VOCs and particle emission from DPF equipped diesel engine during regeneration measured by on-line PTR mass spectrometer

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Emissions from modern diesel engine for automobiles were significantly reduced by progress in combustion technology and emission after treatment devices. In order to reduce fine particle emission, diesel particulate filters (DPFs) have begun to be equipped to diesel engines. DPFs are very effective to reduce fine particles both in number and mass. DPFs are also effective to reduce VOCs (Volatile Organic Compounds) emission significantly. But capacity of DPF to store particles is limited, so DPF must be regenerated periodically to burn stored particles. During such regeneration, nanoparticles are known to be formed downstream of DPF. VOCs emission during regeneration is of interest in view of toxicity and formation mechanism of nanoparticles.

In this work, a HD diesel engine equipped with DPF was investigated by two instruments capable of transient measurements (Fig.1). To measure particle emission, EEPS (Engine Exhaust Particle Sizer) was used to measure particle size distribution in the range between 5 and 500 nm. To measure VOCs, on-line mass spectrometer, PTR-TOFMS (Proton transfer reaction – Time of flight mass spectrometer), was used to measure several VOCs, such as benzene, toluene, acetaldehyde and 1,3-butadiene, which can detect at very low concentration as low as several ppb.

During non-regeneration the DFP effectively reduces fine particles higher than 99.9% by number, with similar particle size distribution to that of engine-out. Several VOCs were undetectable by PTR-TOFMS, which means DPF also reduced VOCs effectively.

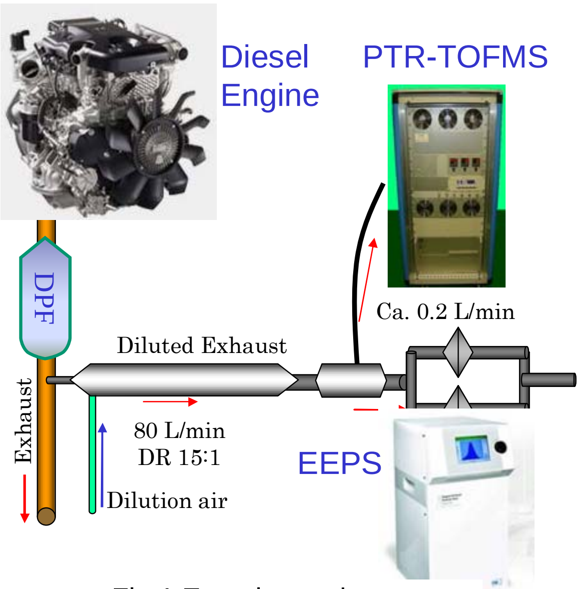


Fig.1 Experimental setup

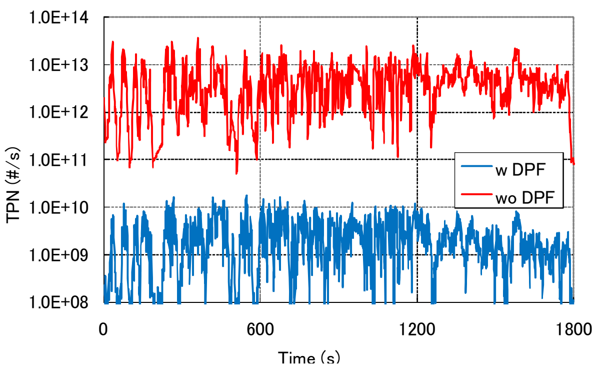
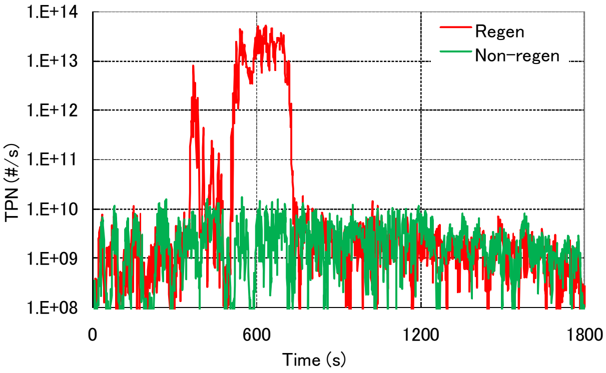
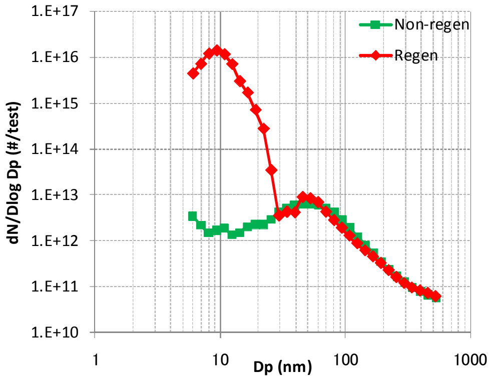


Fig.2 Particle emissions during non-regeneration transient cycle (ETC)

During active regeneration of DPF, fine particle emission increased with nanoparticle formation by nucleation. (Fig.3) Comparison of particle size distribution showed clear nucleation mode with mode diameter ca. 10 nm.



(a) Total particle numbers



(b) Particle size distributions

Fig.3 Comparison of total particle numbers (a) and particle size distributions (b) between non-regeneration and regeneration

Simultaneous VOCs measurement showed that VOCs as well as THC emission increased prior to nucleation of particles then after reduced gradually. (Fig.4) It is suggested that nucleation was caused not by organic compounds rather by inorganic compounds such as sulfate.

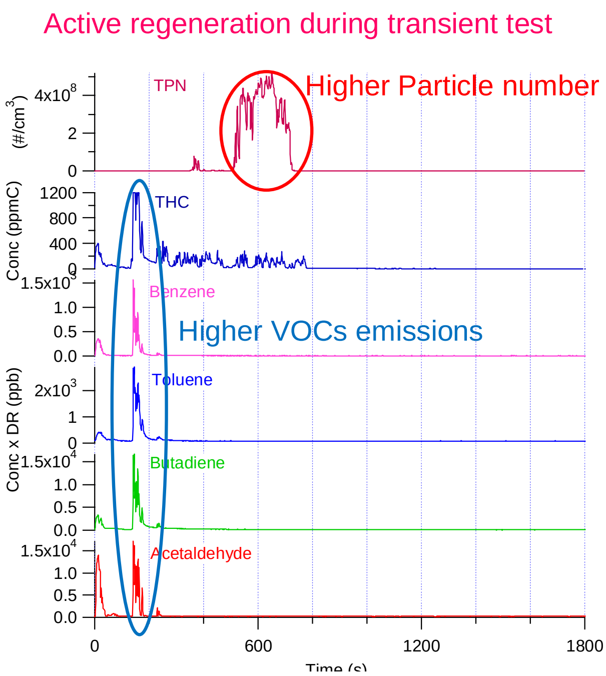


Fig.4 VOCs and THC emission during regeneration

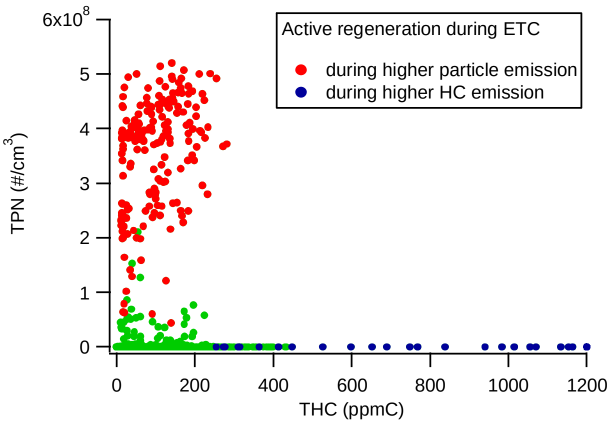


Fig.5 Correlation between THC and TPN during regeneration

Simultaneous measurements of VOCs and fine particles show that during regeneration of DPF fine particles emission increases significantly by nucleation, but almost no increase of VOCs is accompanied with nucleation of particles.

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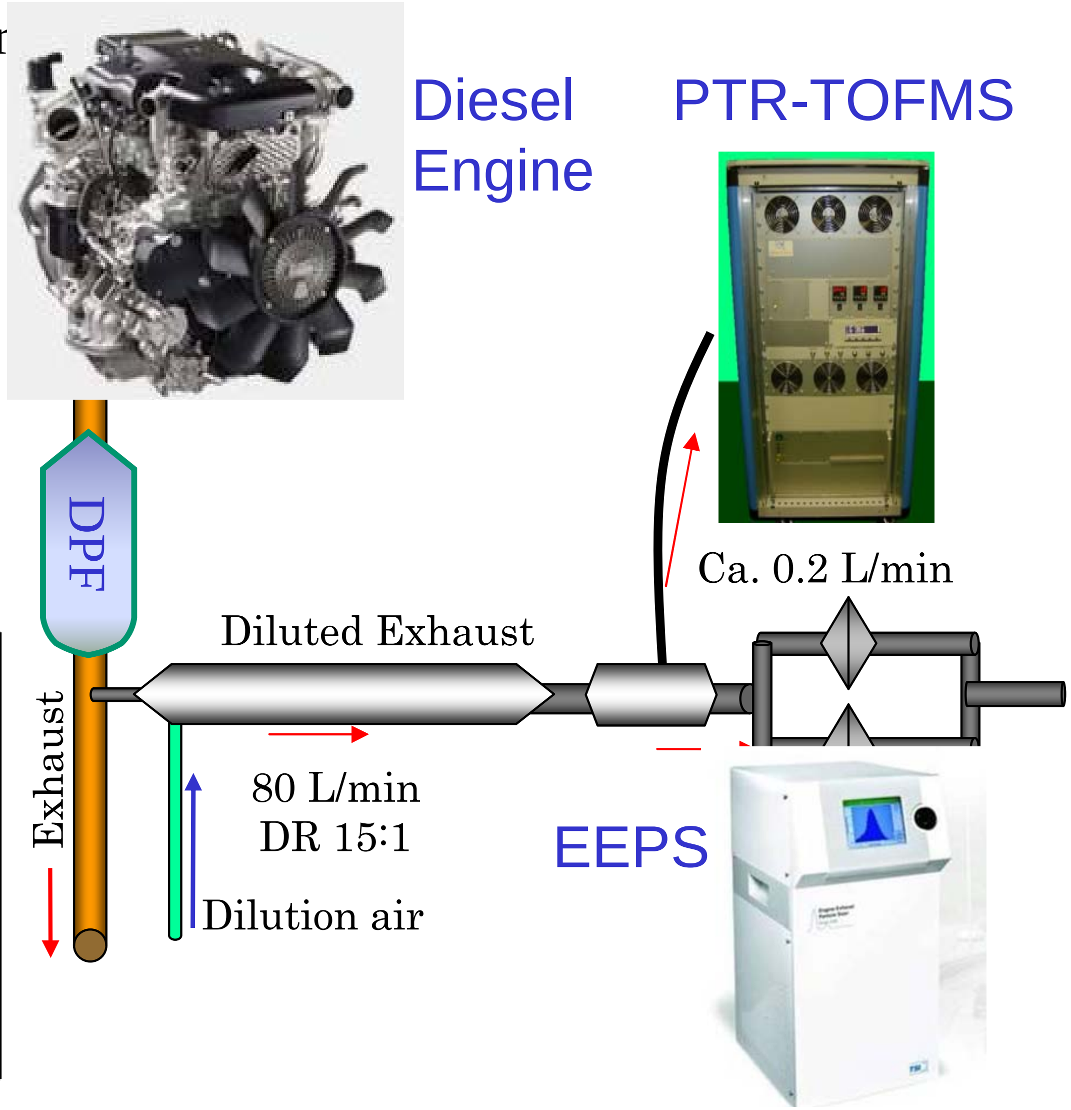
Introduction

- Emission from modern diesel engines for automobiles are significantly reduced by progress in combustion technology and emission aftertreatment devices.
- Emission reduction by diesel particulate filter (DPF)
  - Significant reduction of VOCs as well as particles by DPF
  - Periodical regeneration of DPF increase emission
    - Particle emission
      - Filtering efficiency decrease – Loss of trapped particle layer
    - VOC emission
      - VOCs generation - Oxidation of particles
- Transient emission measurement
  - Regeneration – quite transient process
  - VOCs - PTR-TOFMS
    - benzene, toluene, 1,3-butadiene and acetaldehyde
  - Particle size and number - EEPS

Experimental

- Diesel engine
  - Direct injection Turbo-intercooler
  - Catalyzed Diesel Particulate Filter
- Exhaust sampling
  - Partial flow dilution system
    Dilution Ratio : 15:1 constant
- EEPS - Particles
  - Size range : 5 – 560nm
  - Sampling rate : 0.1 sec
- PTR-TOFMS - VOCs

	Specification
Ionization method	Proton transfer reaction by H_3O^+
Mass spectrometer	High resolution TOF MS
Mass range	1 to 20,000
Mass resolution	ca. 3500 (V-mode)
Data Averaging time	1 sec
Sampling line	Heated sampling line



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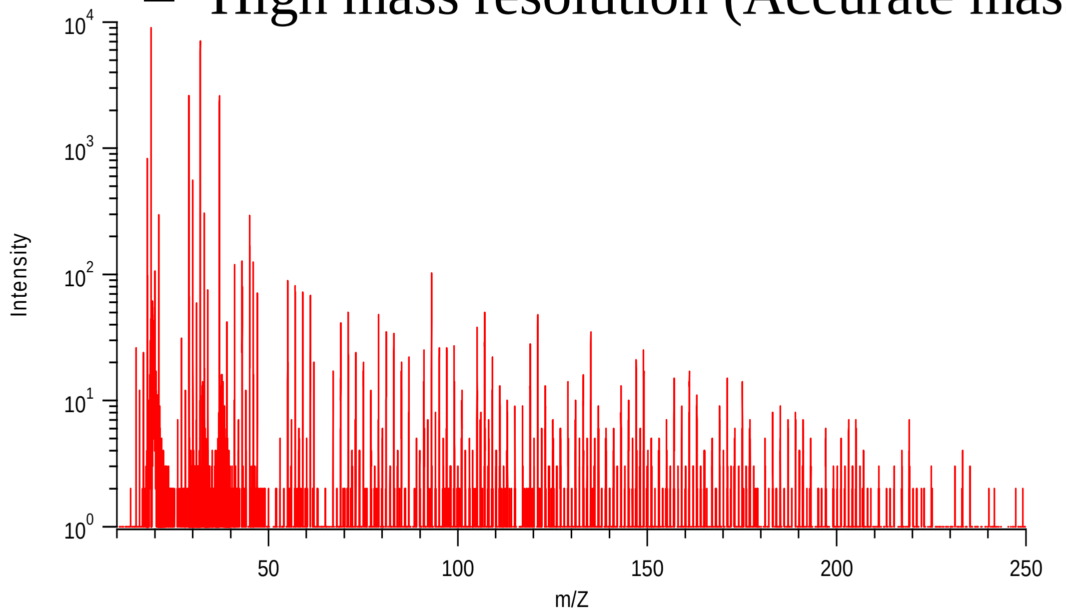
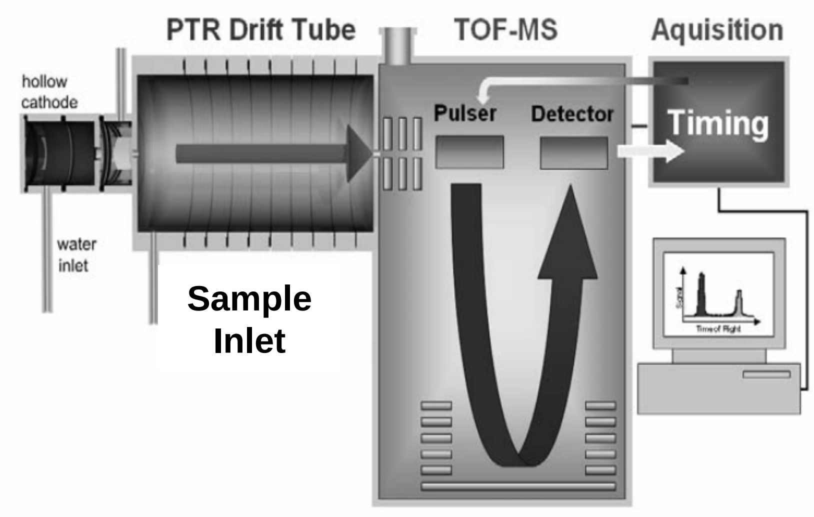
VOCs measurement by PTR-TOFMS

- PTR (Proton Transfer Reaction): Chemical Ionization
  - Wide range of VOCs can be analyzed
  - Suppress fragmentation of ionized molecules

    $H_2O + e^- \rightarrow H_2O{\bullet}H^+ + OH^- + e^-$ (hollow cathode)

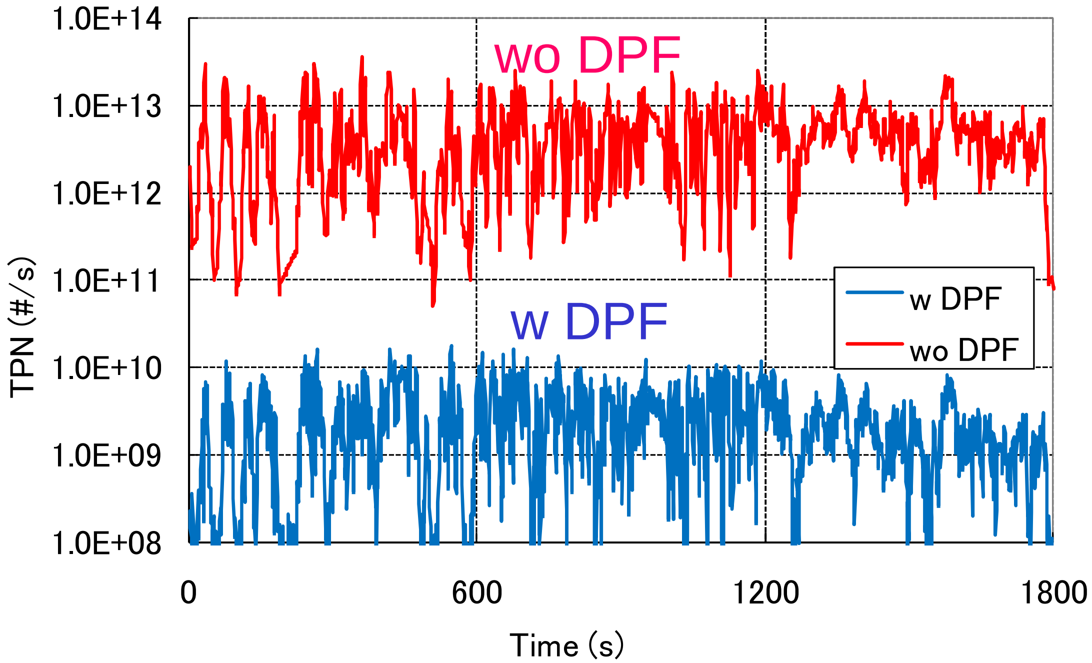
    $VOC + H_2O{\bullet}H^+ \rightarrow VOC{\bullet}H^+ + H_2O$ (PTR Drift Tube)
- TOFMS (Time of Flight Mass Spectrometer)
  - Fast full scan → transient measurement
  - High mass resolution (Accurate mass) → qualification

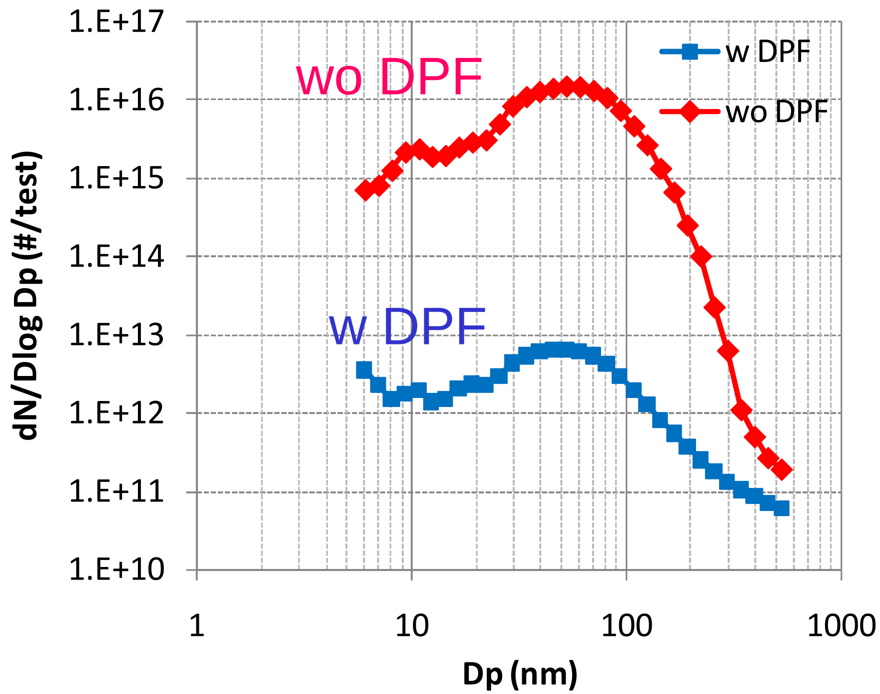




Particle size and number measurement – Non regeneration

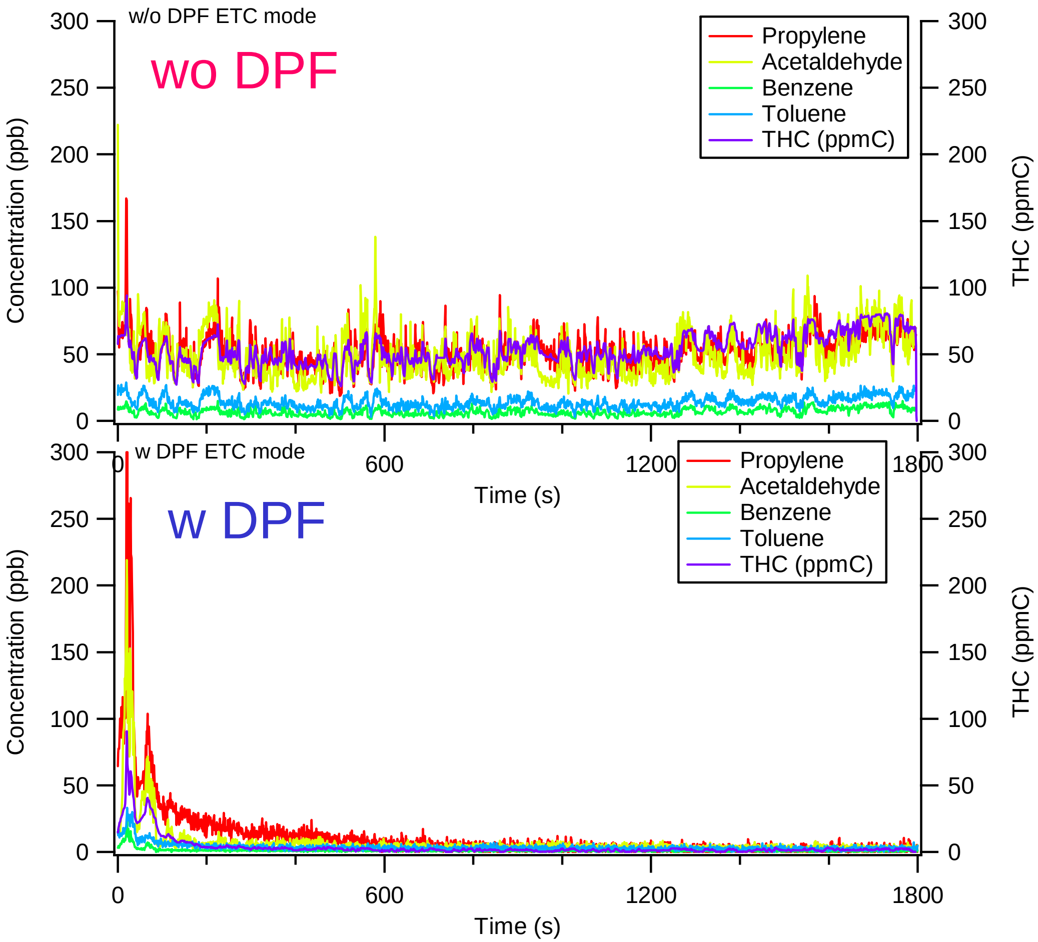
- Particle size and number in transient test cycle
  - Test condition
    - ETC mode , DPF 50% loading, Non-regeneration
  - TPN (Total particle number - solid and volatile particles)
    - With DPF reduced more than 3 orders of magnitude
      -> Filtering efficiency > 99.9%
  - Particle size
    - No significant change in size downstream DPF – mode diameter ca. 50nm

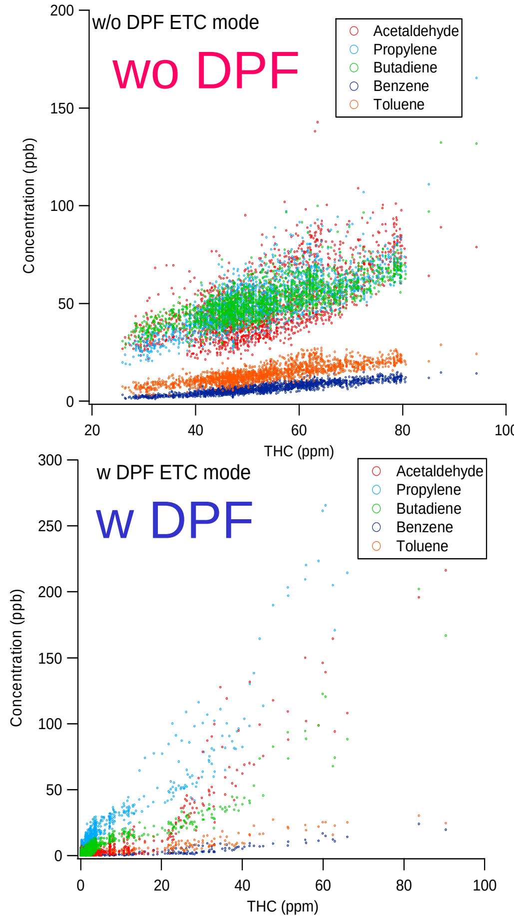




VOCs measurements – Non regeneration

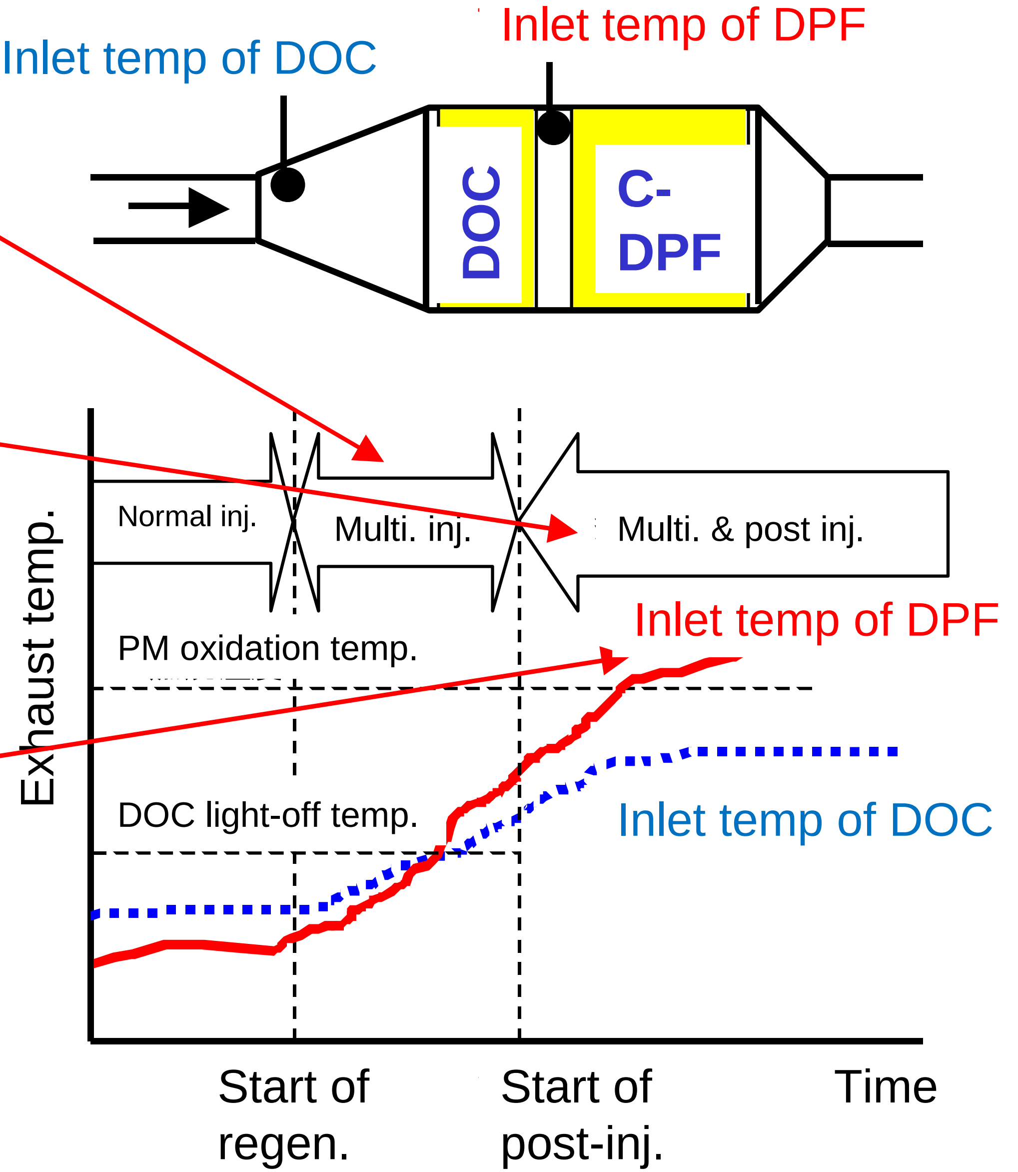
- VOCs emissions measured by PTR-TOFMS
  - With DPF most VOCs are undetected except beginning of tests where DPF is at lower temperature
    - Test condition : ETC mode , DPF 50% loading, Non-regeneration





Active regeneration of DPF

- Active regeneration process
  1. Multiple fuel injection:
     Engine exhaust temperature increase
     → Heating DOC
  2. (After DOC activation)
     Multiple and post fuel injection:
     → Inlet temperature of DPF increase
  3. (After DPF activation)
     Starting oxidation of PM



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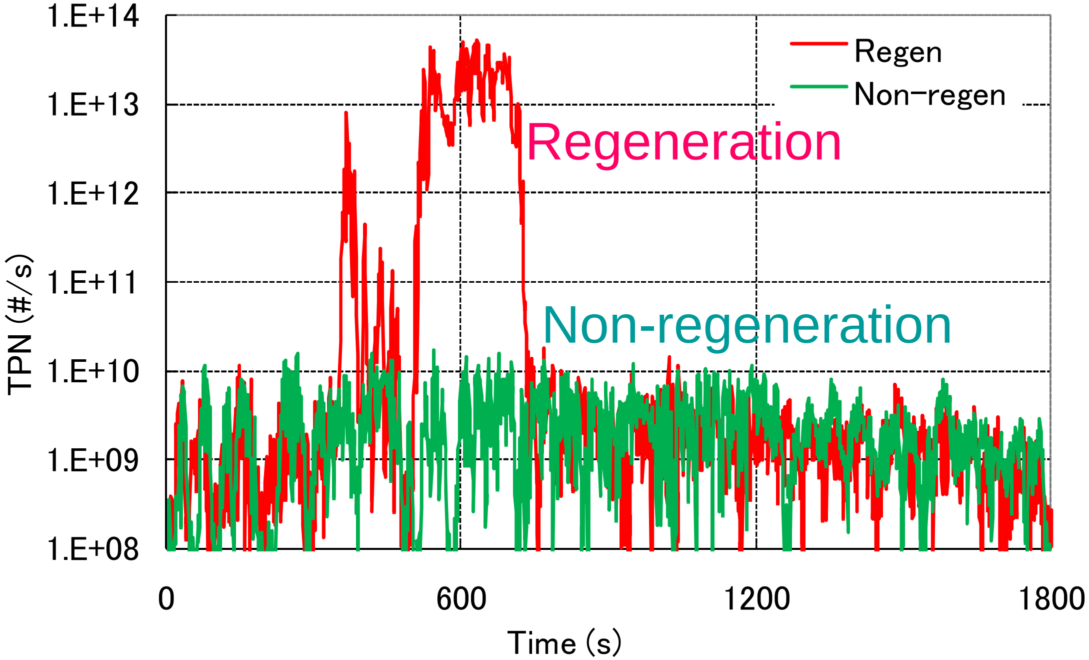
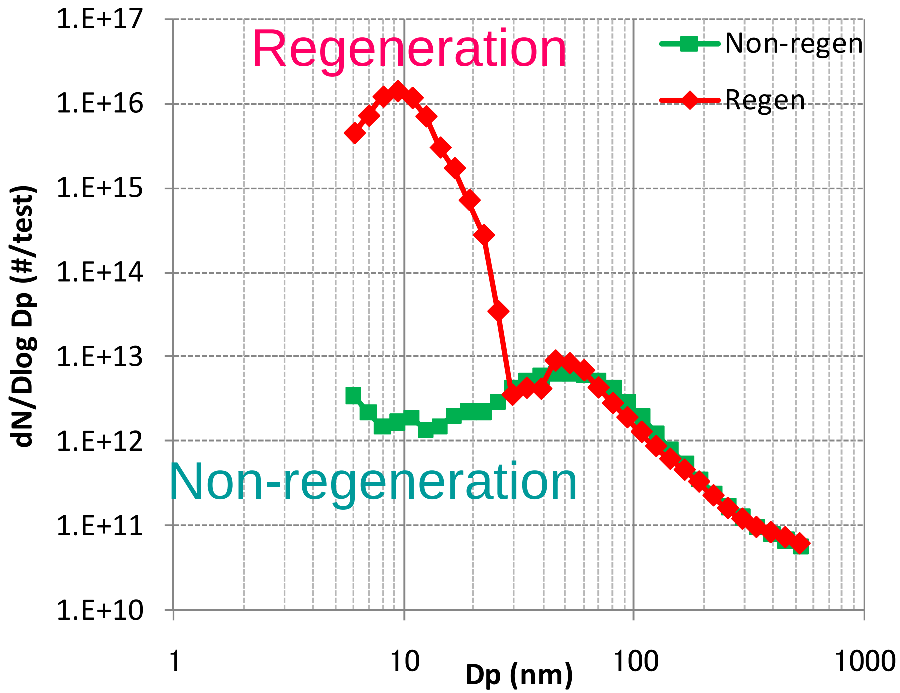
Particle size and number measurement – Regeneration

- Particle size and number during active regeneration
  - Test condition
    - ETC mode , DPF active regeneration
  - TPN increase
    - Particles of Dp < 30nm increase significantly
    - Particles of Dp > 30nm no increase
  - Particle size
    - Bimodal distribution : Mode diameter 10nm and 50nm
      - Nucleation mode particles





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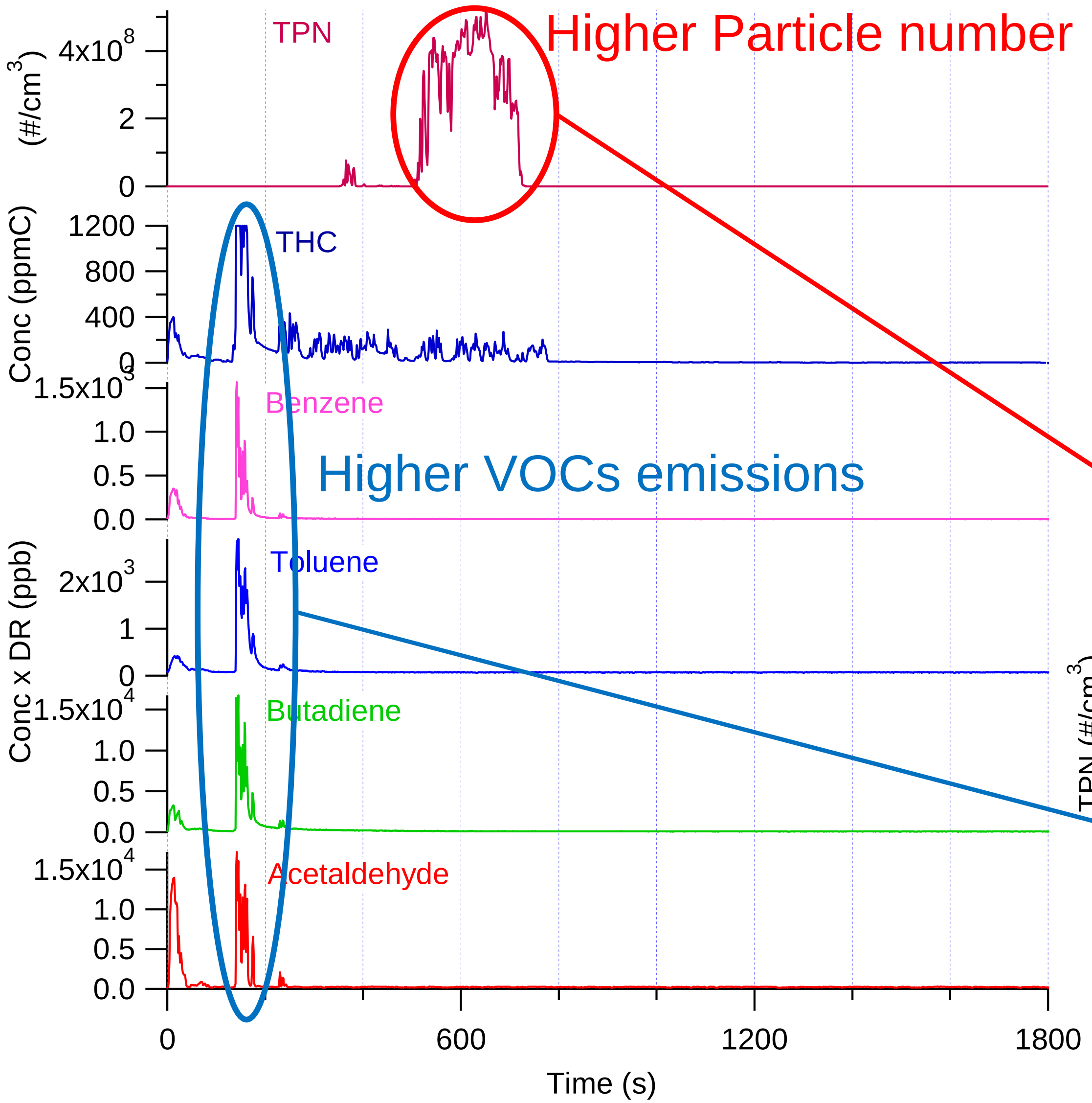
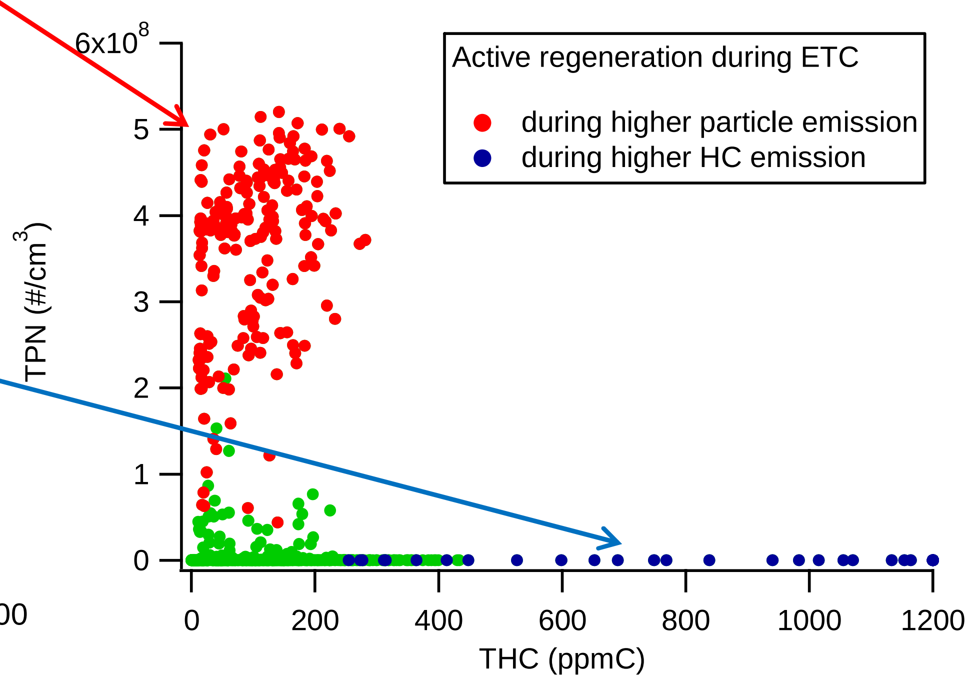
VOCs measurement – Active regeneration

Active regeneration during transient test



- THC and VOCs emission is higher prior to particle increase
  - THC seems to have weak correlation with TPN.
  - VOCs emissions are very low during particle increase



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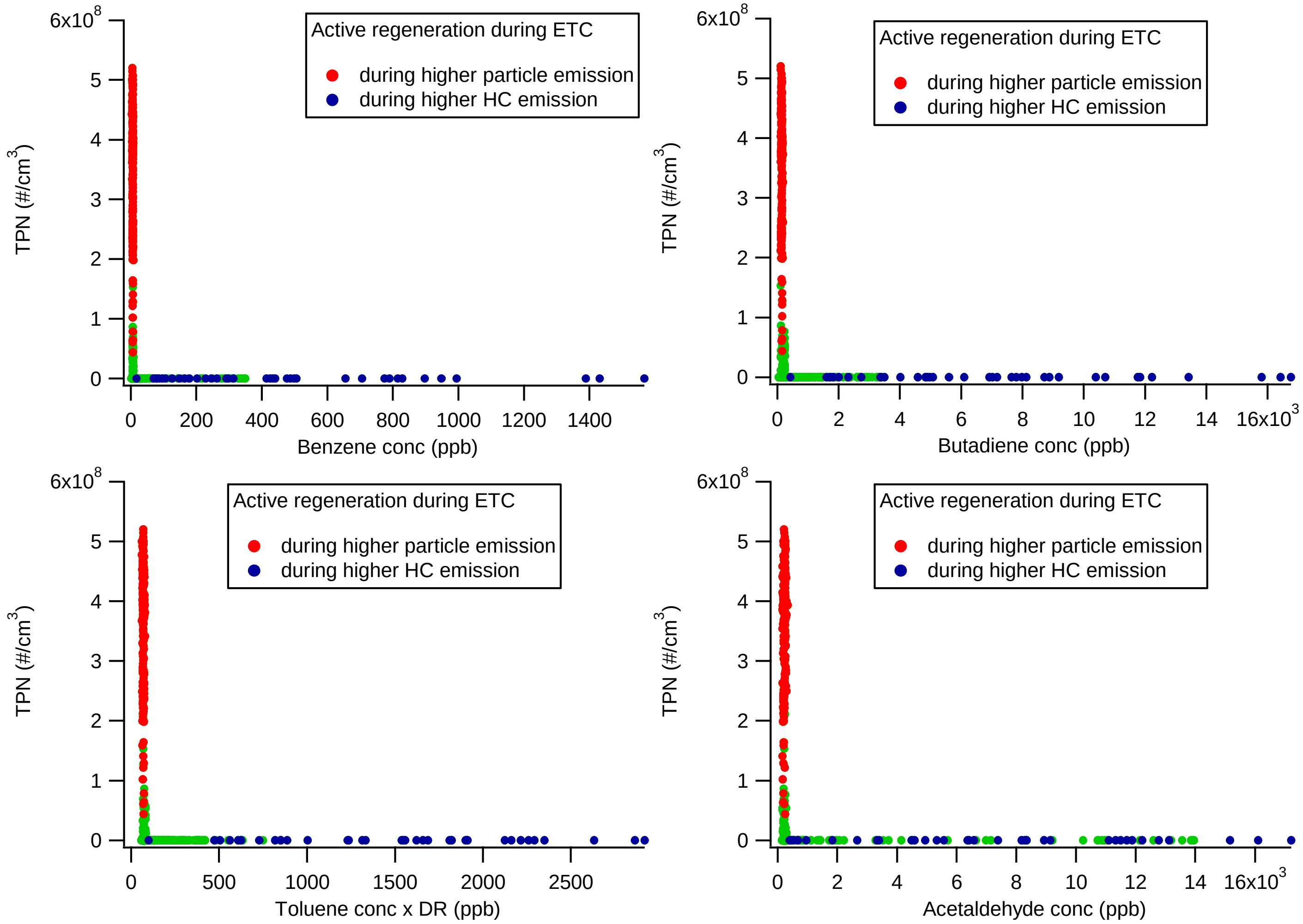
Correlation of VOC concentrations and Particle number

- Higher particle and VOCs emissions occurred independently.
  - During higher particle emissions lower VOC concentrations were observed.



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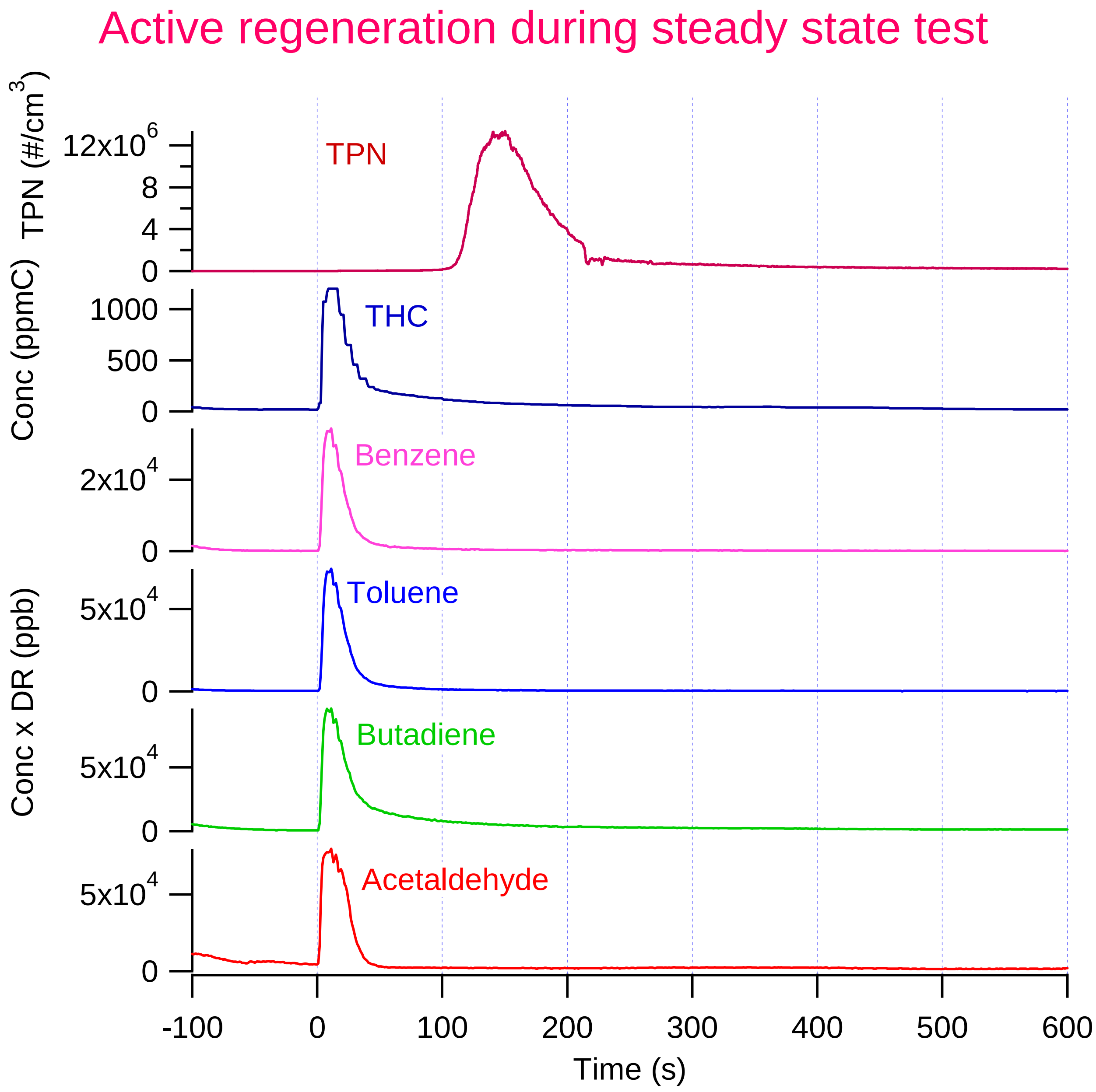
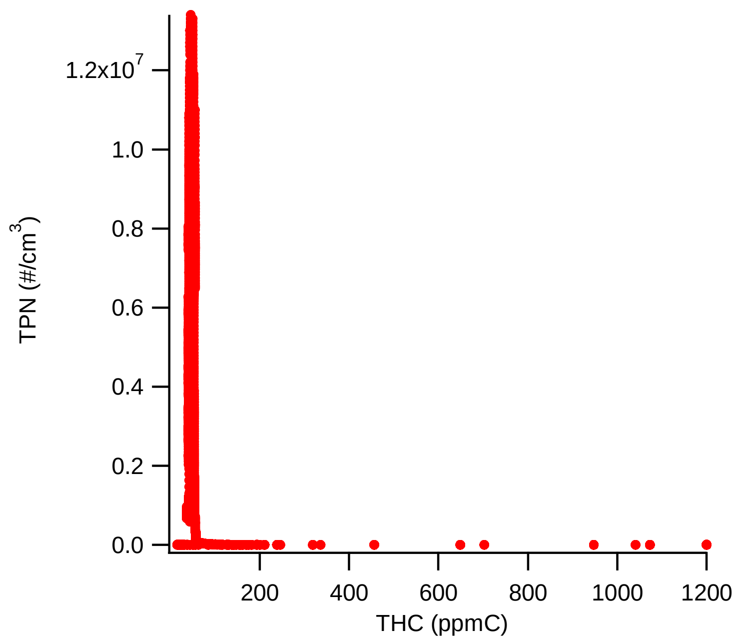
Active regeneration in steady state test

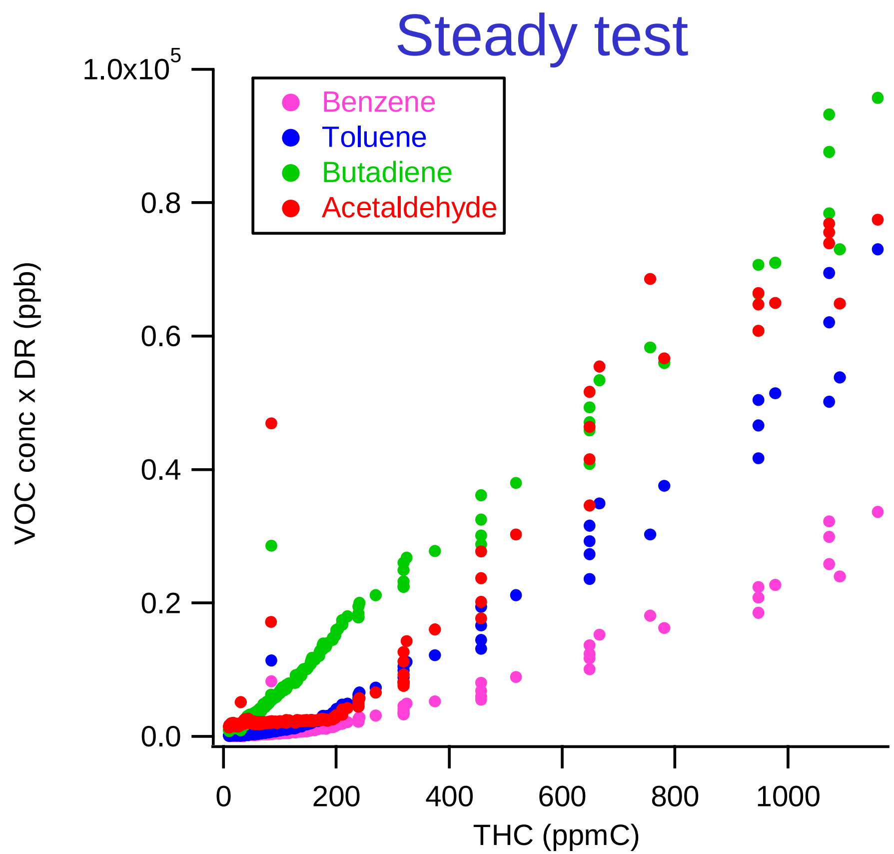


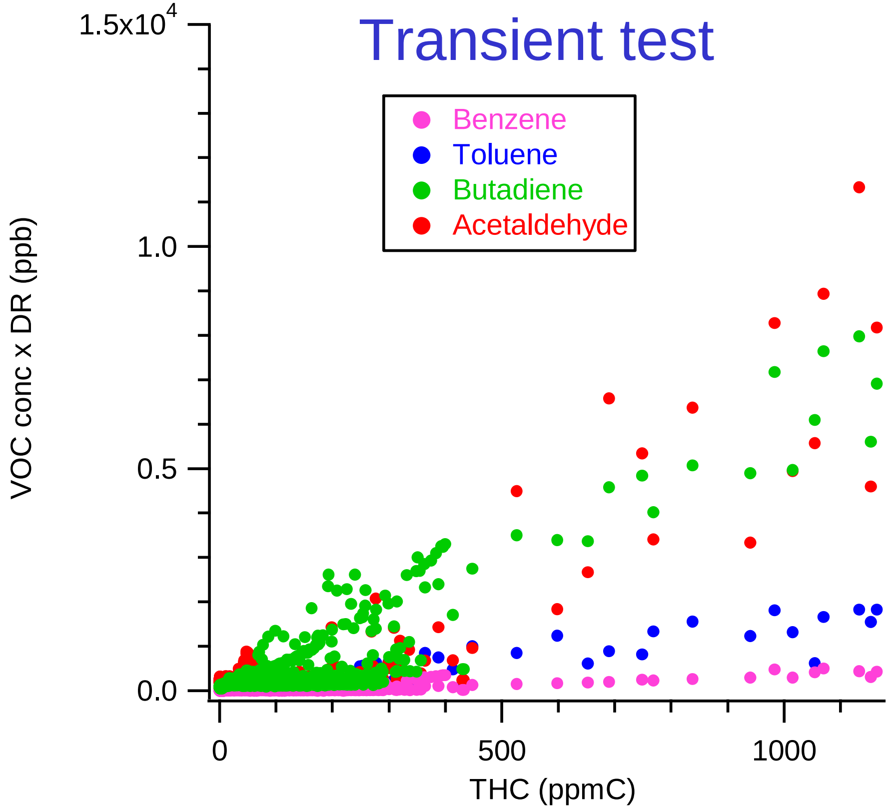
- THC and VOCs concentrations
  - decreasing during TPN increase
  - higher at the beginning of regeneration
- Particle increase is not caused by HC or VOCs emissions.



VOC emissions during regeneration

- Correlation of VOCs and THC
  - Benzene, Toluene, Butadiene – linear better correlation
  - Acetaldehyde – rather scattered correlation





Conclusion

- Simultaneous measurement of VOCs emission and particle size
  - Particle emission by EEPS
    - During regeneration total (solid and volatile) particle number increases
  - VOC emission measured by PTR-TOFMS
    - PTR-TOFMS measures VOCs of ppb level concentration in transient tests
  - No increase of the VOC emissions accompanied with particle emission increase
    - Higher before particle emission increase
    - Lower during particle increase
  - THC emission generally correlates with the VOC emissions
    Transient measurements of VOCs provide valuable information of speciated compounds.

- Future issues
  - Calibration and quantification of additional compounds
  - Sampling of lower volatile compounds
  - Reduction of background concentration of dilution