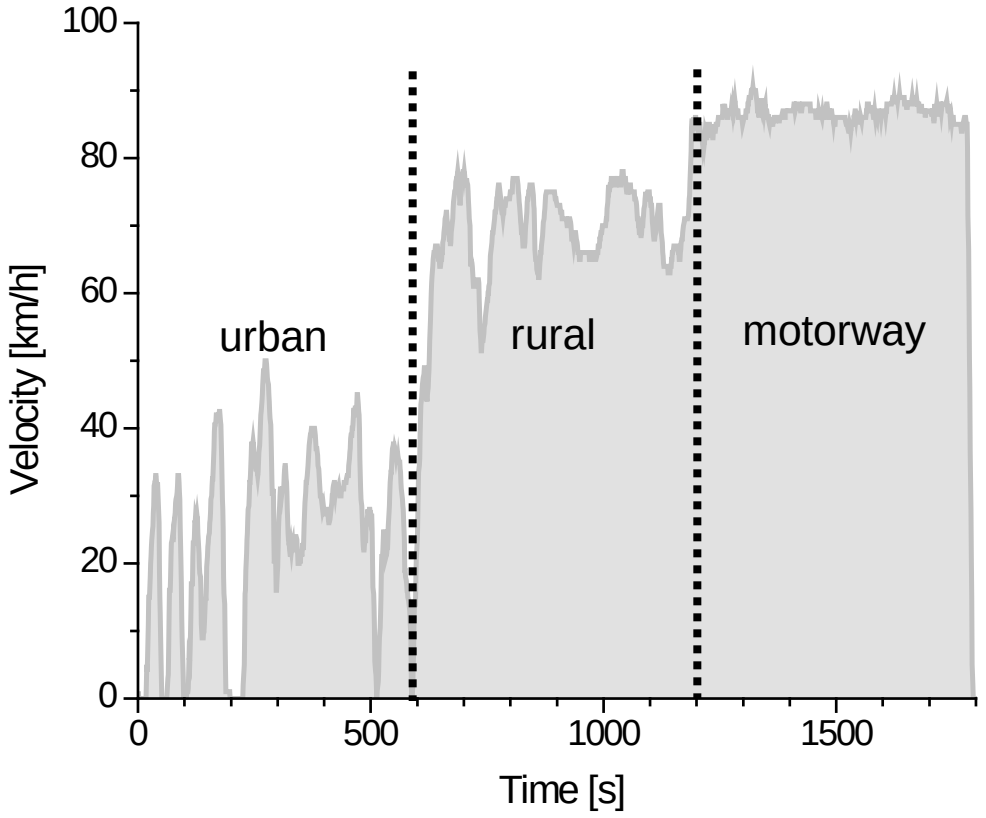
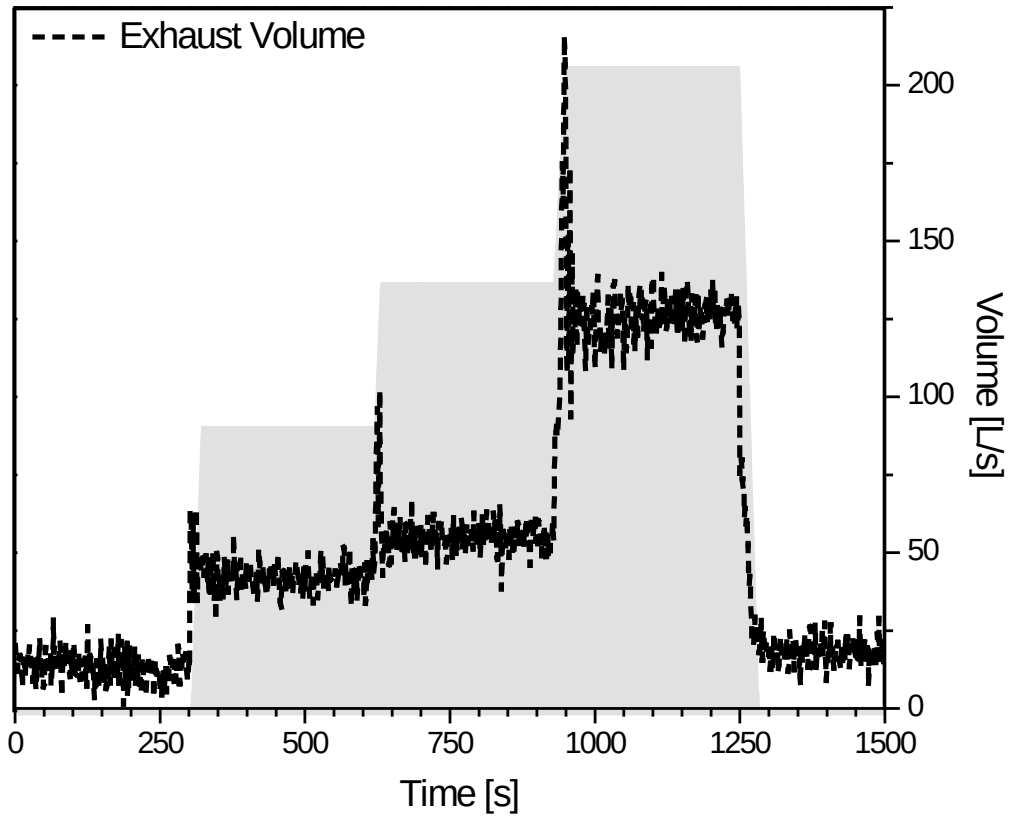
European Transient Cycle (ETC); cold start & hot start



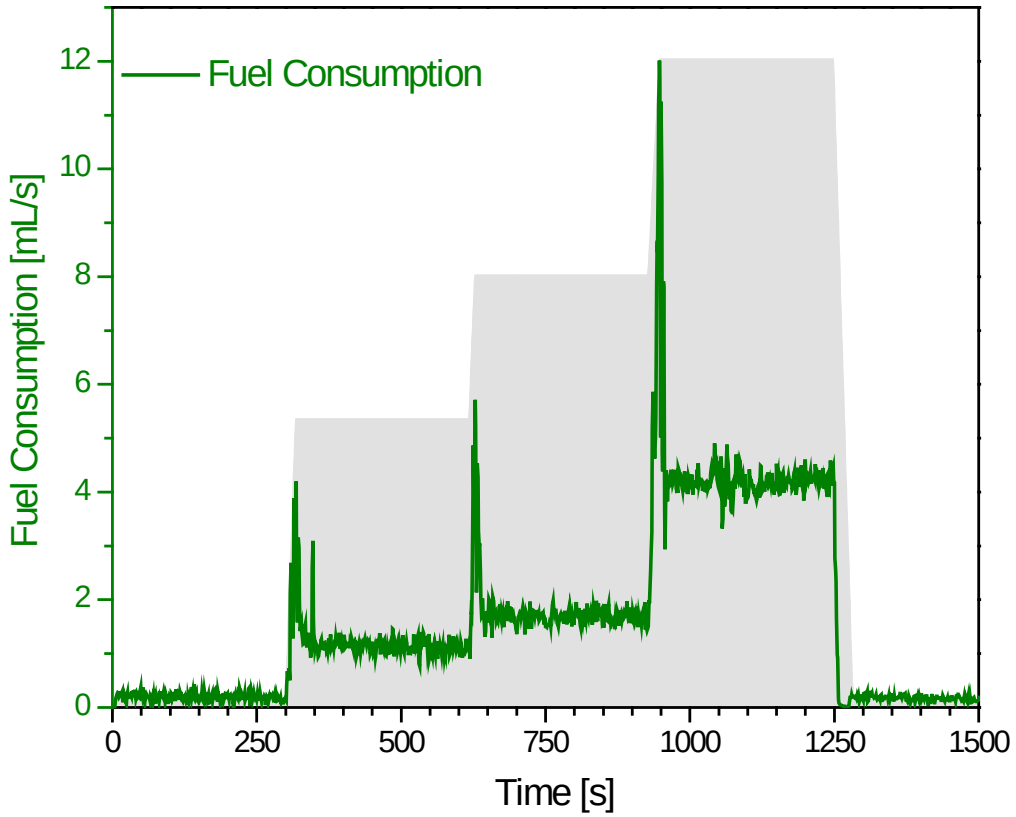
European Transient Cycle (ETC); cold start & hot start



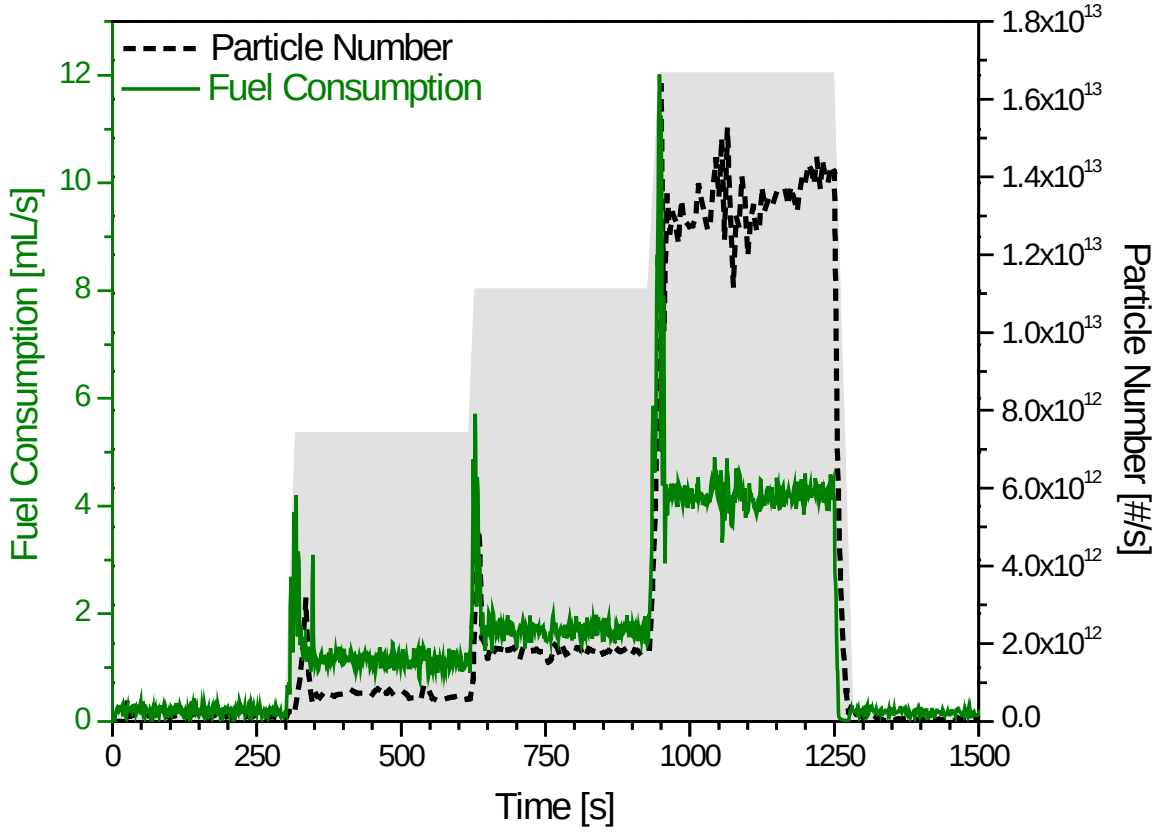
Exhaust Volume



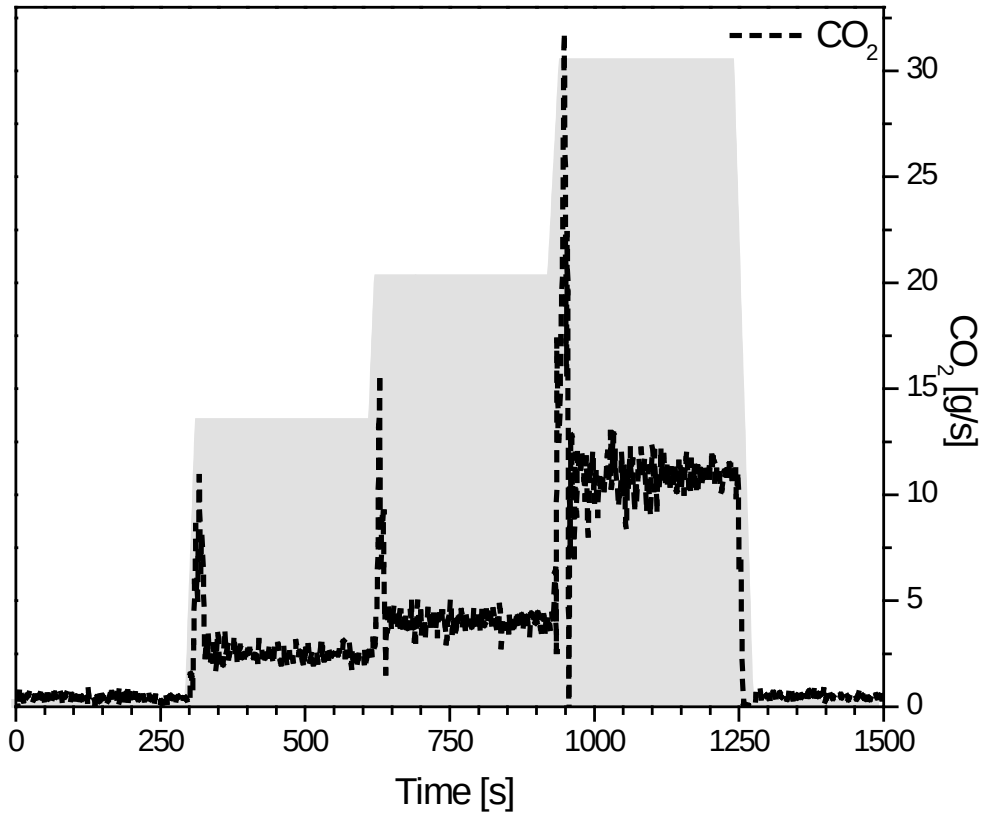
Fuel Consumption



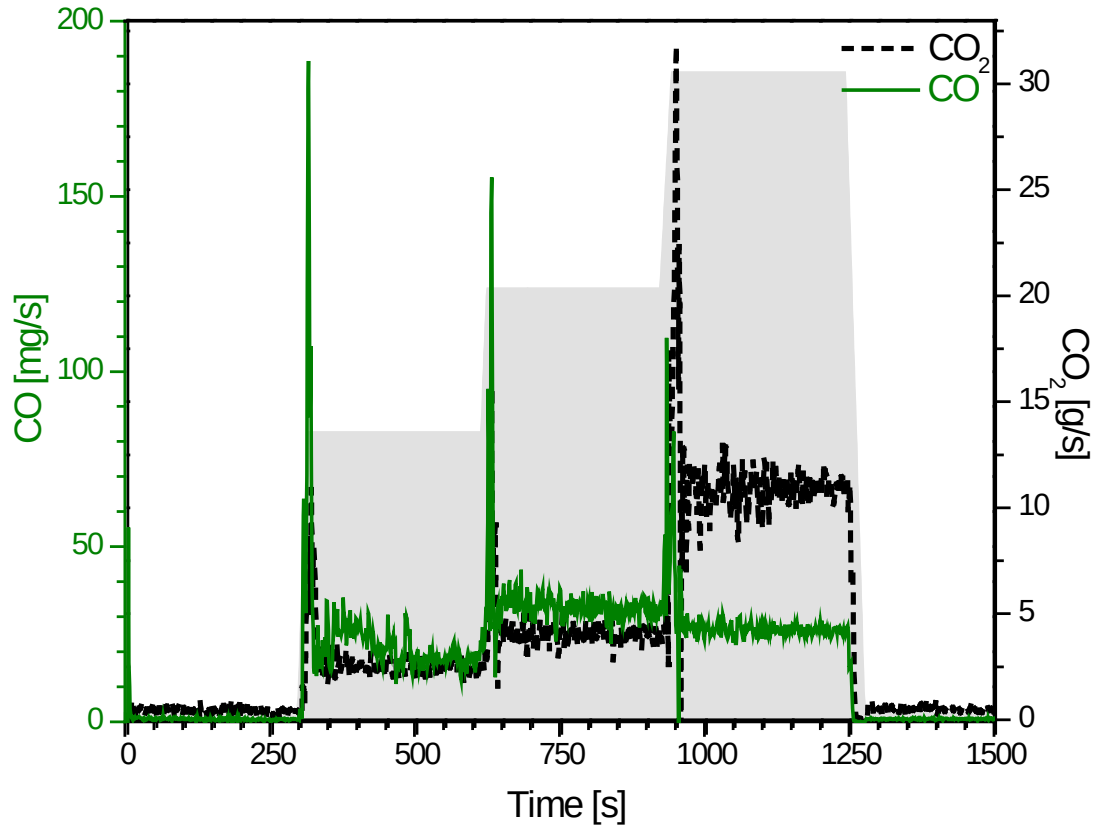
Fuel Consumption & Particle Number



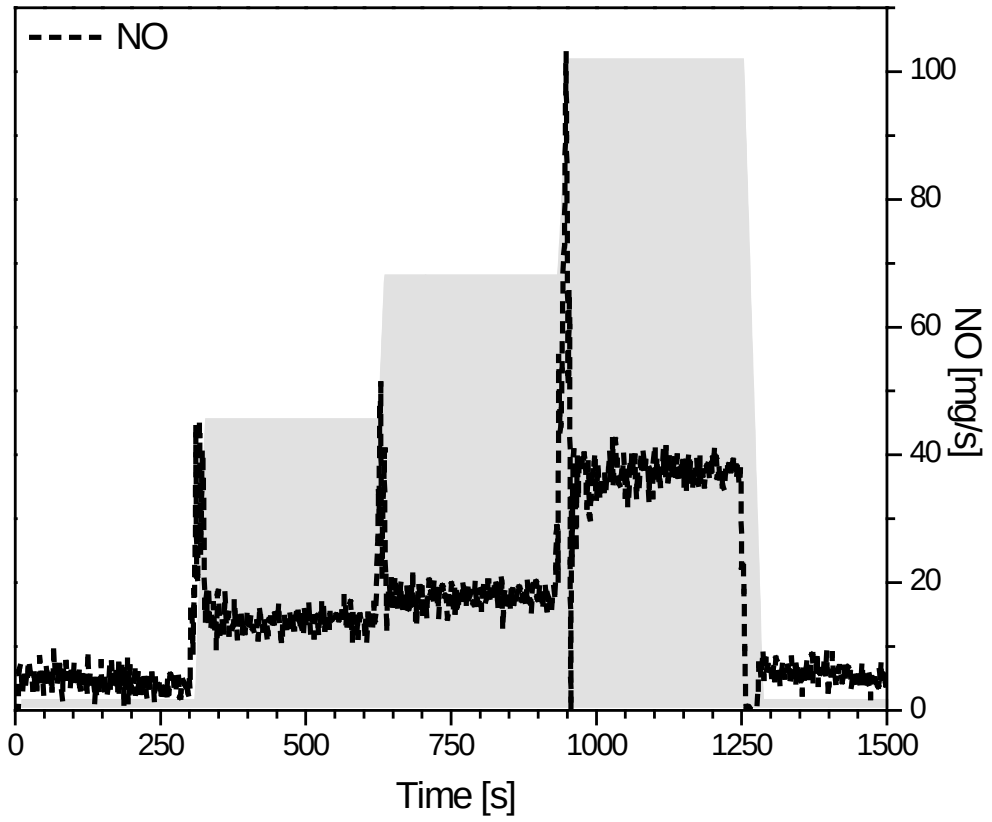
CO_2



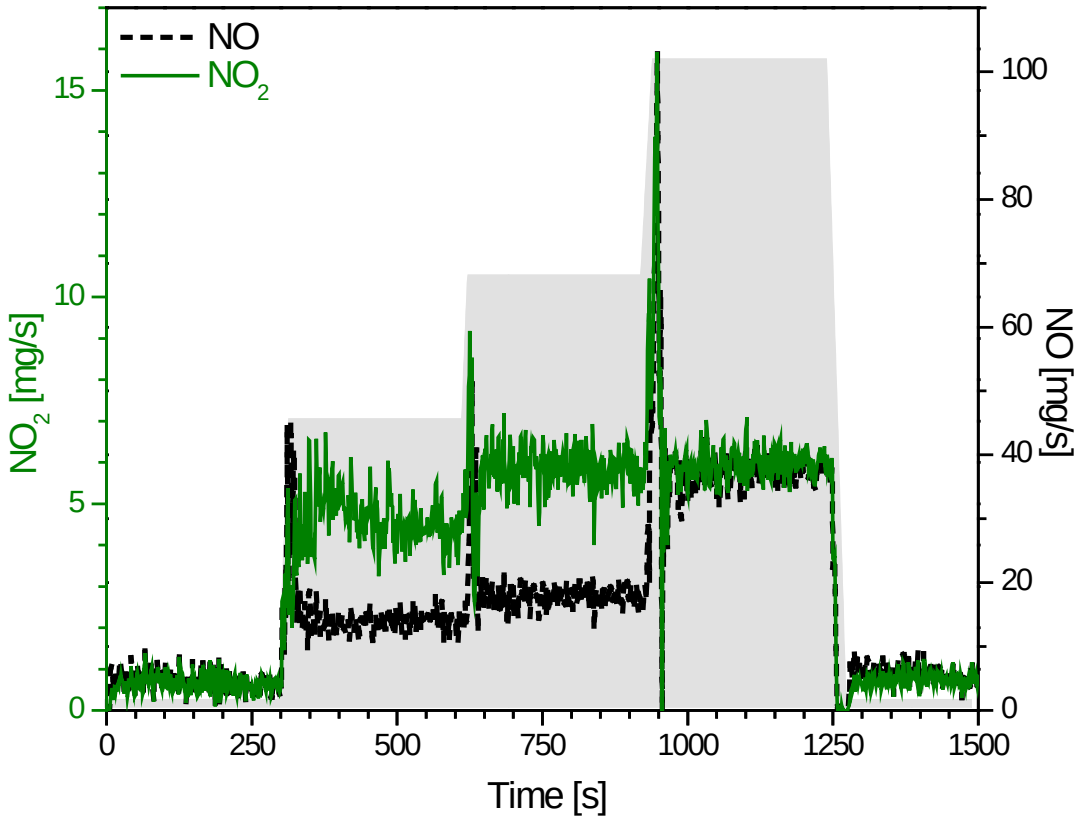
CO_2 & CO


CO [mg/s]
CO2 [g/s]
Time [s]
CO2
CO
0
50
100
150
200
0
5
10
15
20
25
30
0
250
500
750
1000
1250
1500

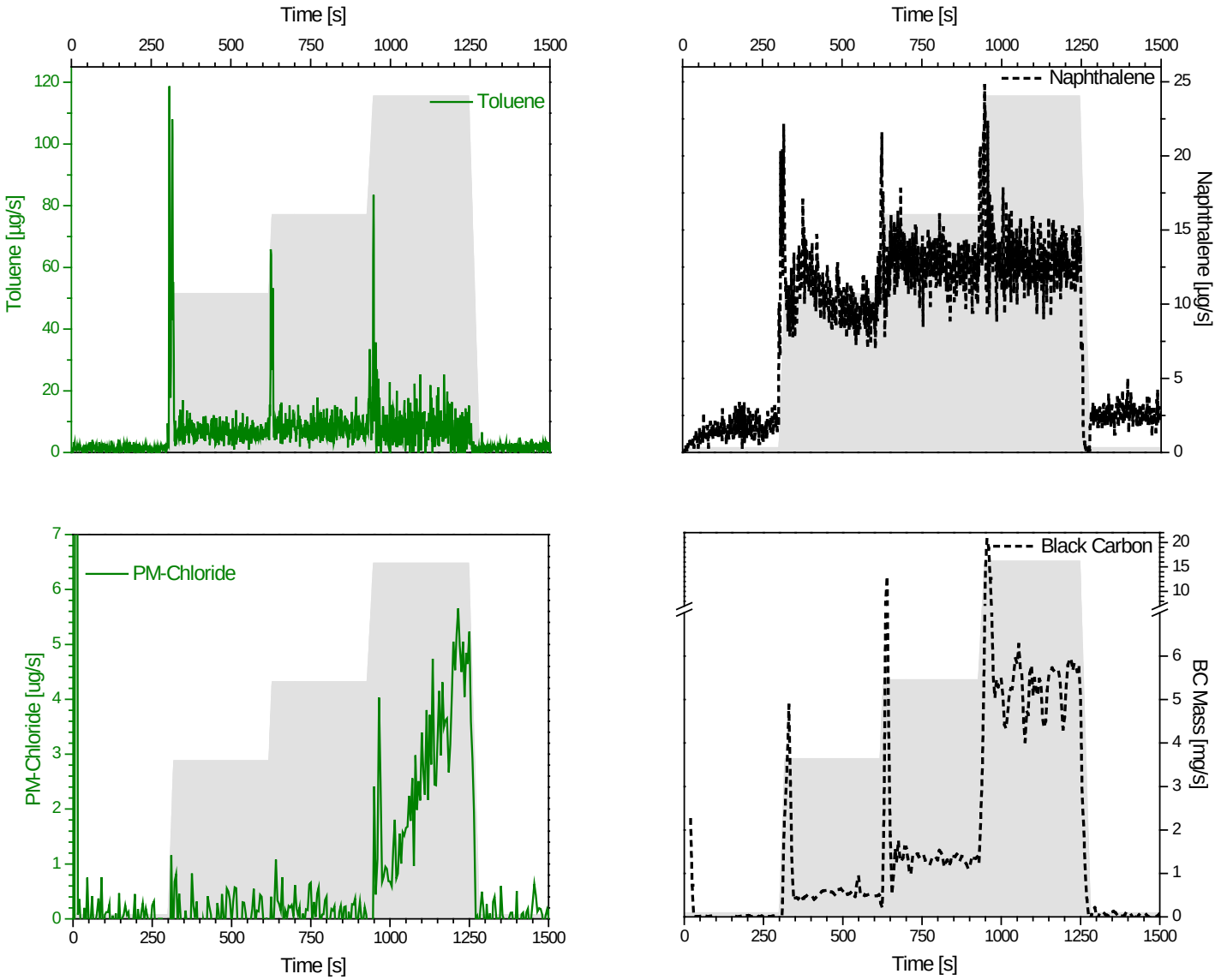
NO



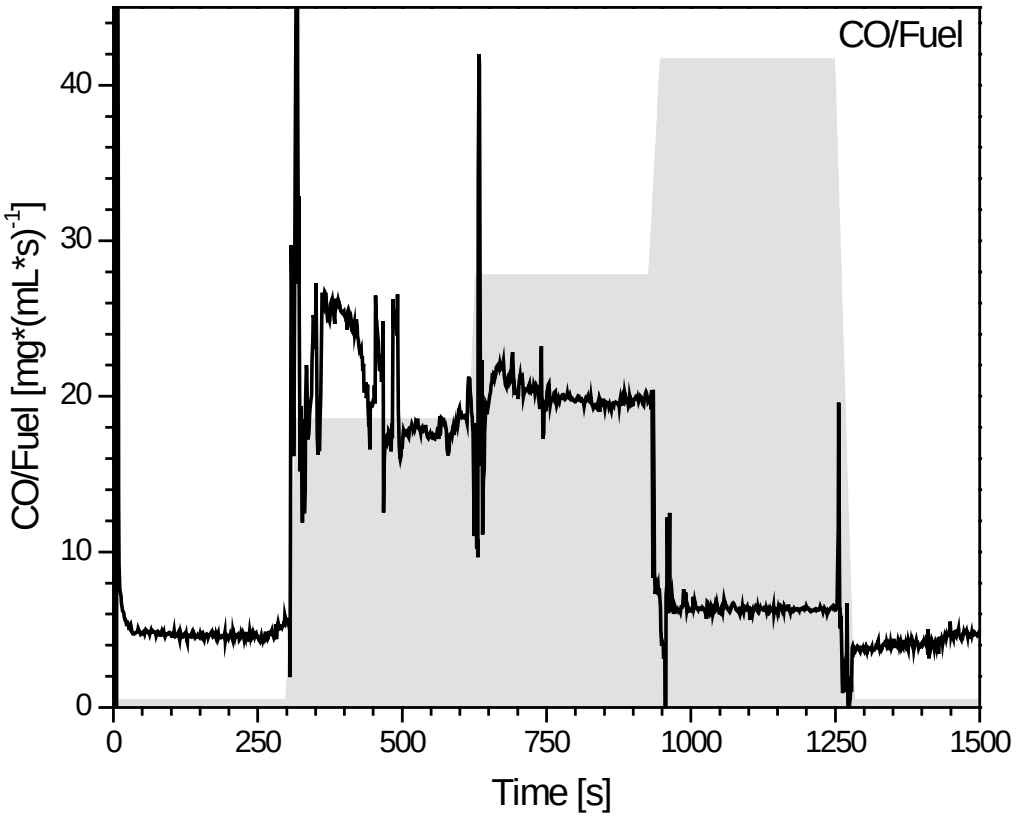
NO & NO_2


NO
NO2
NO2 [mg/s]
NO [mg/s]
Time [s]
0
5
10
15
0
20
40
60
80
100
0
250
500
750
1000
1250
1500

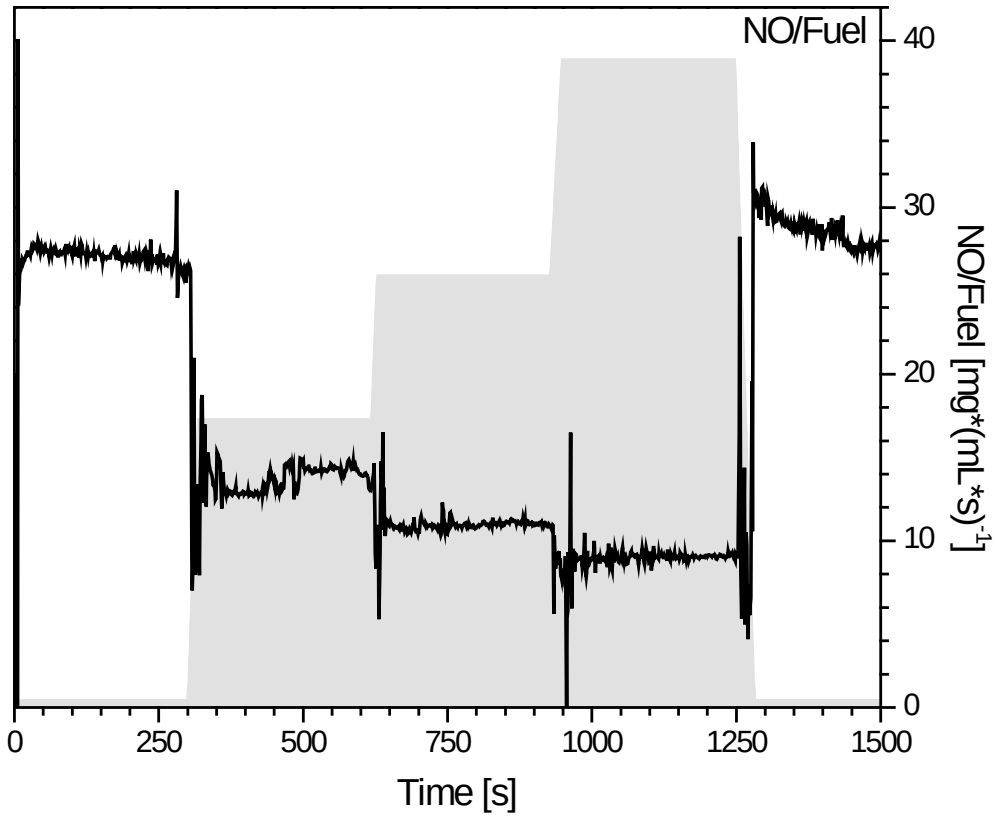
Time-resolved Emission



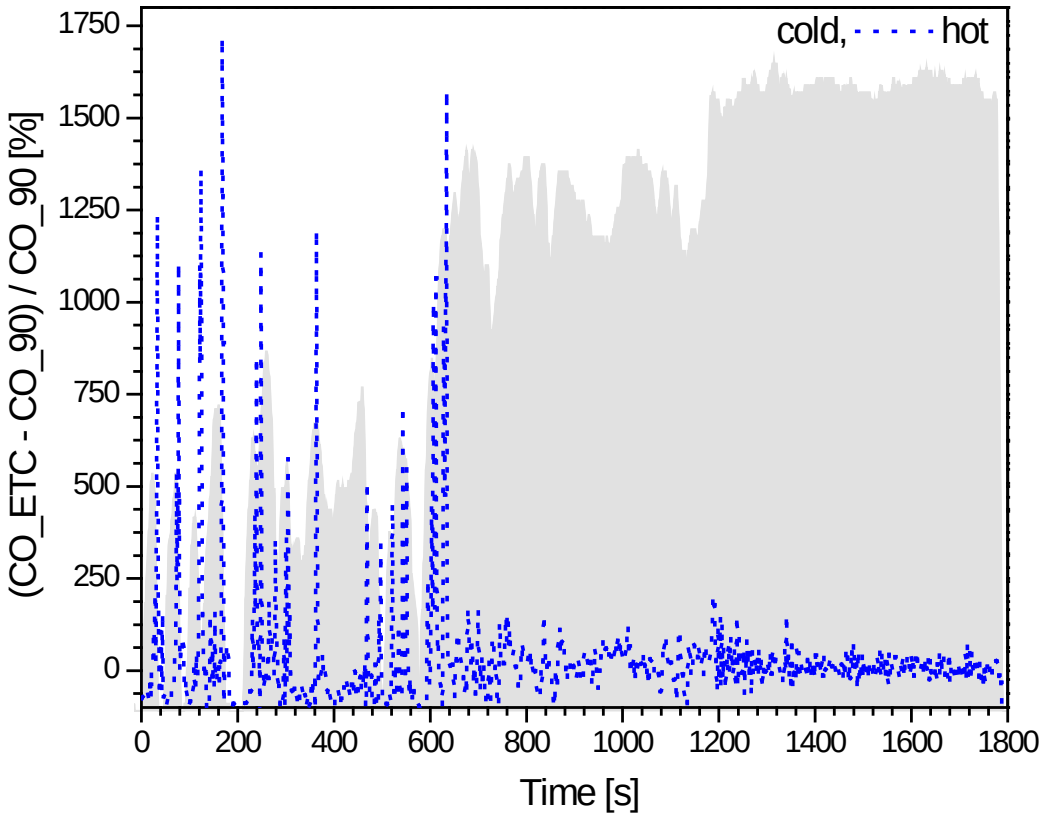
CO / Fuel


CO/Fuel
CO/Fuel [mg*(mL*s)-1]
Time [s]
0
10
20
30
40
0
250
500
750
1000
1250
1500

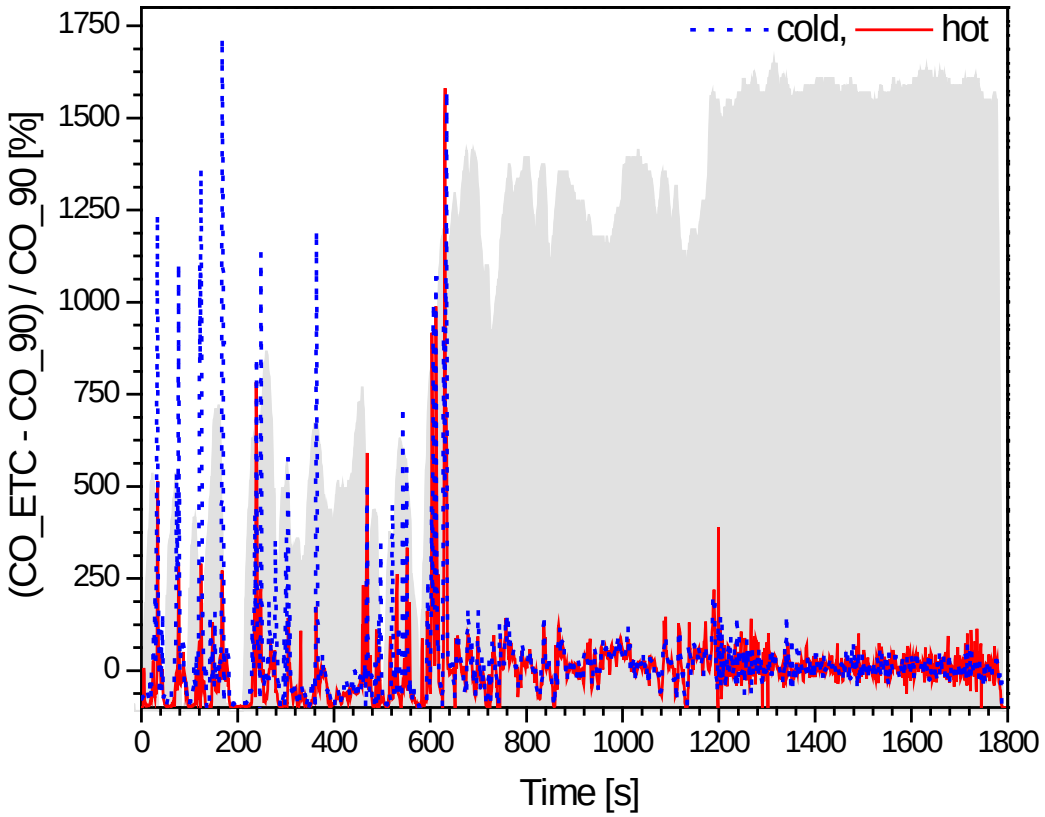
NO / Fuel


NO/Fuel
0
250
500
750
1000
1250
1500
Time [s]
0
10
20
30
40
NO/Fuel [mg*(mL*s)-1]

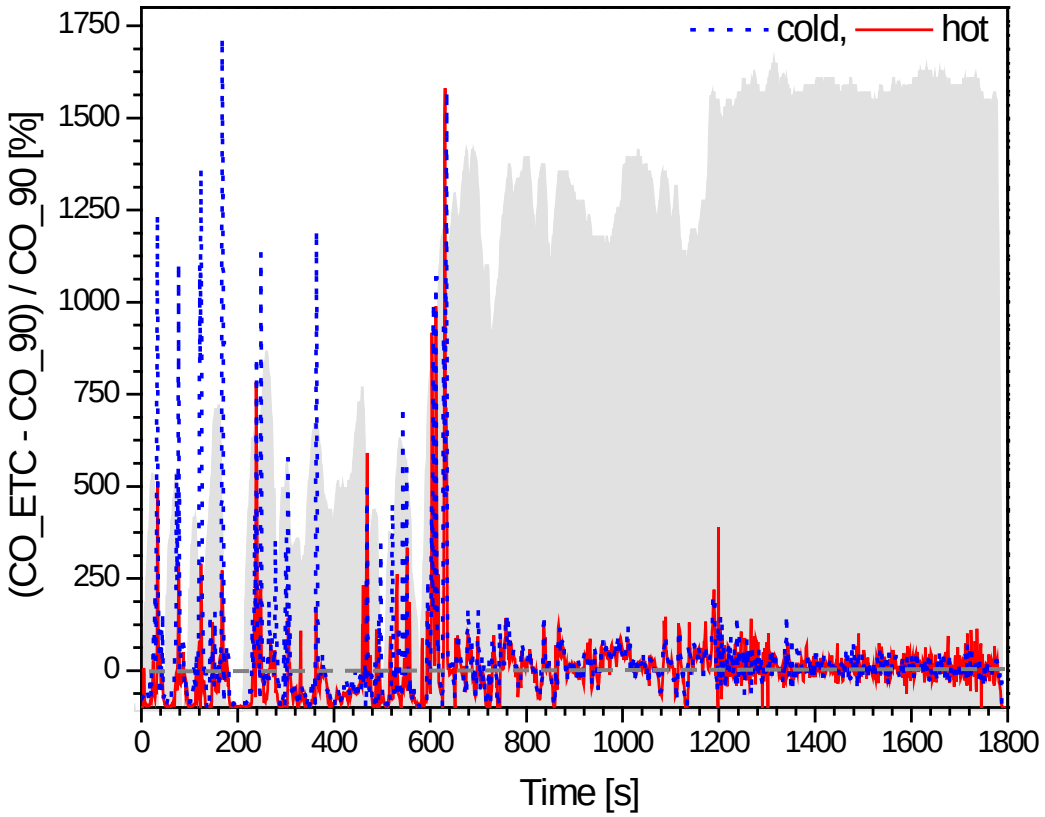
Cold/Hot Start norm. High Speed



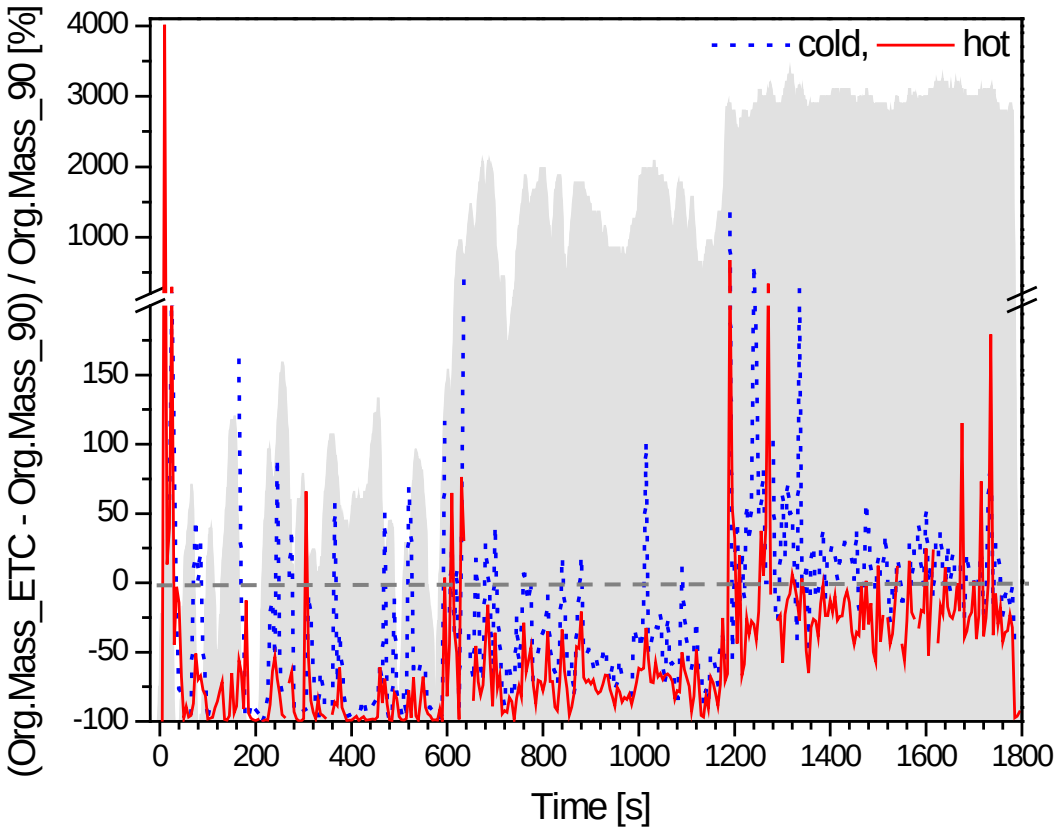
Cold/Hot Start norm. High Speed



Cold/Hot Start norm. High Speed



Cold/Hot Start norm. High Speed



Cold/Hot Start norm. High Speed