Formation of “white soot” by diesel cars equipped with particle filters

Christian Ehlers[1], D. Klemp[1], F. Rohrer[1], A. Wahner[1], H. Dörksen[2], S. Simon[2], L. Menger[3], R. Strey[3]

In urban areas one of the main particle sources is road-traffic, especially the emissions of particles from diesel-cars. For new diesel-cars particle traps have been established to reduce the particle emissions.

WHITE SOOT

For diesel-cars without a particle trap a filter sample taken at the exhaust pipe will be black. When sampling at the exhaust pipe of a modern diesel-car equipped with a particle trap the filter will remain white, but when the sampling is done with a cooled filter (approx. 5°C) the filter will gain in weight. The material which is sampled on the filter is called by us “white soot”. For further clarification the filter samples were analyzed using the EC/OC-Method.

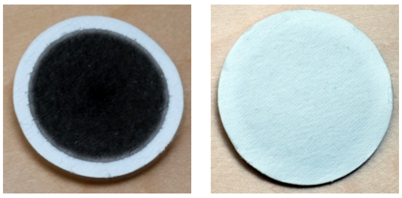


Figure 1: Black soot (left), white soot (right)

The EC/OC-Method

For the analysis of aerosol samples a method to determine the organic and elemental carbon content was developed. The first methods to analyze the carbon content of aerosol samples have been developed years ago [*Cadle et al.*, 1980]. Based on this principle an optimized system to analyze the carbon contents of ambient air samples as well as exhaust samples was developed in Research Center Jülich.

Samples are heated in an oxygen-atmosphere up to max 800°C (see Figure 2). Organic carbon compounds (**OC**) are evaporated and oxidized in a Pt-catalyst at 500°C. Elemental carbon (**EC**) is directly oxidized in the oven at higher temperatures. The resulting concentrations of CO_2 and H_2O are detected by a cavity-ringdown-spectrometer. Using this highly sensitive detection-method minimal sample mass was reduced to 3 µg.

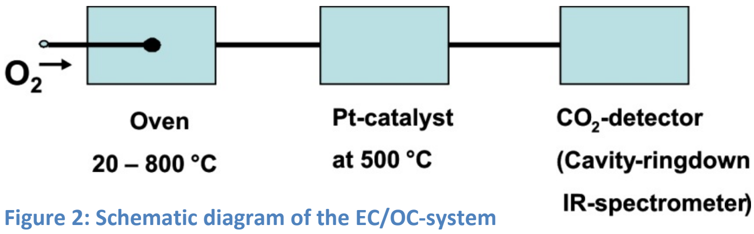


Figure 2: Schematic diagram of the EC/OC-system

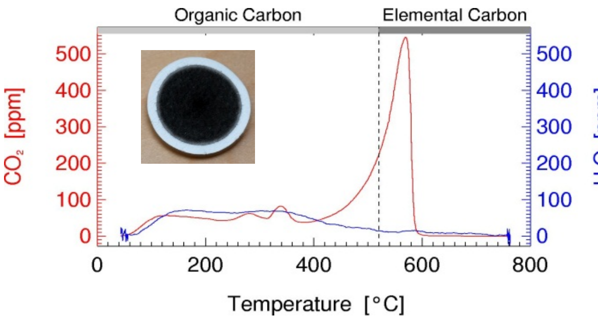


Figure 3: Thermogram of black soot

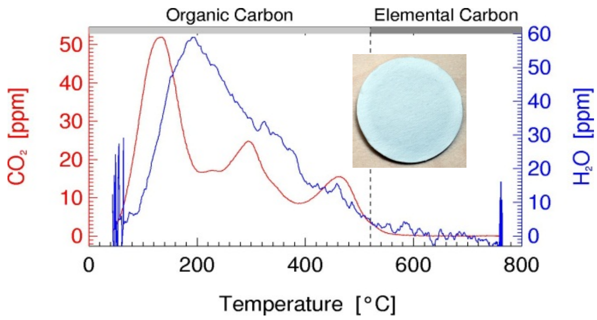


Figure 4: Thermogram of “white soot”

The OC- and EC-fractions are determined by the temperature profile of the oven and the water concentration. Figure 4 shows comparable concentrations of CO_2 and H_2O for the OC compounds whereas the EC compounds are not accompanied by H_2O-signals.

[1] Forschungszentrum Jülich – IEK8 Troposphäre – correspondence: c.ehlers@fz-juelich.de
[2] University of Cologne
[3] Trier University of Applied Sciences

Conditions in a particle trap

The "black soot" thermogram showed CO_2-Signals originating from organic compounds evaporating at temperatures between 100 and 500°C. In normal operation the temperatures in the particle trap of a diesel car are in the same region. Only every few hours the trap is heated up (e.g. by injection of additional fuel) to regenerate the trap by combustion for some minutes.

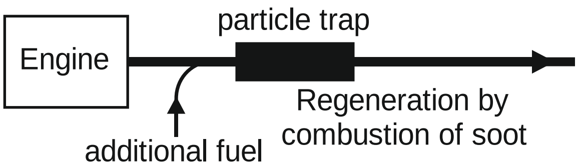


Figure 5: Schematic diagram of a particle trap

During the period of normal operation particles are collected in the particle trap. The temperatures in the particle trap are high enough so that organic compounds can evaporate and pass the trap. As mentioned before, these compounds can be sampled using a cooled filter.

First evaluation

For evaluation of the hypothesis that white soot is also formed in the ambient air, an experiment running a modern diesel car equipped with a particle trap was performed in a confined environment. The concentrations should be comparable to inner-city and hotspot-conditions, the runtime of the experiment should be approximately one hour, to have enough sampling time for the collection of filter samples. And furthermore, there should not be serious changes in temperature and humidity. A big garage (4000m³ Volume) was found to be closest to these needs.

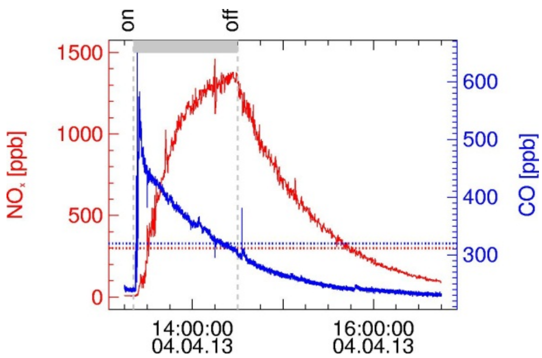


Figure 6: Gas-phase concentrations in the "chamber" (dotted lines represent averaged concentrations from Bonn Bad Godesberg, hotspot concentrations in cities are even larger)

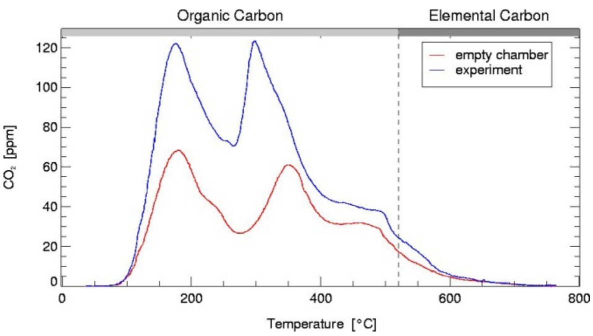


Figure 7: The OC-fraction shows a significant rise between the empty garage (red) and the experiment (blue).

	Total [µg/m³]	Elemental Carbon [µg/m³]	Organic Carbon [µg/m³]
Empty chamber	24.6	2.7 ± 0.6	21.9 ± 1.2
Experiment	41.8	3.8 ± 0.8	37.8 ± 1.6
Rise	17.2	1.1	15.9

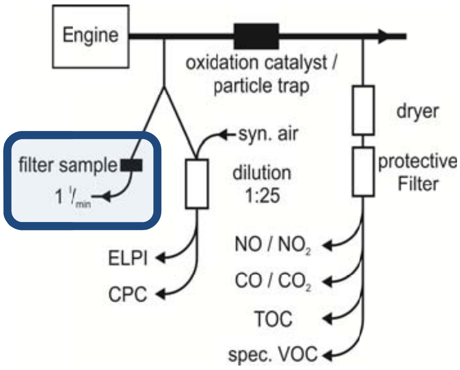
The concentrations determined via the EC/OC-Method showed a significant increase in organic compounds, whereas the change in EC concentrations cannot be regarded as significant.

These results lead to the conclusion, that modern diesel-cars equipped with a particle trap are still emitting organic compounds which lead to a "production" of particles in the atmosphere. A possible solution could be the implementation of an additional oxidation catalyst behind the particle trap to oxidize the organic emissions. We also investigated, if the use of alternative fuels could be another possible solution.

Alternative Fuels

Within a cooperation-project with the University of Cologne and the University of Applied Sciences Trier the influence of alternative Fuels emission properties of diesel-cars was investigated.

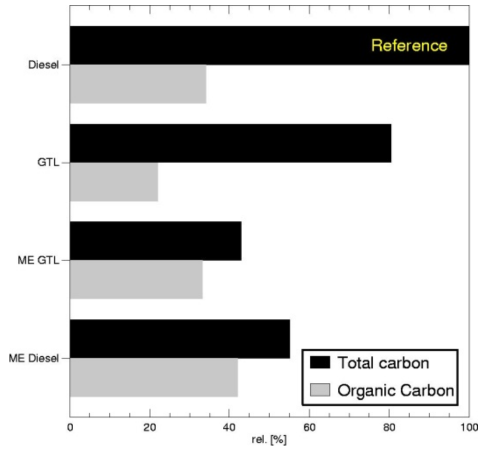
At the University of Cologne Water-in-Diesel-Microemulsions were developed [*Bemert and Strey*, 2007]. These microemulsions are stable and can be used like conventional diesel without further modifications of the car. At the University of Applied Sciences Trier studies with a test-engine running on a diesel-water emulsion showed reductions in Particle mass up to 40% [*Simon et al.*, 2013].



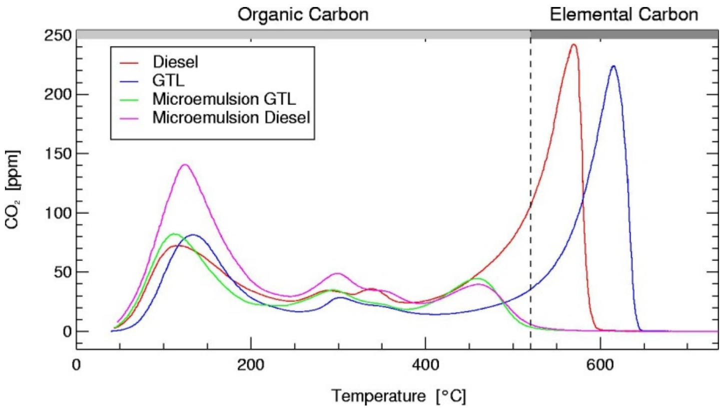
the exhaust-

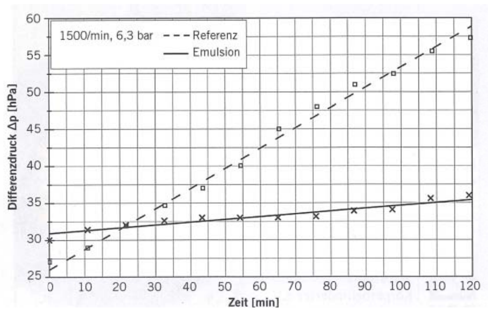
For the study presented here a standard car (BMW 530D E39) was run on Diesel, GTL and the corresponding microemulsions. The car was run on a chassis-dynamometer following the WLTP test cycle. The filters for the results presented here were sampled directly behind the engine in front of the particle trap as shown in Figure 8.

Our study showed a significant reduction in particle mass by a factor of two. Furthermore, a change in particle composition was observed (Figure 10). The EC/OC-analysis revealed that the reduction in particle-mass was attributed to a nearly complete elimination of the elemental carbon (black soot), whereas the organic carbon compounds showed even a slight increase. These results agree very well with results from the engine lab. In Trier they found a significant reduction in the rise of differential pressure over the particle trap as shown in Figure 11. The reduced differencial pressure can be explained with the lowered emissions of elemental carbon compounds.



tal-mass of





er

Conclusions

Our studies showed that modern diesel cars equipped with a particle trap emit organic compounds which form “white soot” in ambient air.

The use of microemulsion-fuels can be advantageous for cars equipped with particle traps as the reduction of elemental carbon can prolong the span between the necessary regenerations of the particle trap and in consequence save fuel.

Furthermore, the results showed for all fuels the necessity to reduce the emissions of low-volatile organic compounds to avoid the generation of “white soot”. Possibilities which should be further investigated would be the implementation of an additional oxidation catalyst behind the particle filter or the reduction the amount of organic coating on the particles by means of engine management.

Literature

Bemert, L., and R. Strey (2007), Diesel-Mikroemulsionen als alternativer Kraftstoff, in *Bunsen Tagung*, edited.

Cadle, S. H., P. J. Groblicki, and D. P. Stroup (1980), Automated carbon analyzer for particulate samples, *Analytical Chemistry*, *52*(13), 2201-2206.

Simon, C., H. Dörksen, and H. Dornbusch (2013), Schadstoffreduzierung durch Diesel-Wasser-Emulsionen, *MTZ - Motortechnische Zeitschrift*, *1*, 72-77.

Formation of „white soot“ by diesel-cars equipped with particle filters

2013-06-24 | Christian Ehlers, D. Klemp, F. Rohrer, A. Wahner, H. Dörksen, S. Simon, L. Menger, R. Strey

JÜLICH FORSCHUNGSZENTRUM

Formation of „white soot“ by diesel-cars equipped with particle filters

- Motivation
- The EC/OC-method
- First evaluation
- Influence of alternative fuels
- Conclusion

Motivation

- investigation of the consequences of road-traffic emissions for air quality in urban areas
- emissions from diesel-cars represent a substantial source for particles

➢ particle traps to reduce emissions

black soot from diesel-car without particle trap

Motivation

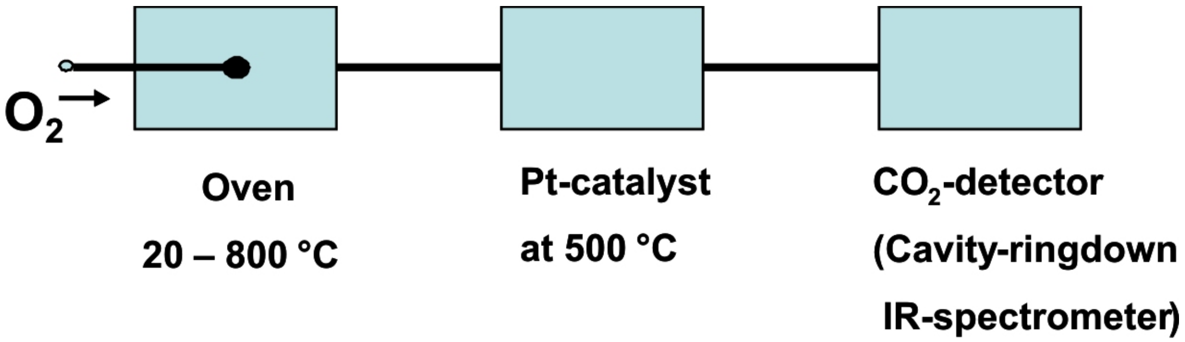
- investigation of the consequences of road-traffic emissions for air quality in urban areas
- emissions from diesel-cars represent a substantial source for particles

➢ particle traps to reduce emissions

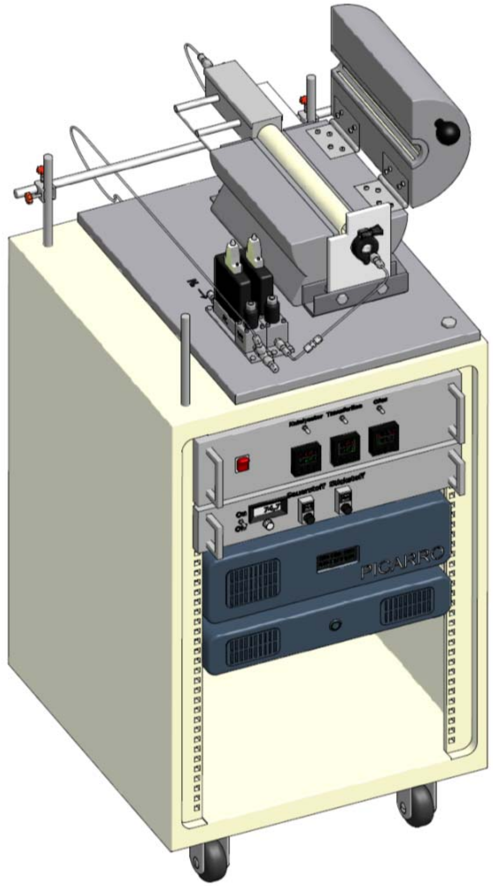
sample taken behind a particle trap
cooled filter → gain in weight

➔ "white soot"

The EC/OC-method

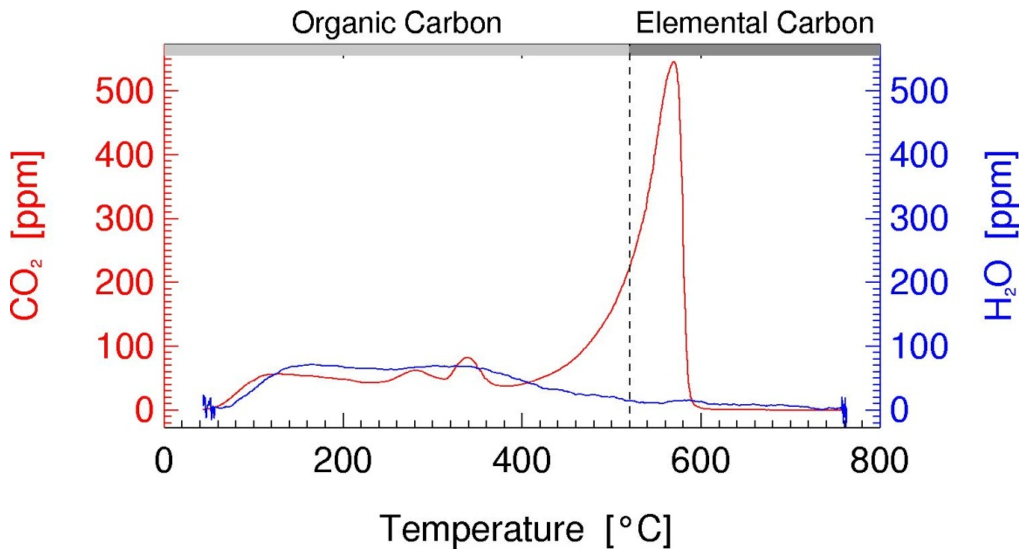


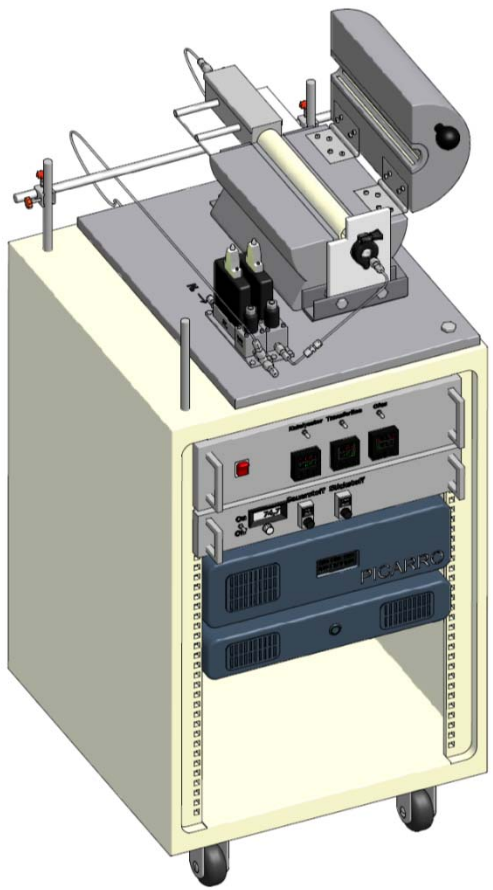
- quartz-filter-samples are heated (max. 800°C)
- carbon-compounds are oxidized in oxygen-stream
- detection of H_2O & CO_2 by cavity-ringdown



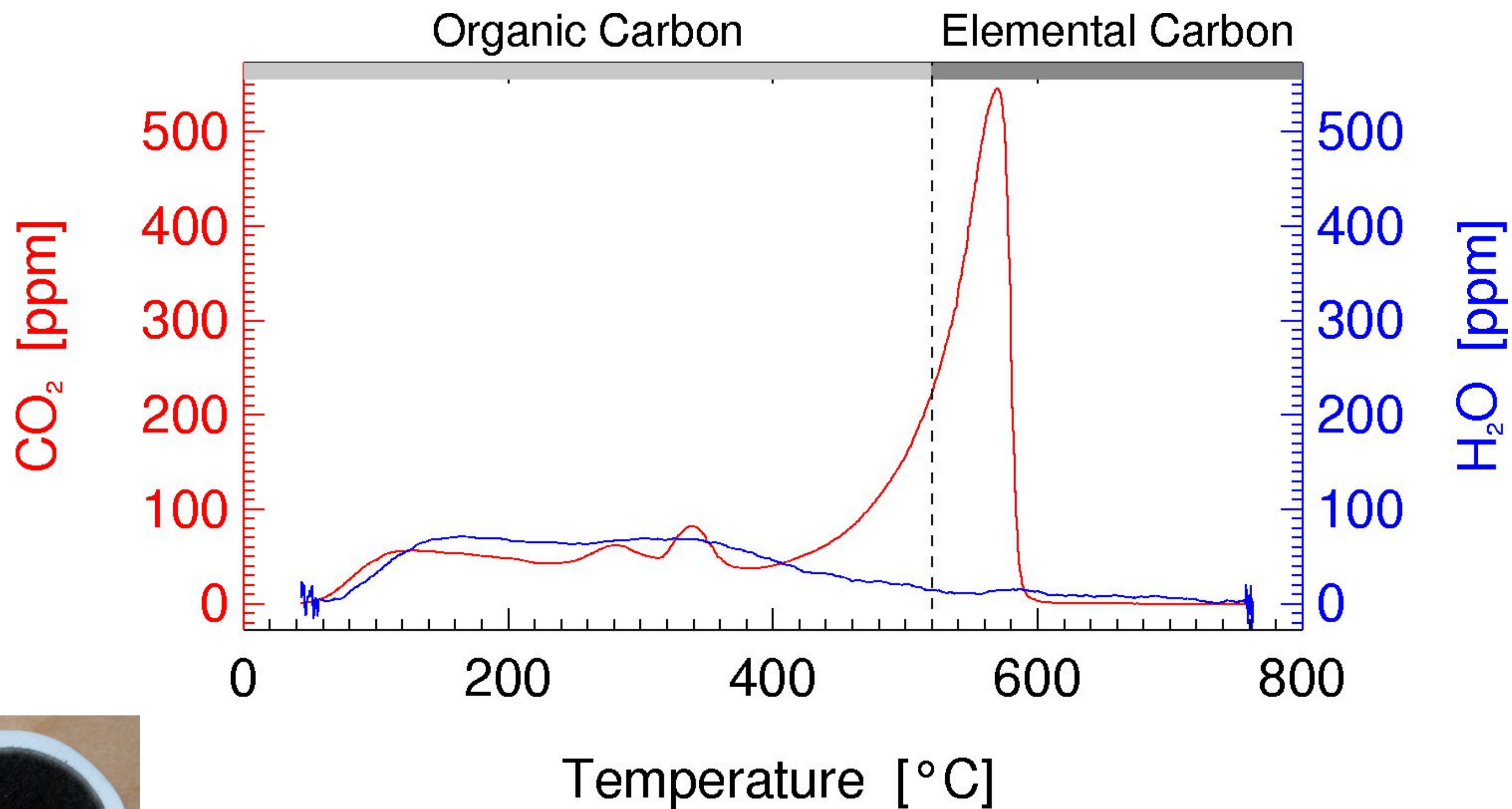
The EC/OC-method

- detection limit ≈ 3 µg C (1 µg EC / 2 µg OC)
- determination of organic (**OC**) and elemental carbon (**EC**) by temperature profile and water-concentration

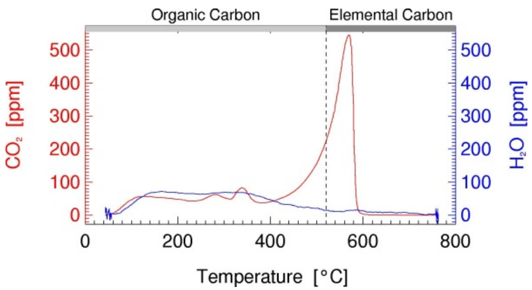


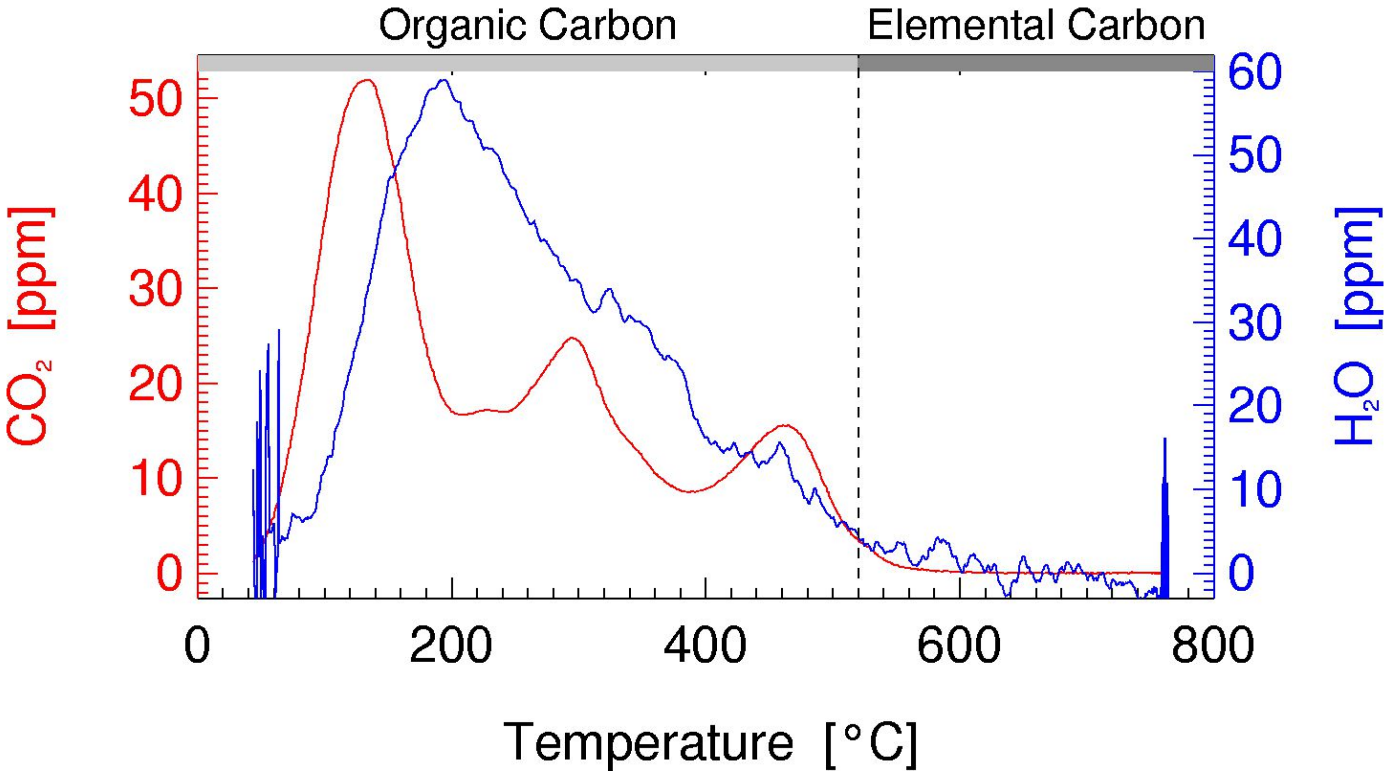


The EC/OC-method

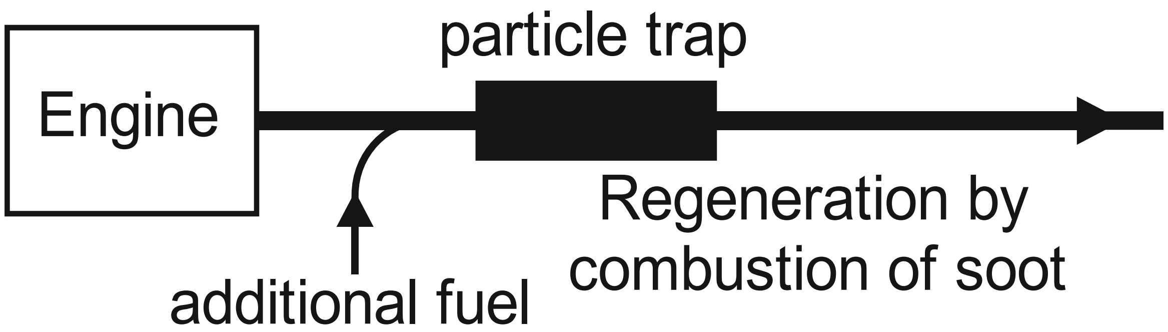


The EC/OC-method

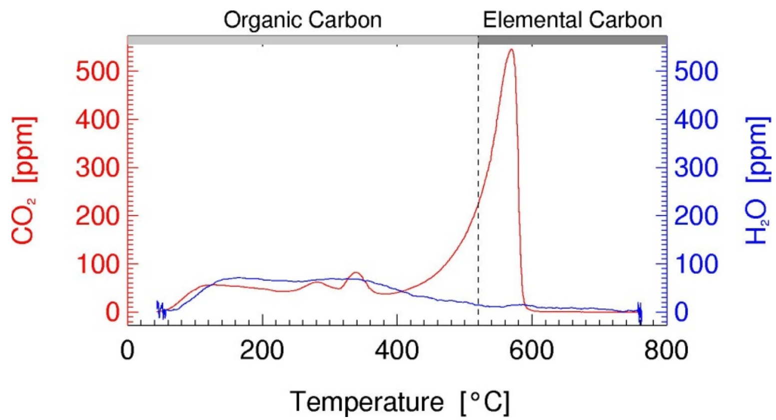




Particle trap

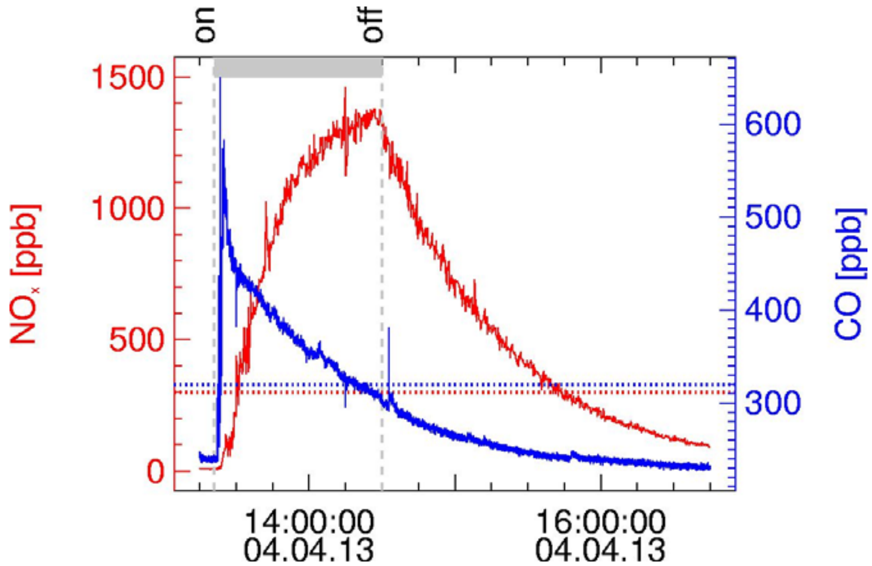


- regeneration (every few hours)
  - heating up to 500 – 600 °C to burn particles
- normal operation
  - temperatures in range of 100 – 500°
  - organic compounds can evaporate



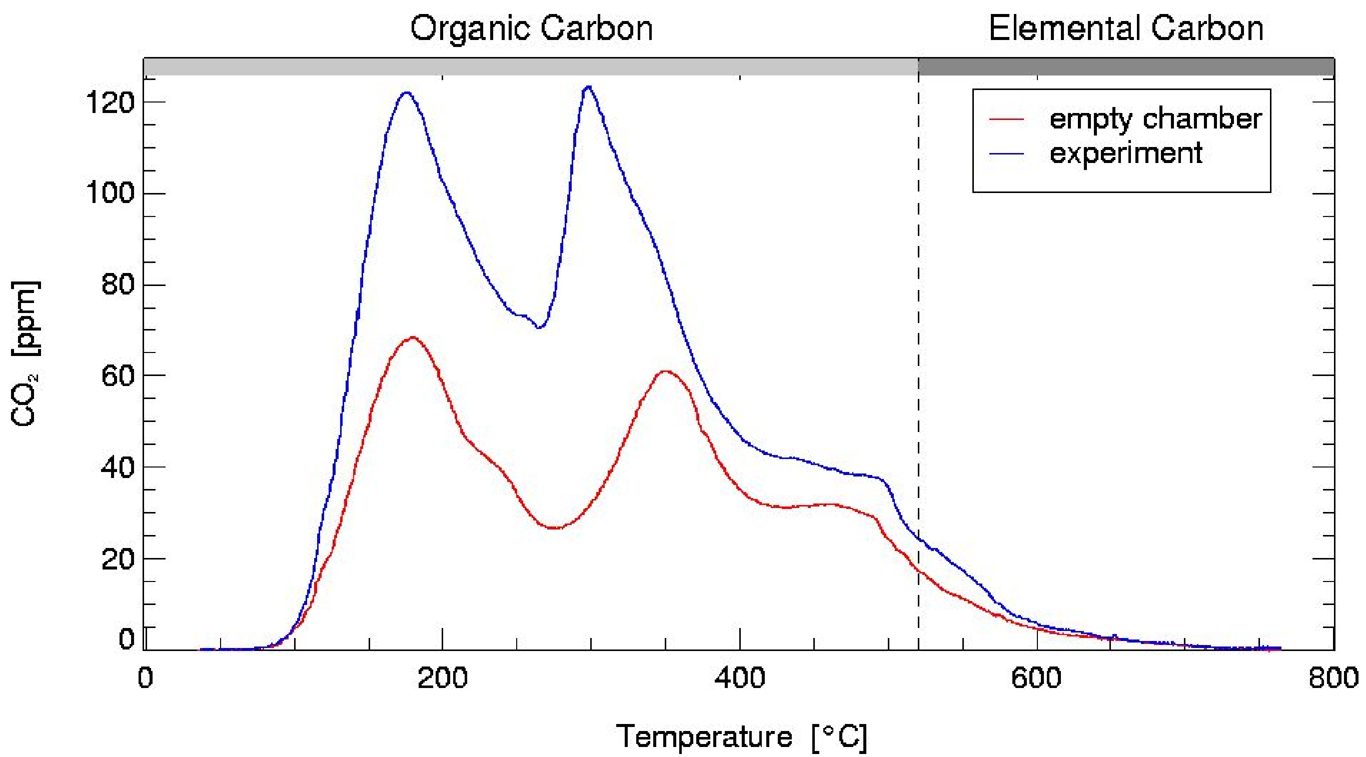
First evaluation

- test in a confined environment
  - concentrations comparable to inner-city conditions
  - runtime of approx. one hour
- diesel-car equipped with particle trap
  - ➢ tests showed no direct particle emissions from exhaust pipe above cutoff-limit of CPC (5 nm)



dotted lines: Bonn Bad Godesberg (mean values)

Particle mass (**EC/OC-method)**



	total-concentration [µg/m³]	elemental carbon-concentration [µg/m³]	organic carbon-concentration [µg/m³]
Empty chamber	24.6	2.7 ± 0.6	21.9 ± 1.2
Experiment	41.8	3.8 ± 0.8	37.8 ± 1.6
Rise	17.2	1.1	15.9

First evaluation - results

- diesel cars equipped with particle traps produce emissions leading to an increase in organic particle mass
- organic compounds are emitted
  - large hydrocarbons
  - not monitored by standard gas-phase analytics
  - “anthropogenic **secondary aerosols**” (without need for oxidation)

JÜLICH FORSCHUNGSZENTRUM

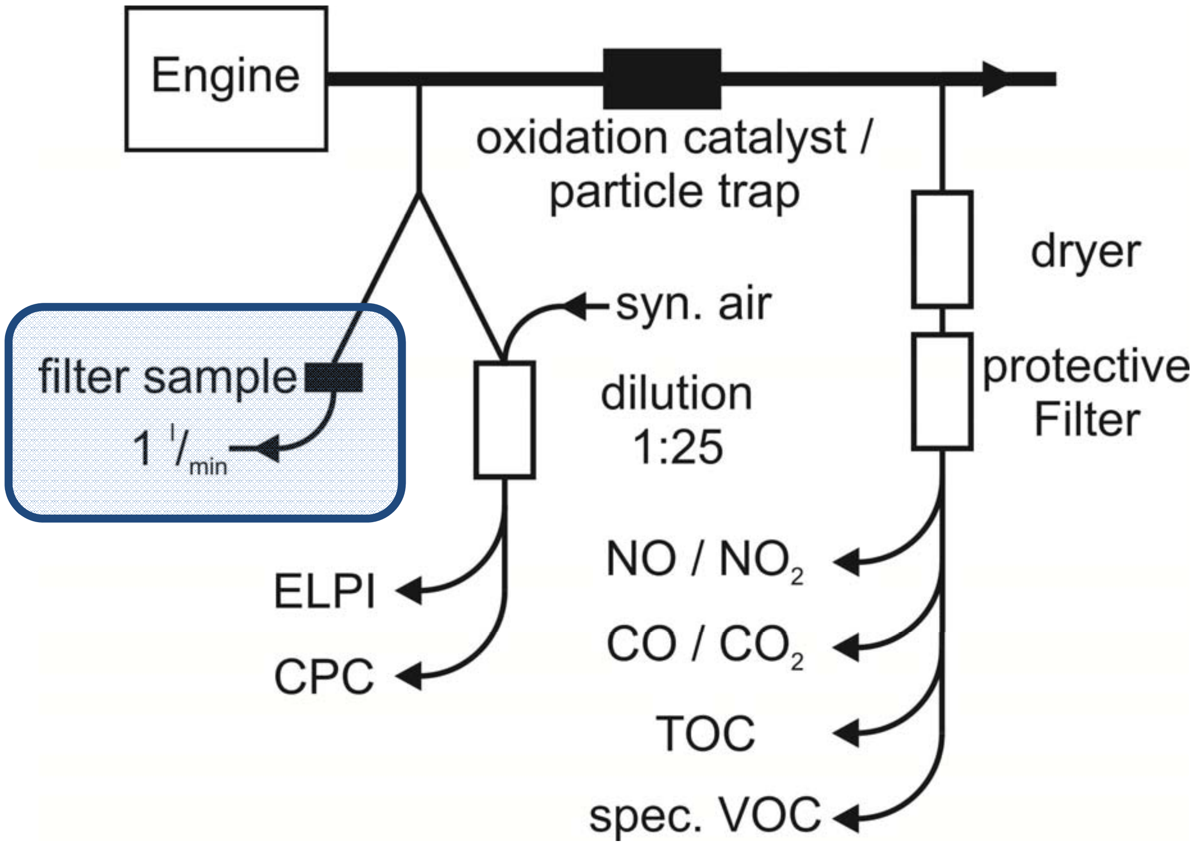
Alternative fuels

- water-in-diesel microemulsions
  - stable microemulsion
  - can be used like conventional diesel
  - no modifications on car / engine necessary
  - emission-reductions proven for test-engines (diesel-emulsion 10%):
    - PM reduction up to 40 %[1]

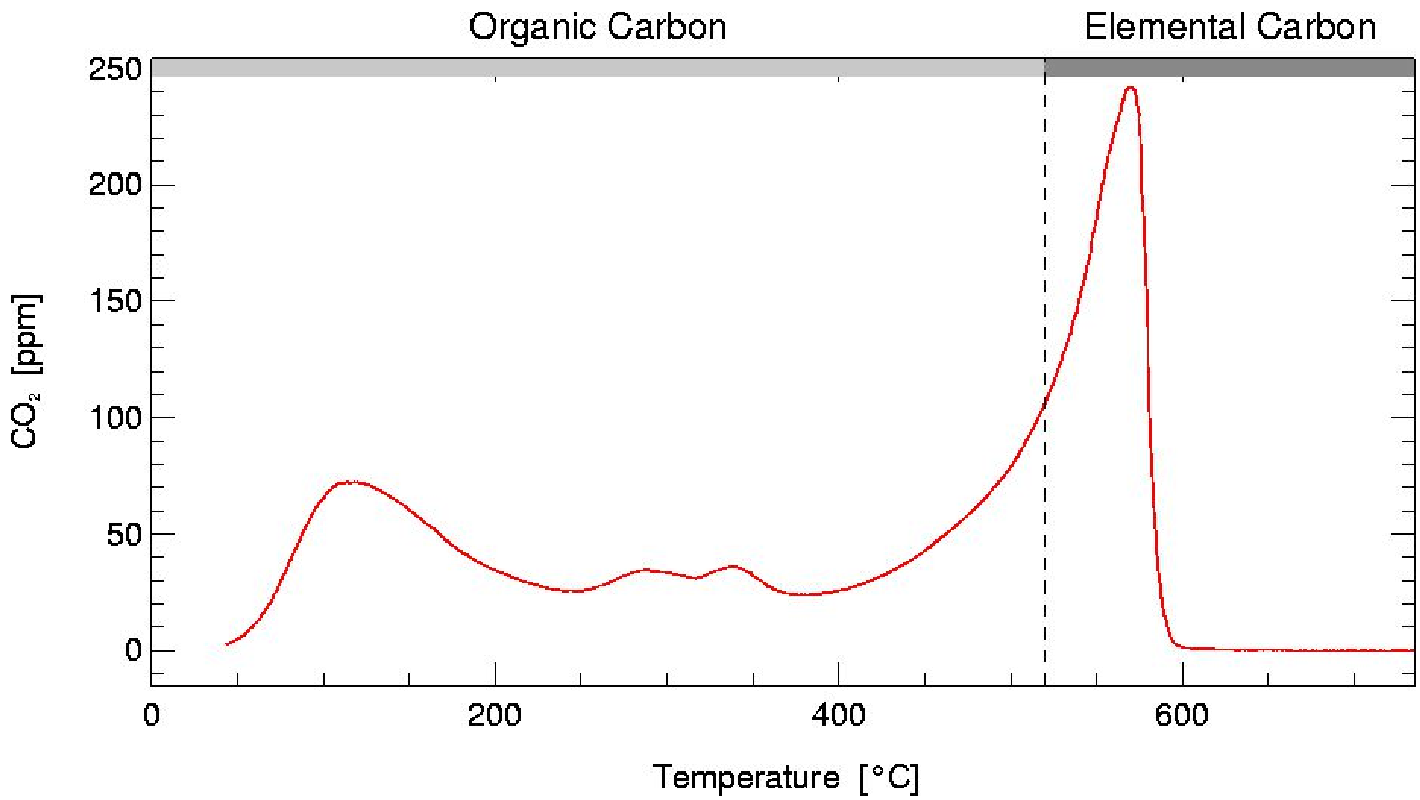
- Microemulsions
  - University of Cologne, Prof. R. Strey, L. Menger
- Test-stand
  - Trier University of Applied Sciences, Prof. C. Simon, H. Dörksen

[1][MTZ 01|2013, S. 72 – 77]

Alternative fuels – exhaust measurements

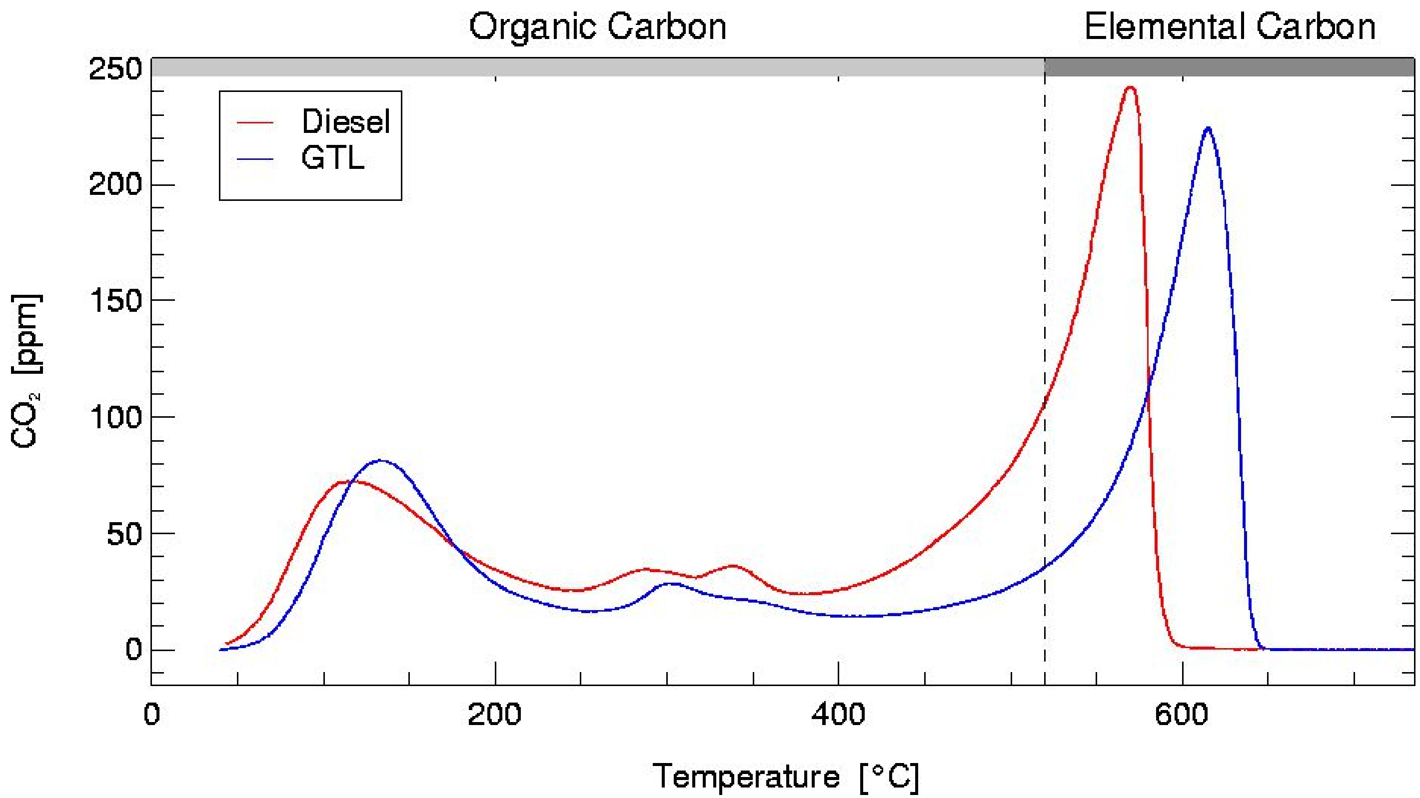


EC/OC - results

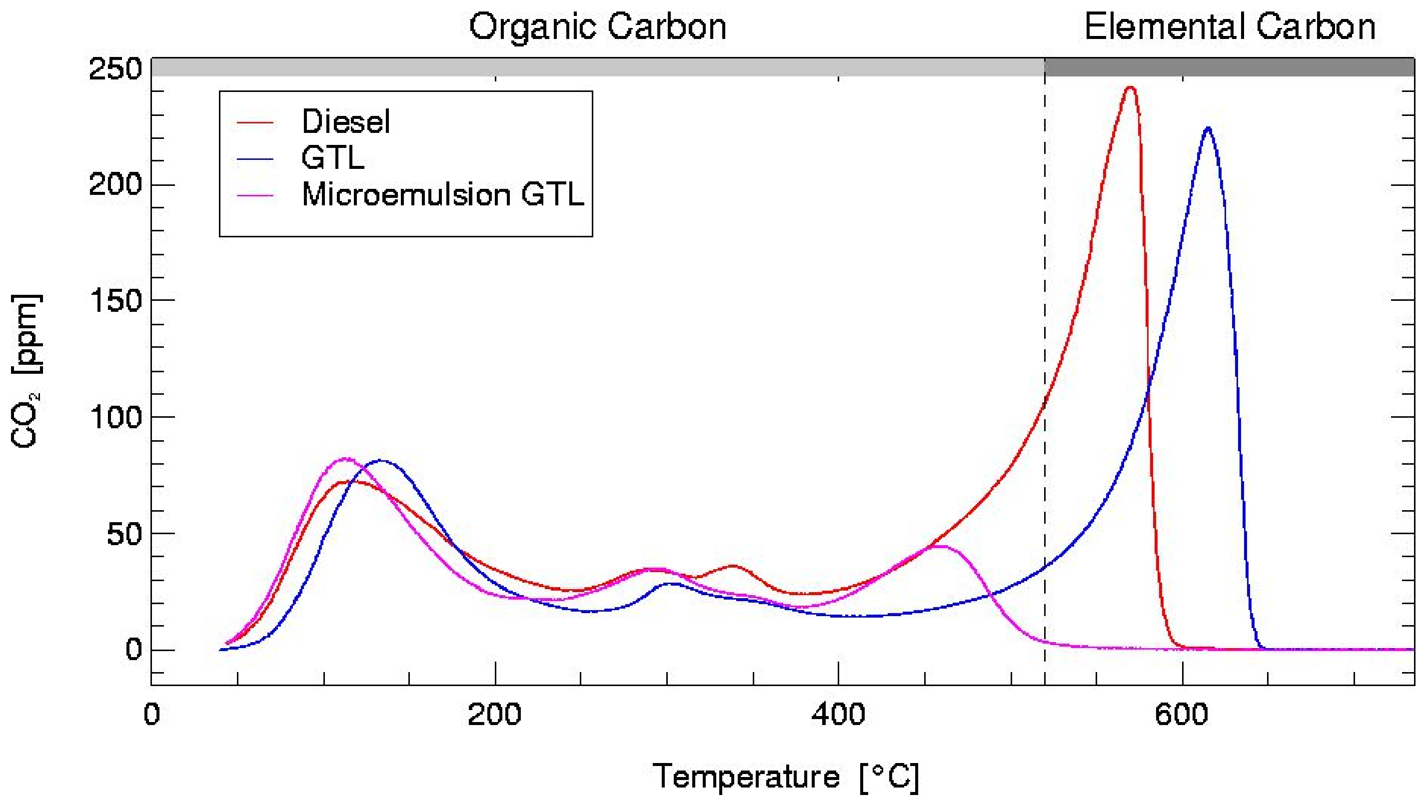


Mitglied der Helmholtz-Gemeinschaft

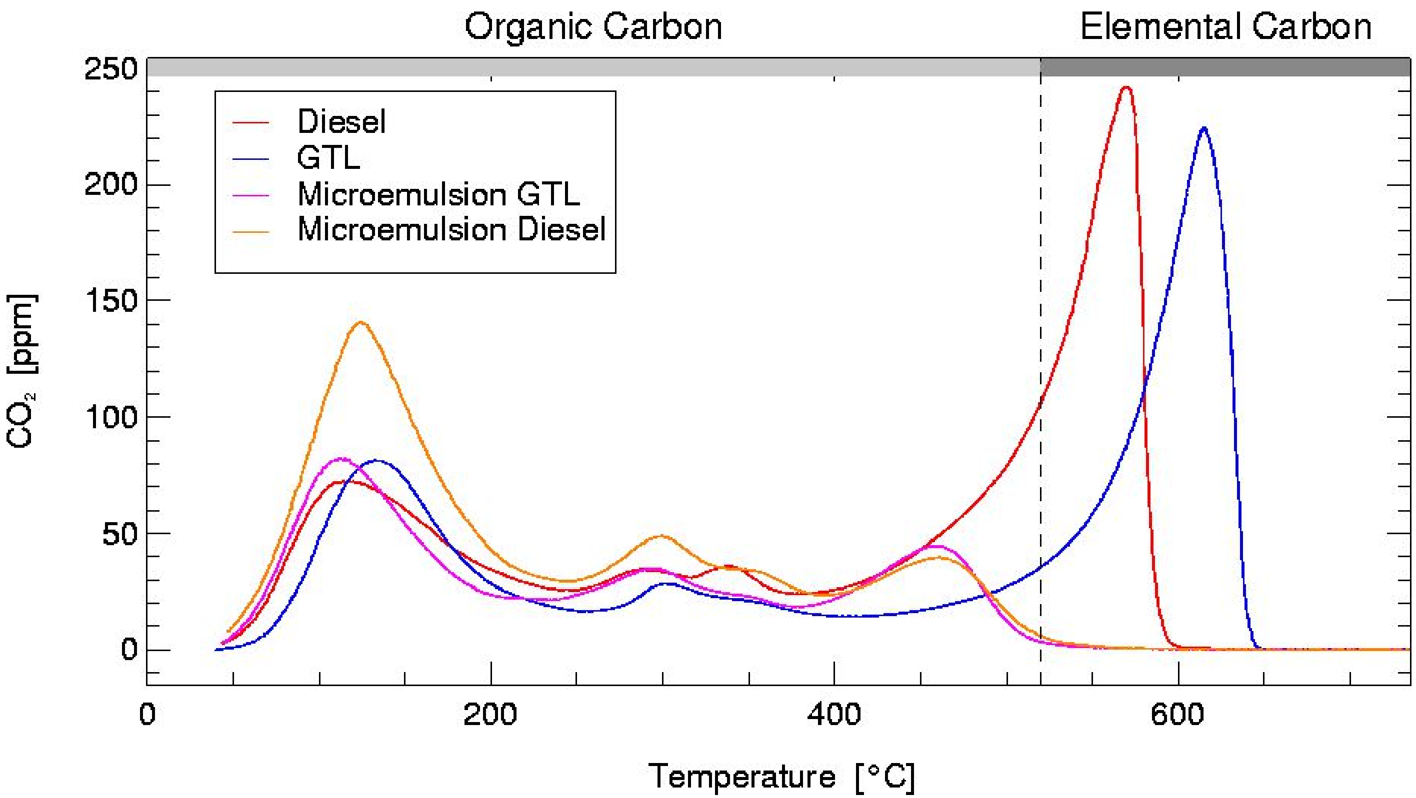
EC/OC - results



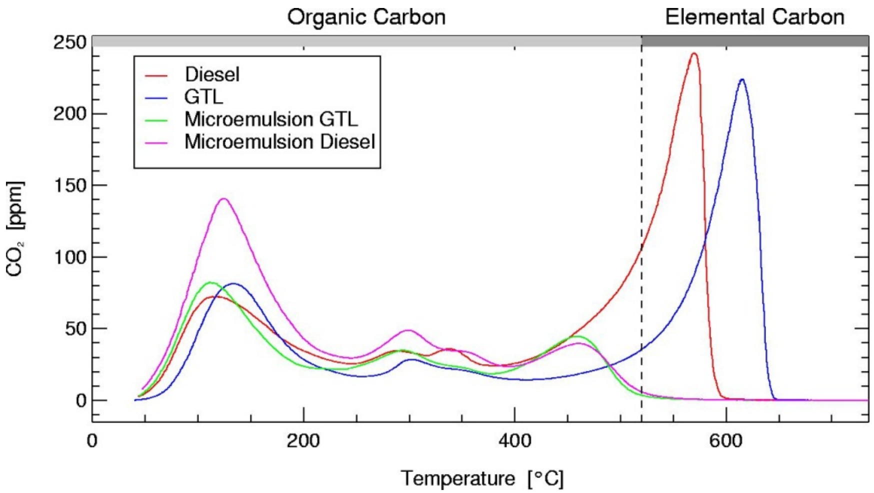
EC/OC - results

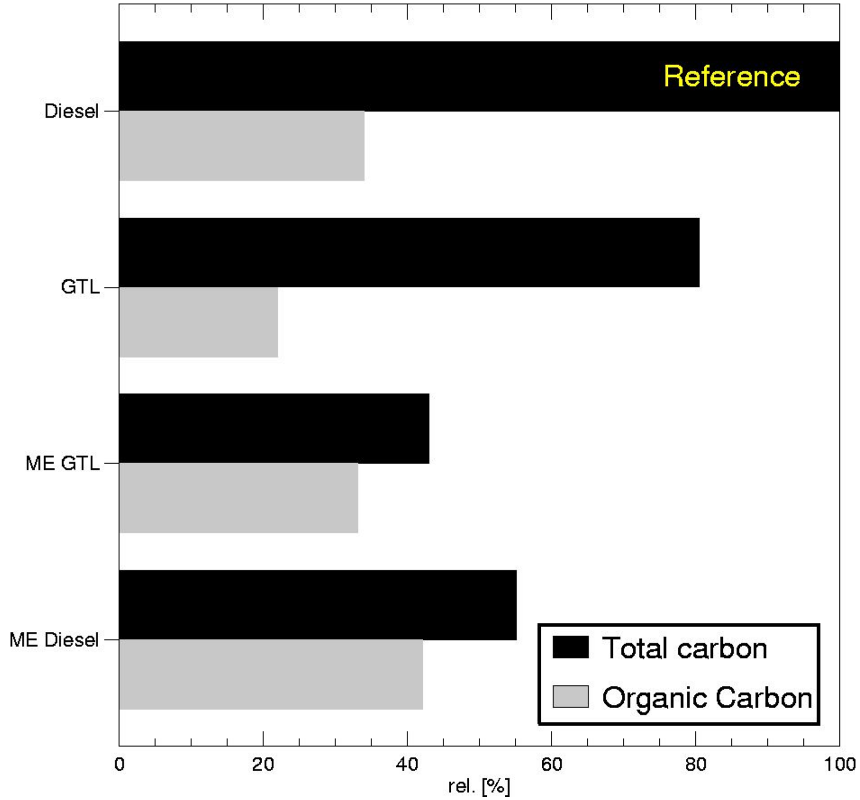


EC/OC - results



EC/OC - results





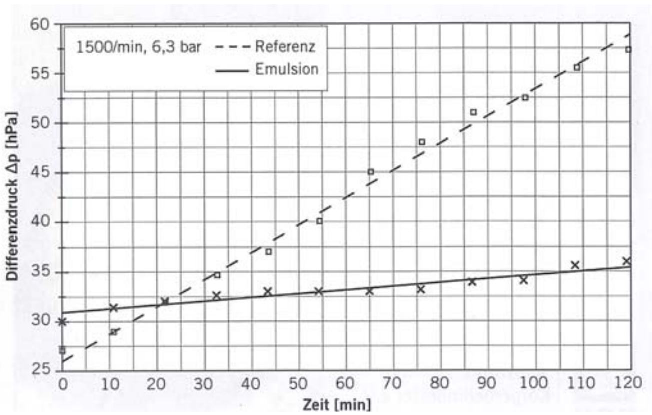
- Mass reduction by factor two with Microemulsions
- Reduction of elemental carbon emissions
- Nearly constant organic compounds

Alternative fuels - results

- reduction in particle mass by factor of two
  - ➢ only at elemental carbon (→ black soot)
  - ➢ no reduction in organics
    → no change in “white soot” precursors

➢ Advantages for particle trap regeneration

- similar results at engine test stand:
  - ▪ lowered pressure-rise with emulsion
  - ➢ less need for particle-trap regeneration



[MTZ 01|2013, S. 72-77]

Mitglied der Helmholtz-Gemeinschaft

Conclusion

- diesel-cars equipped with particle traps "produce" particles
  - emissions of large hydrocarbons need to be reduced (e.g. by additional catalyst)
- Water-in-Diesel-Microemulsions can reduce emissions of black soot (elemental carbon)
  - advantages for particle-trap regeneration
- effect of particle formation / growth ("white soot") needs to be further investigated