Hilfe1

EMPA

Materials Science & Technology

Electron microscopic analysis of metal-bearing particle emissions from diesel engines

A. Liati, P. Dimopoulos Eggenschwiler, D. Schreiber

Laboratory of Internal Combustion Engines, Empa

Folie 1

Hilfe1 Diese Folie enthält zwei Mastergruppen (Master und Titelmaster), welche den Corporate-Design-konformen Auftritt definieren. Der jetzt zugewiesene Empa-Master 1 sieht für die Titelfolie das Empa-Logo vor. Den weiteren Folien ist kein Logo zugewiesen. Für längere Vorträge mit Zwischentiteln empfehlen wir, den Folien mit Zwischentiteln den Empa-Master 2 (mit Logo unten rechts) zuzuweisen. Dazu öffnen Sie via Ansicht > Aufgabenbereich > Foliendesign-Entwurfsvorlage rechts die Masterauswahl. Nun markieren Sie im linken Ansichtsfenster die Folien, denen Empa-Master 2 zugewiesen werden soll (mindestens zwei, ansonsten für den ganzen Satz Empa-Master 1 verwendet wird). Weitere Hilfe erhalten Sie bei Monika Ernst, 4995 (Empa, Dübendorf)

M. Ernst; 04.02.2005

Outline

- Brief Introduction on ash PM
- Analytical techniques for the study of ash
- Sampling methods/setup
- Two case studies:

i. Ash depositions in diesel particulate filters

ii. Ash sampled directly from the exhaust stream

- Summary – Conclusive remarks

ASH: Non-combustible PM in diesel exhaust

Chemical component

- Metal additives in lubricating oil
- Metal additives (traces) in fuel

Mechanically transported fragments

- Metal fragments (engine wear)

Analytical techniques

Methods (macro-, micro-, nano-scale):

- Macroscopic study (on dissected DPFs)
- Optical microscopy
- X-ray diffraction analysis
- Scanning electron microscopy (SEM) – EDX
- Transmission electron microscopy (TEM) - EDX

Morphology (surface features, shape, size), chemical composition ⇨

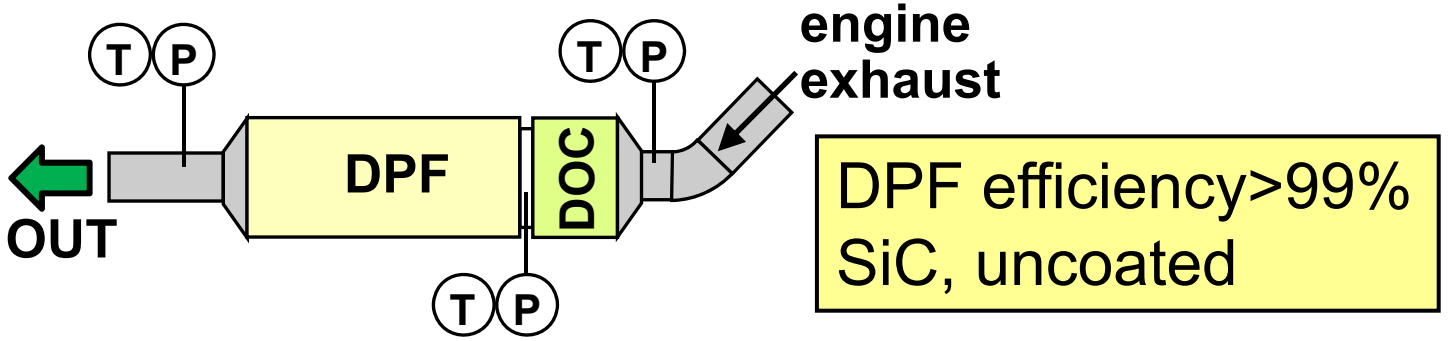
Health effects (epidemiological / toxicological) ⇨

Important for validating and developing mitigation measures/strategies

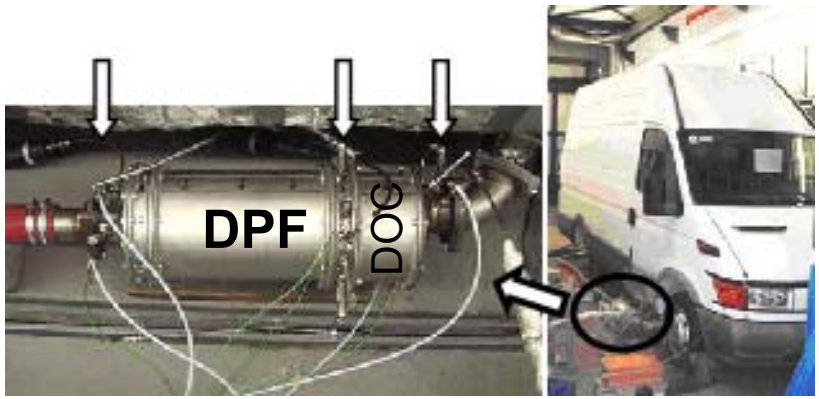
Sampling methods / setup

- Ash depositions in diesel particulate filters
- Ash sampled directly on TEM grids

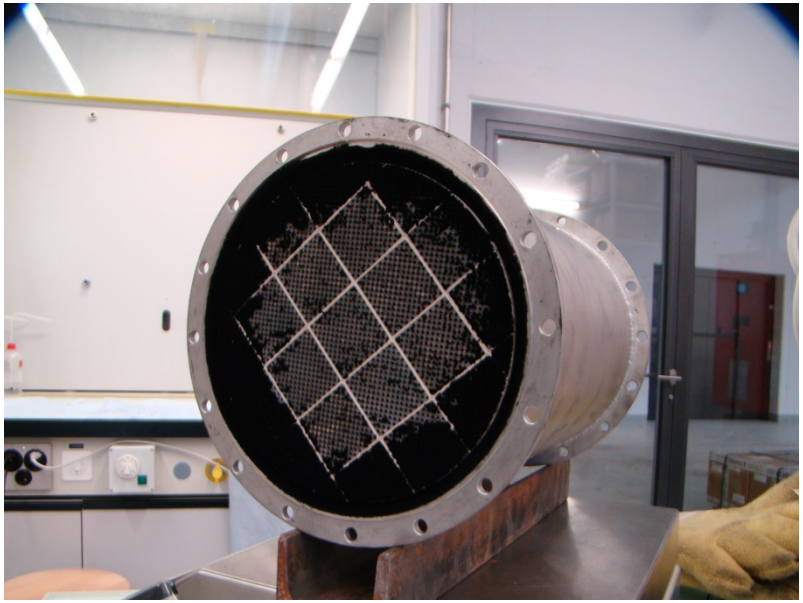
Sampling setup

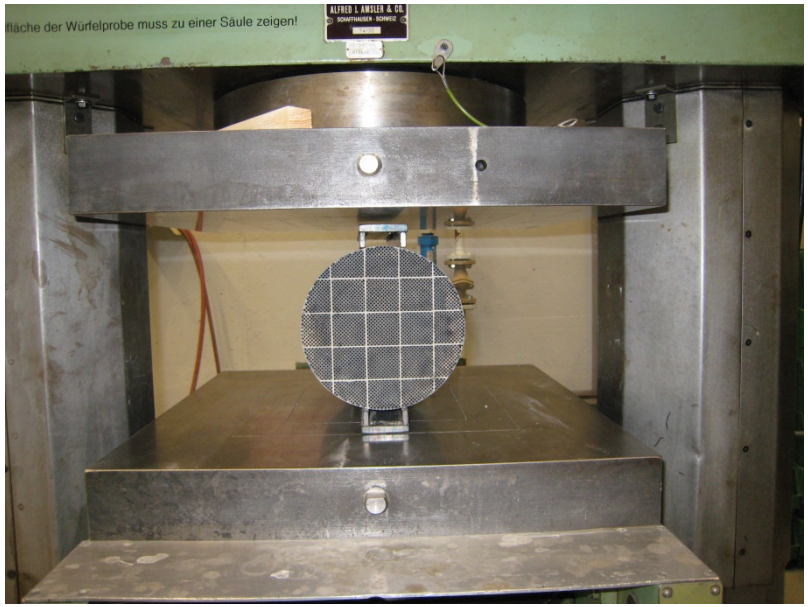


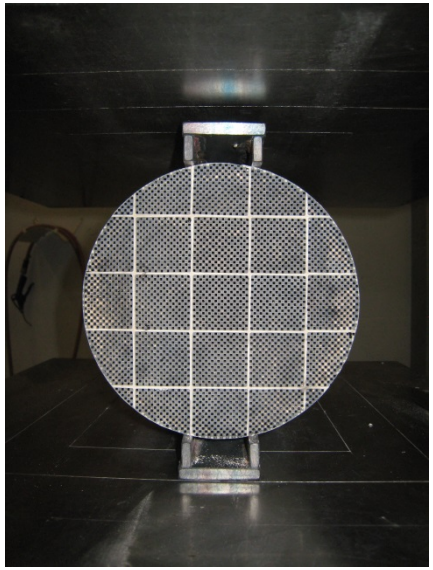
DPF efficiency>99%
SiC, uncoated

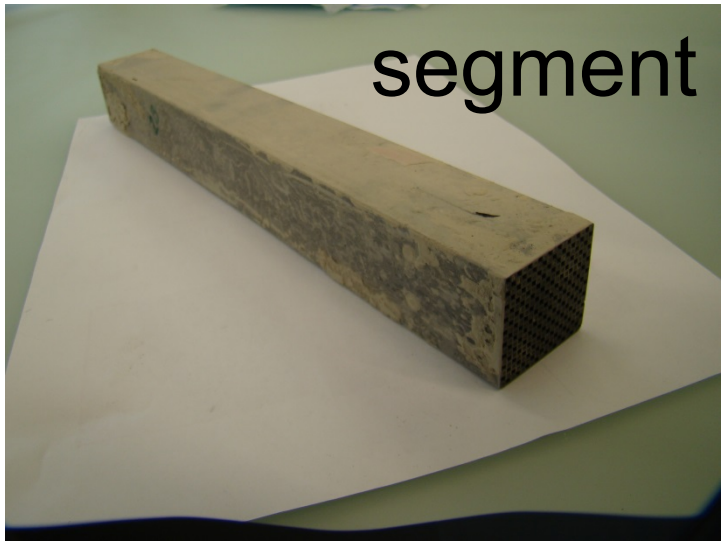


Disassembling the DPF

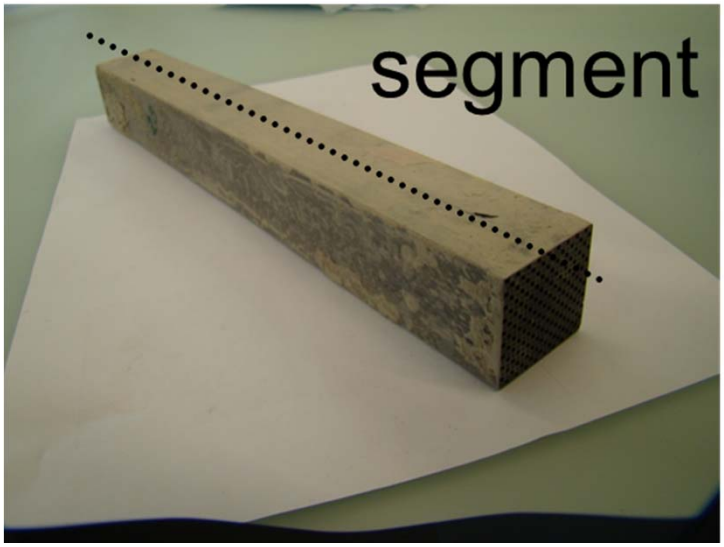








Embed filter segments into epoxy to stabilise loose particles



without epoxy

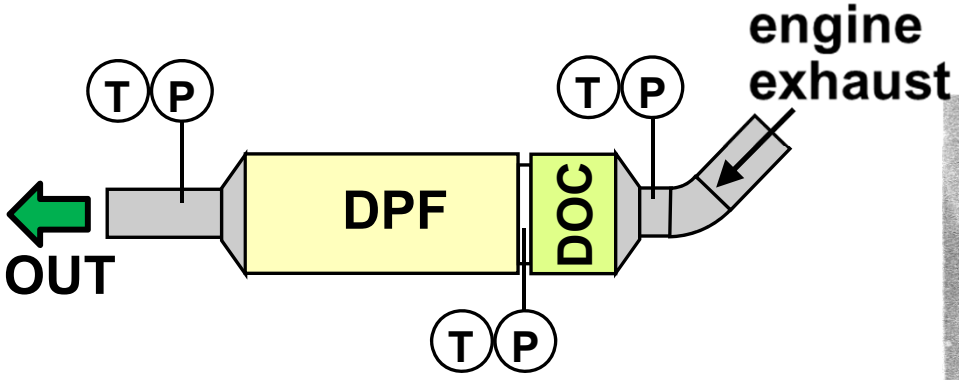
INFLOW

1cm

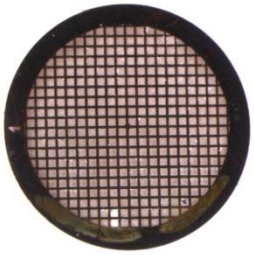
with epoxy

INFLOW

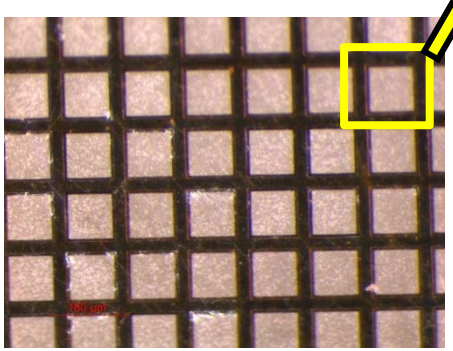
Sampling of PM directly from the exhaust stream on TEM grids



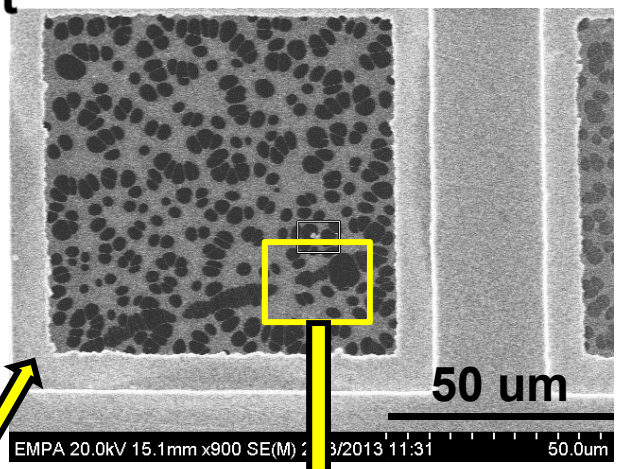
TEM grid

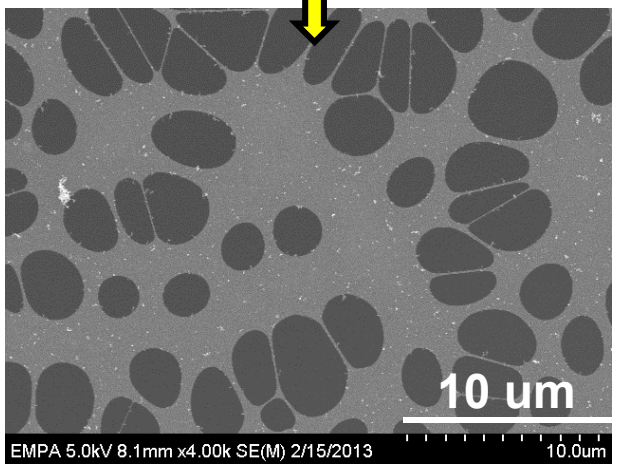


3mm

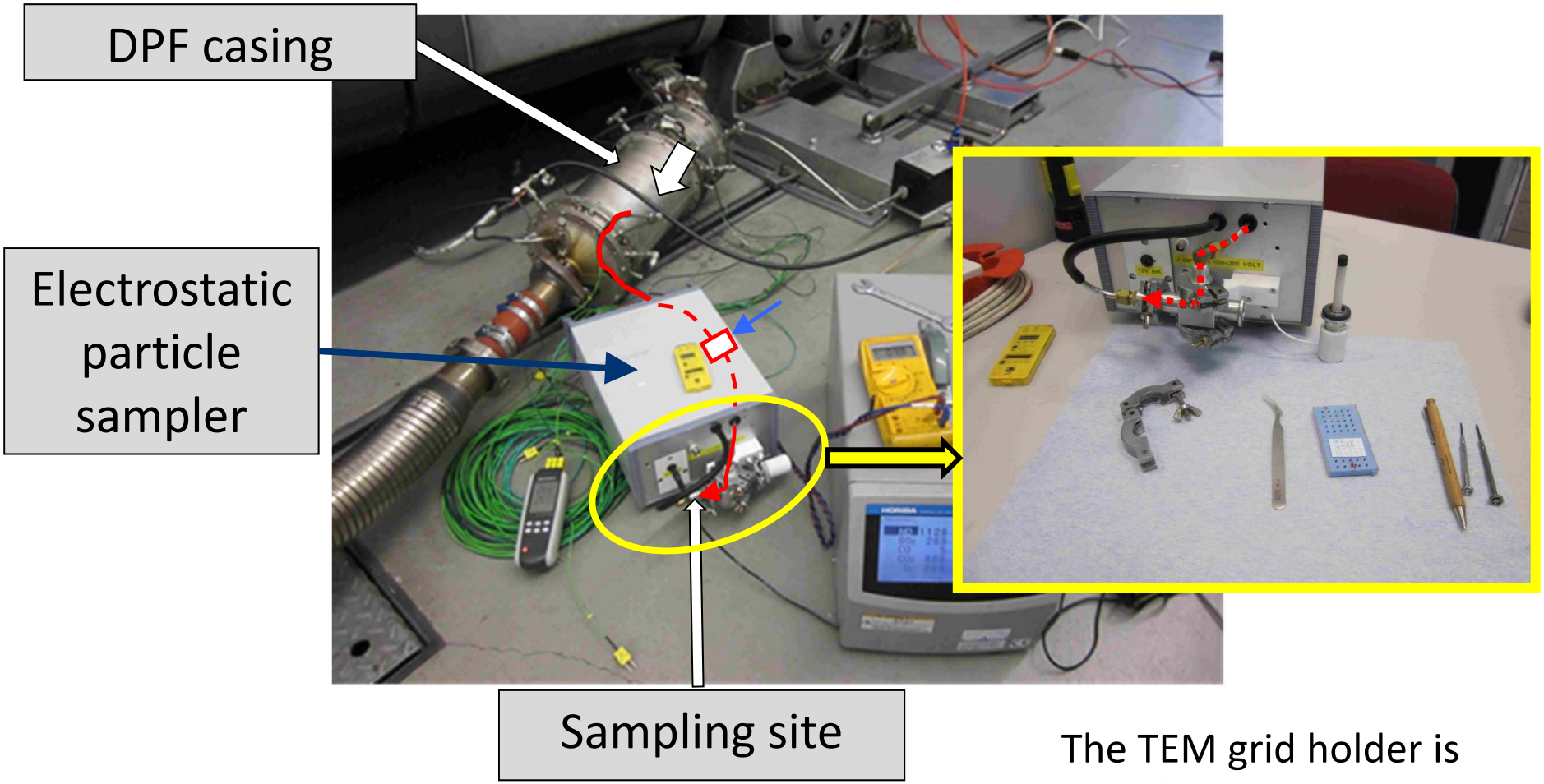


200 um



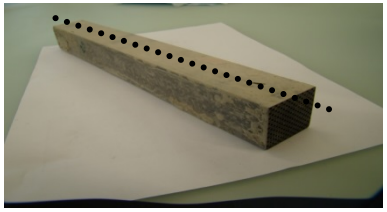


Sampling of PM directly from the exhaust stream on TEM grids



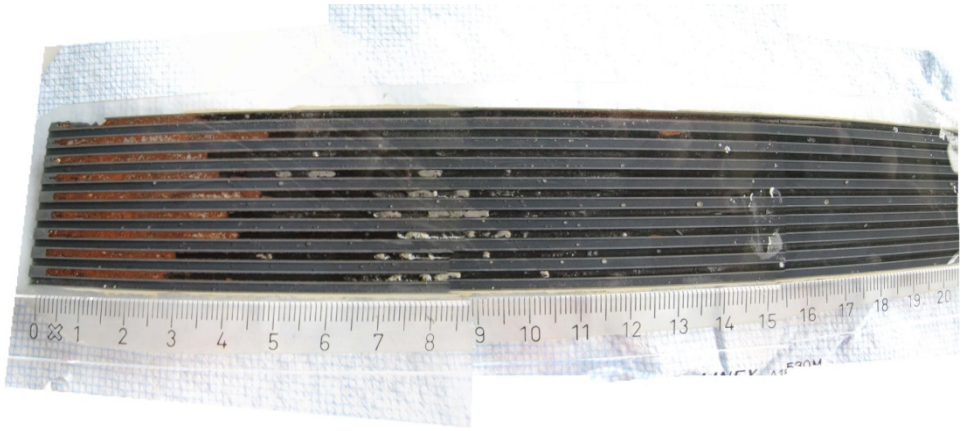
The TEM grid holder is heated/under high voltage

RESULTS: Ash deposits in DPF: channels start filling up with ash from the plugged ends toward the inflow



DPF segment

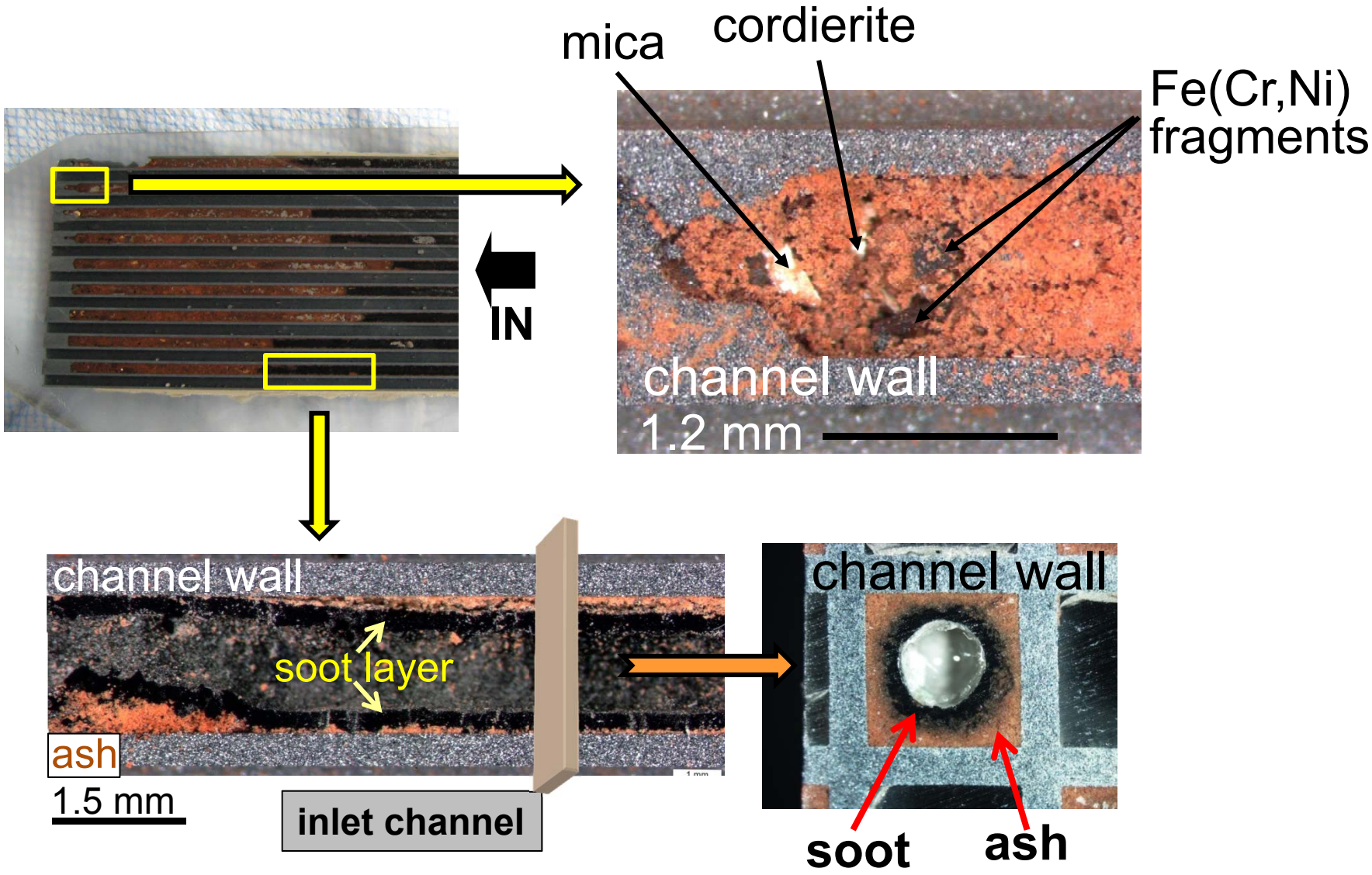
out



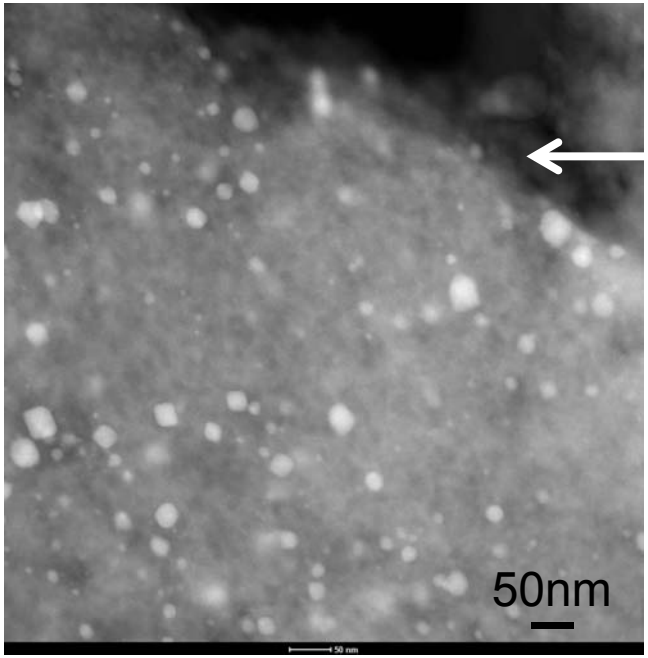
in

Section of a filter segment parallel to the flow direction – ca. 3-5 cm (ca. 15% of the effective filter volume) from the plugged ends are filled up with ash.

Diesel Particulate Filter - Assembly



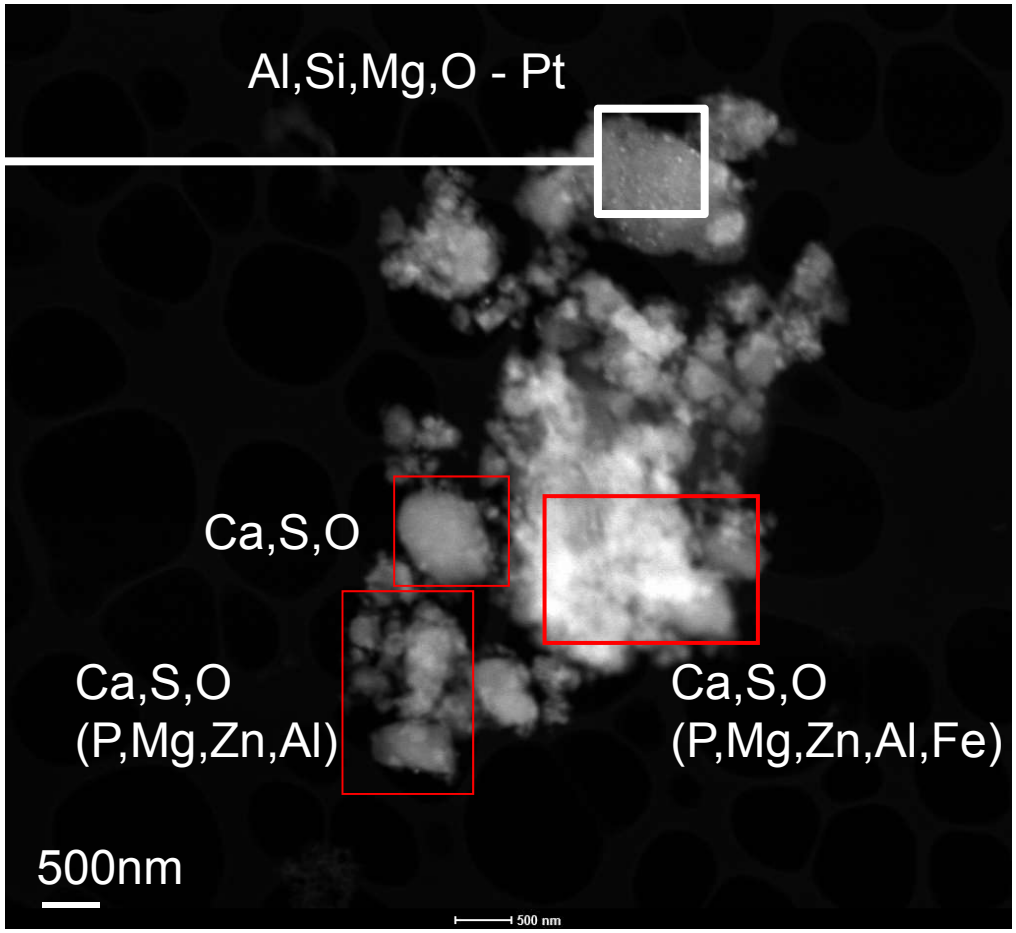
Ash aggregates consist predominantly of Ca,P,Mg,Zn,O,S,Al,Fe-bearing phases and of fragments detached from the DOC



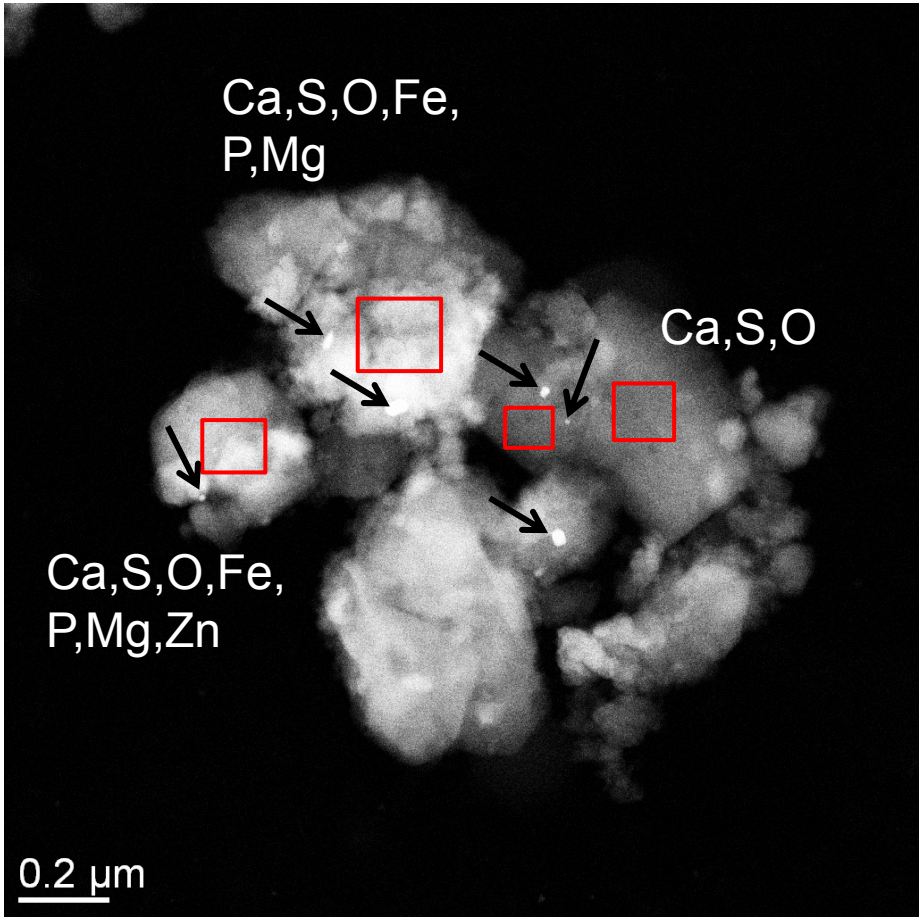
DOC substrate with Pt particles (bright)

(Pt: 40-5nm)

TEM-image of ash aggregates

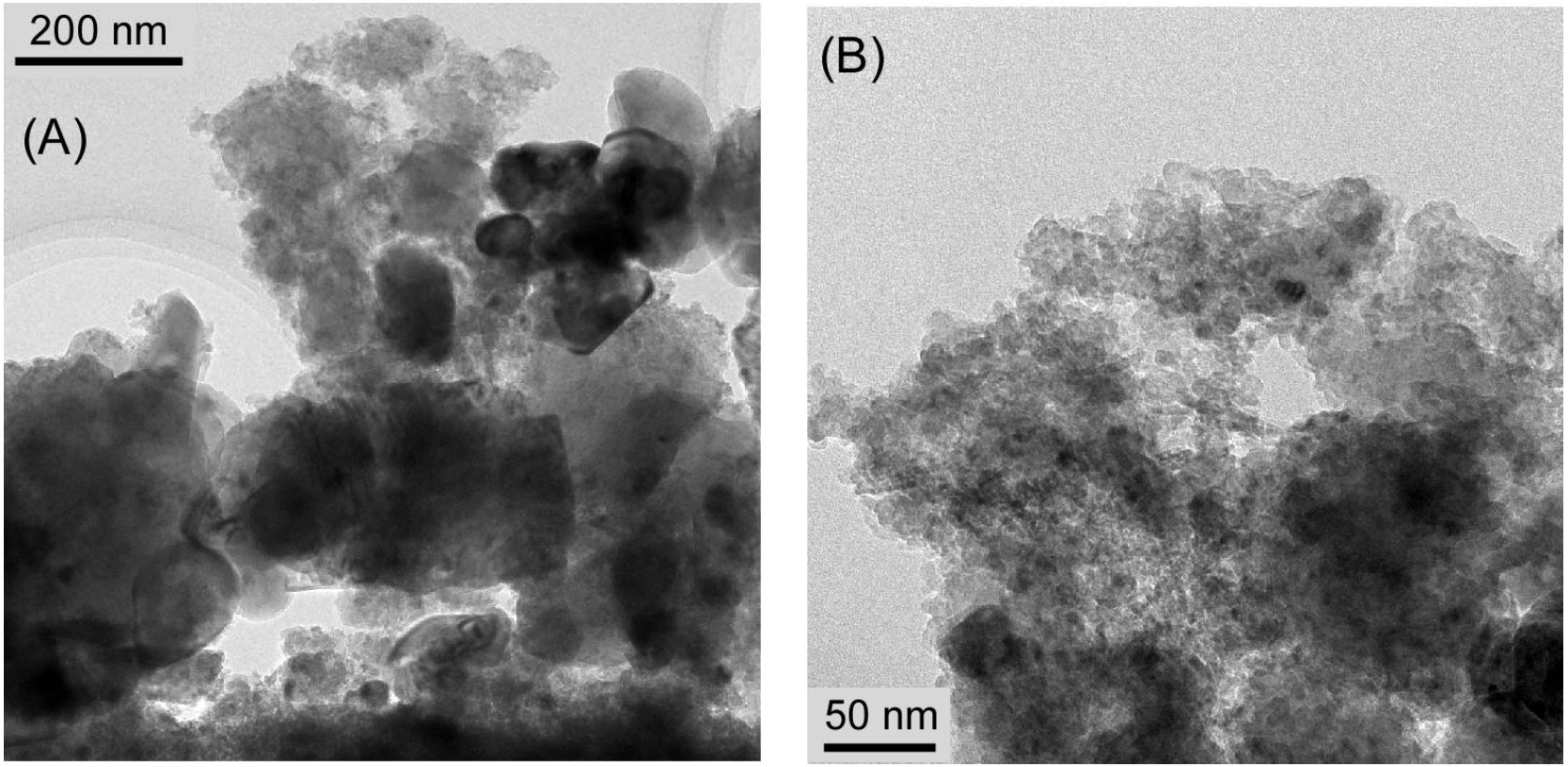


Ash aggregates (Ca,P,Mg,Zn,O,S,Al) with dispersed Pt-particles (without their substrate)



TEM-image of ash aggregates

Ash particle cpnstituents of aggregates have sizes of ~170-60nm, down to ~7nm



TEM images (STEM, BF mode) of individual ash particles

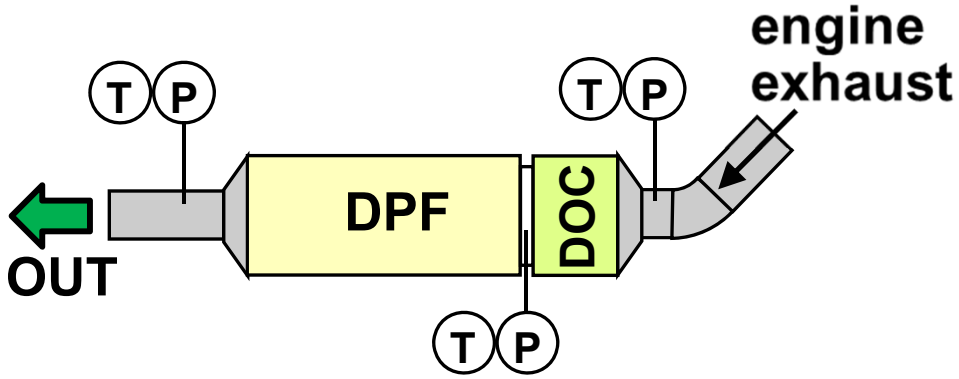
Summary for ash depositions in DPF

- Ash forms powdery aggregates (a few μm to 100s of μm large), deposited at the rear part of the DPF and on channel walls along the DPF.

- Ash consists of Ca,P,Zn,Mg,S (lube oil-related), Fe,Cr,Ni,Cu (engine wear), noble metals: Pt,Pd (DOC), Al,Mg,Si (DOC, intumescent mat).

- The primary particle constituents of the ash aggregates range in size between ~170-60nm, down to ~7nm.

RESULTS FROM SAMPLING DIRECTLY ON TEM GRIDS

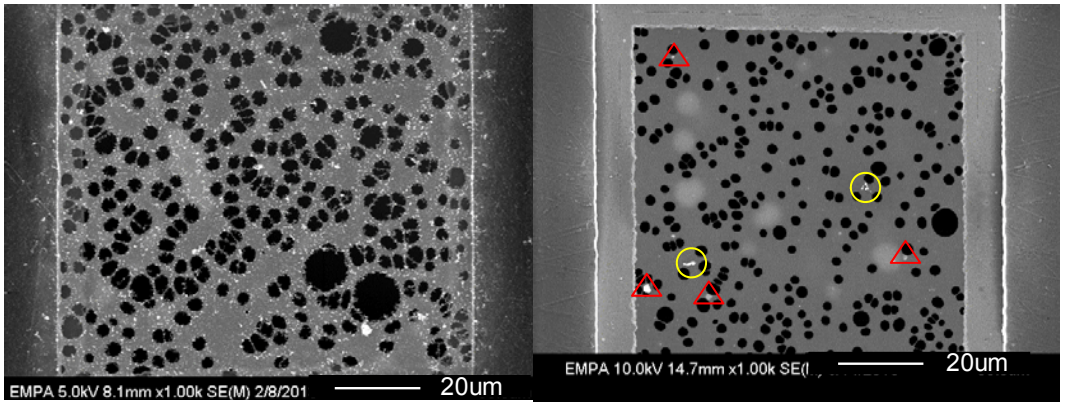


- DPF was new before the experiment; efficiency>99%
- SiC, uncoated
- Degreened - Loaded with soot for ~2000 km (speed: 70km, 5th gear)
- Sampling: normal operating conditions, at steady state operation.

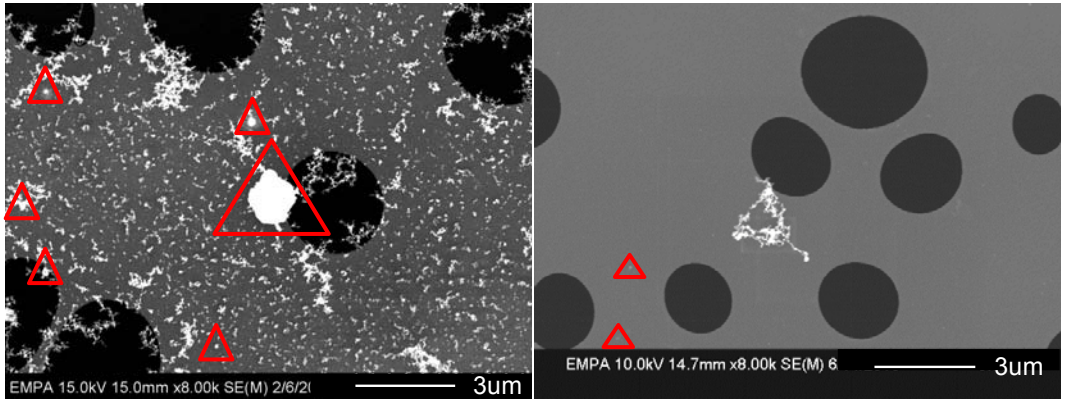
pre-DPF (3 min-diluted)	post-DPF (5-10min-undiluted)

Dramatic decrease of PM after the DPF

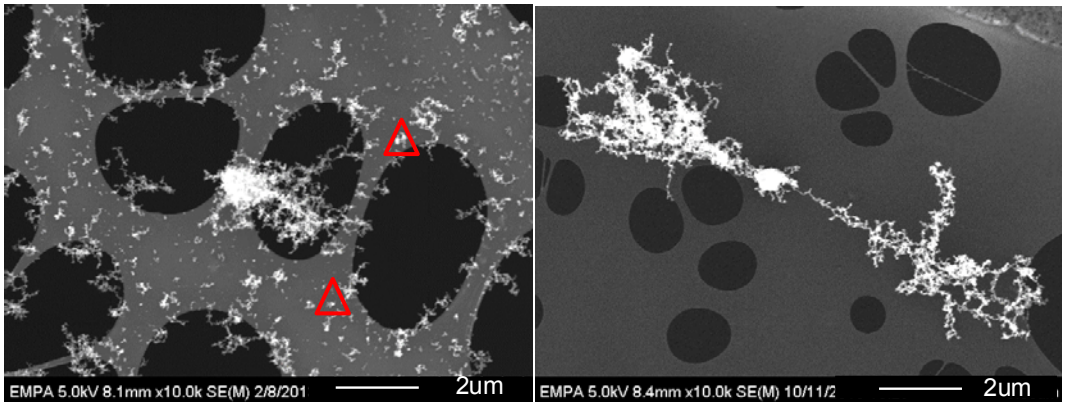
1000x



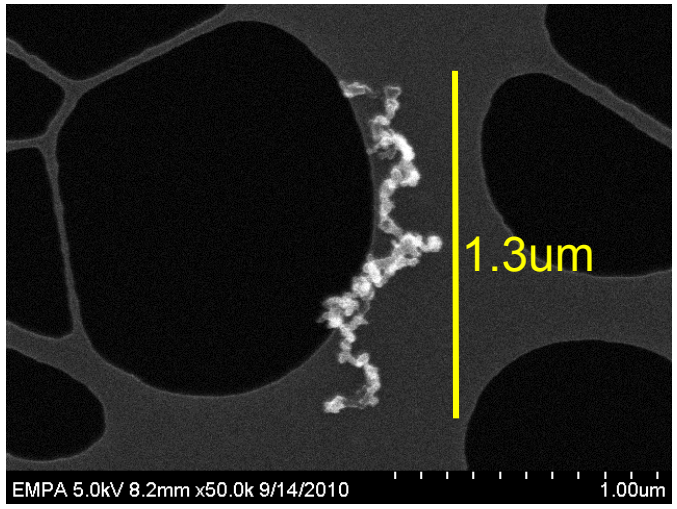
8000x

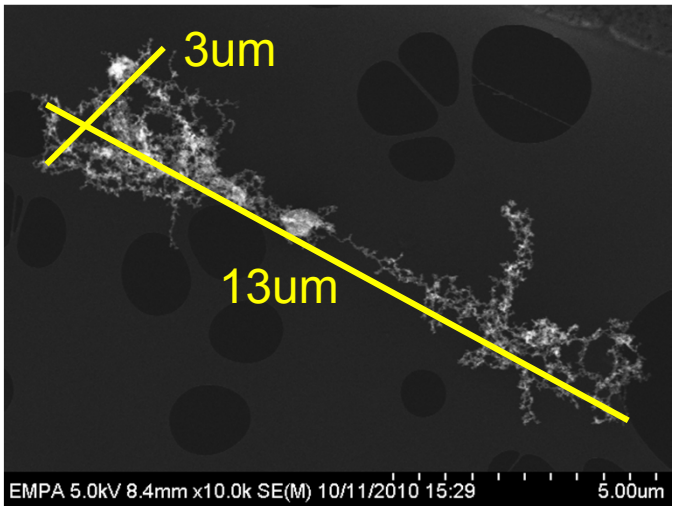


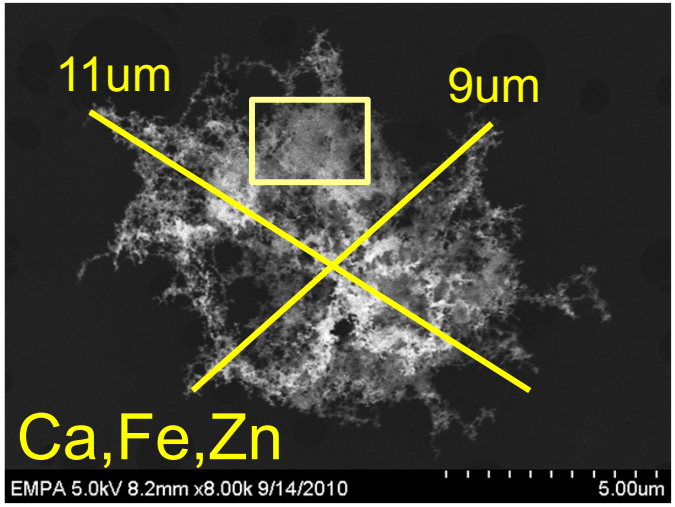
10000x



Soot agglomerates that escape the DPF are usually large and ash-bearing

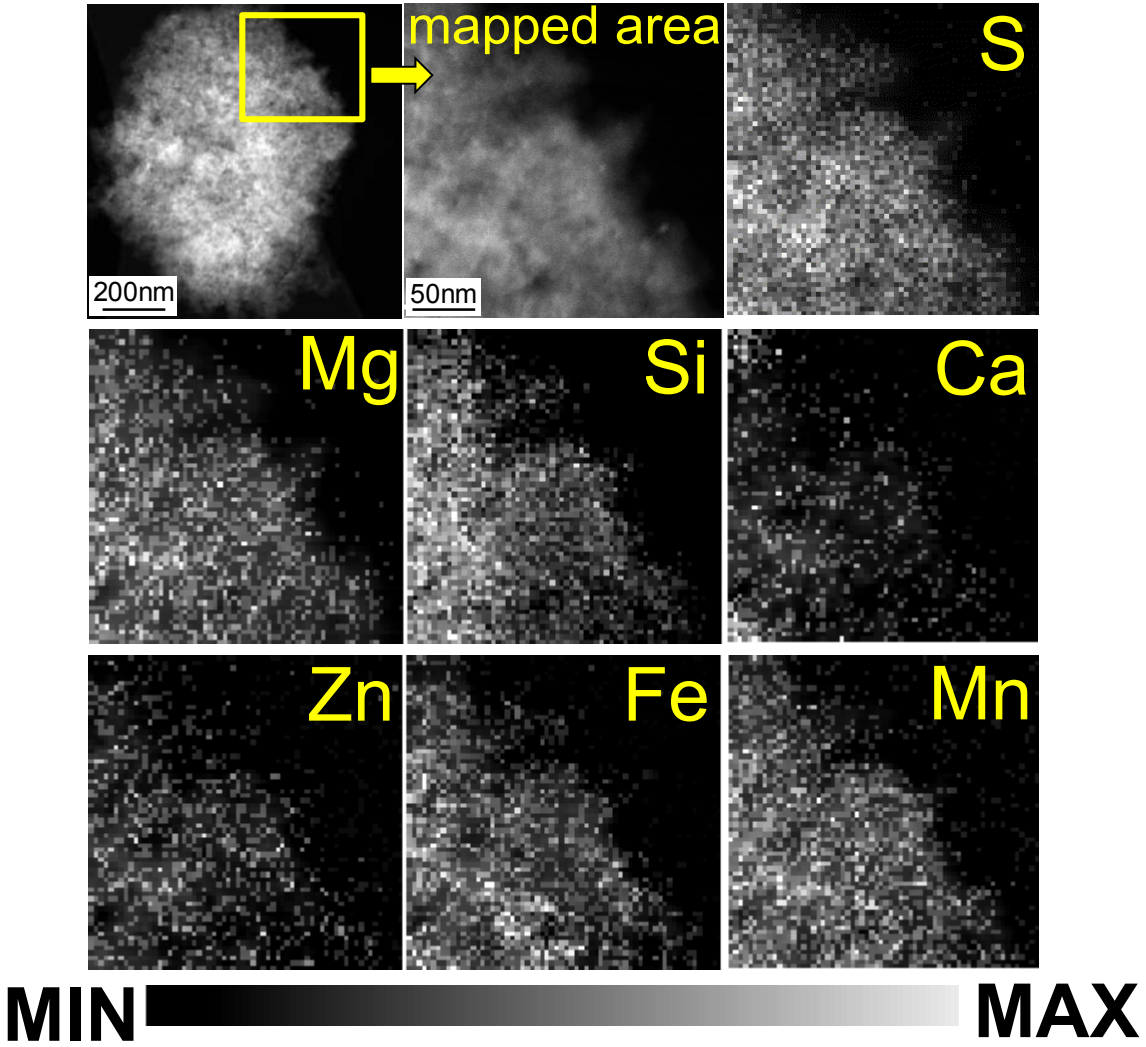




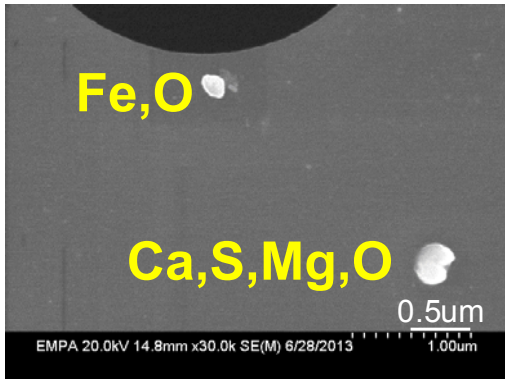


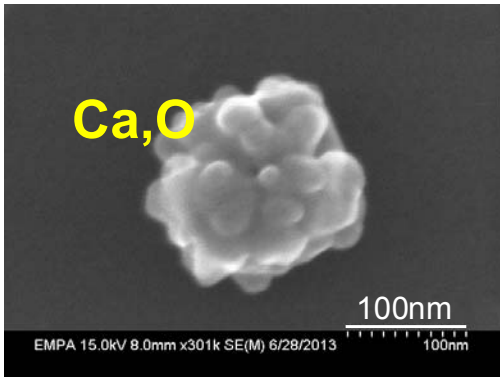
SEM images of samples collected downstream of the DPF (5-10 min sampling time – undiluted).

TEM-element mapping of aoot agglomerate with attached ash (S,Mg,Si,Ca,Zn,Fe,Mn)

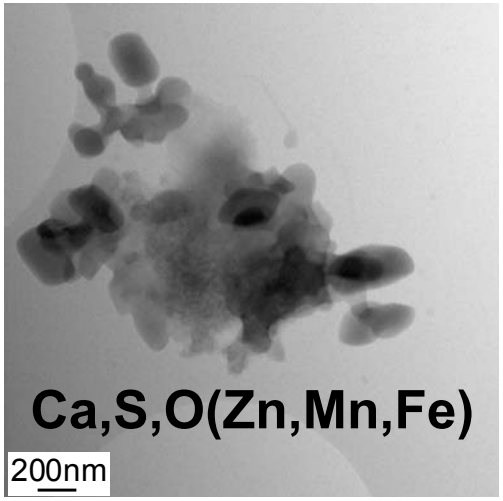


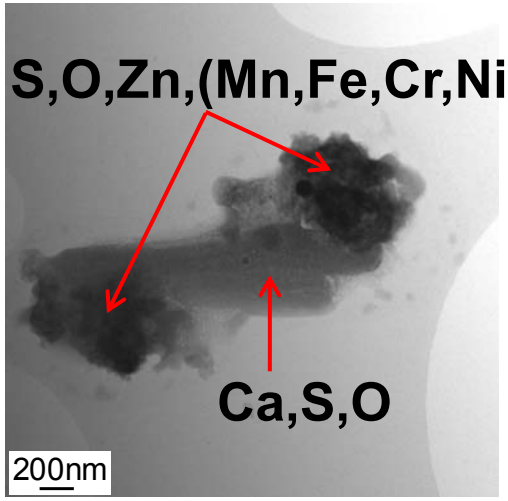
Ash aggregates not attached onto soot can escape the DPF





SEM images of ash collected downstream of the DPF

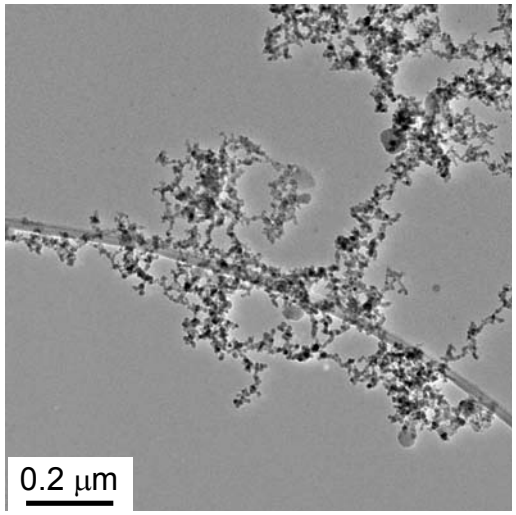


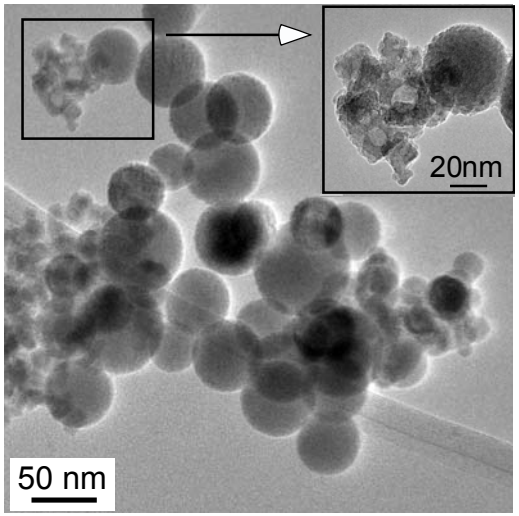


TEM images of ash collected downstream of the DPF

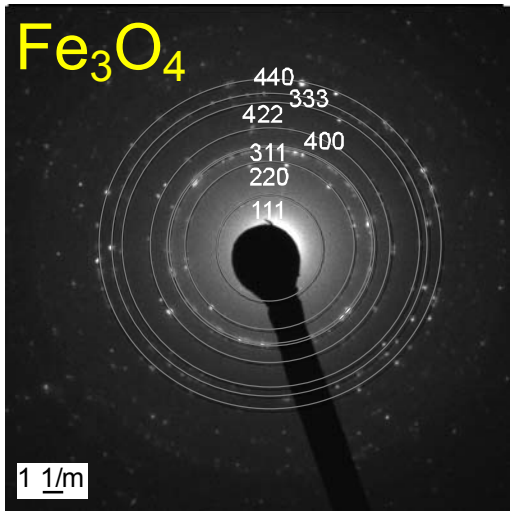
Fe-oxide nanoparticles can form by in-cylinder melting of steel fragments

TEM images

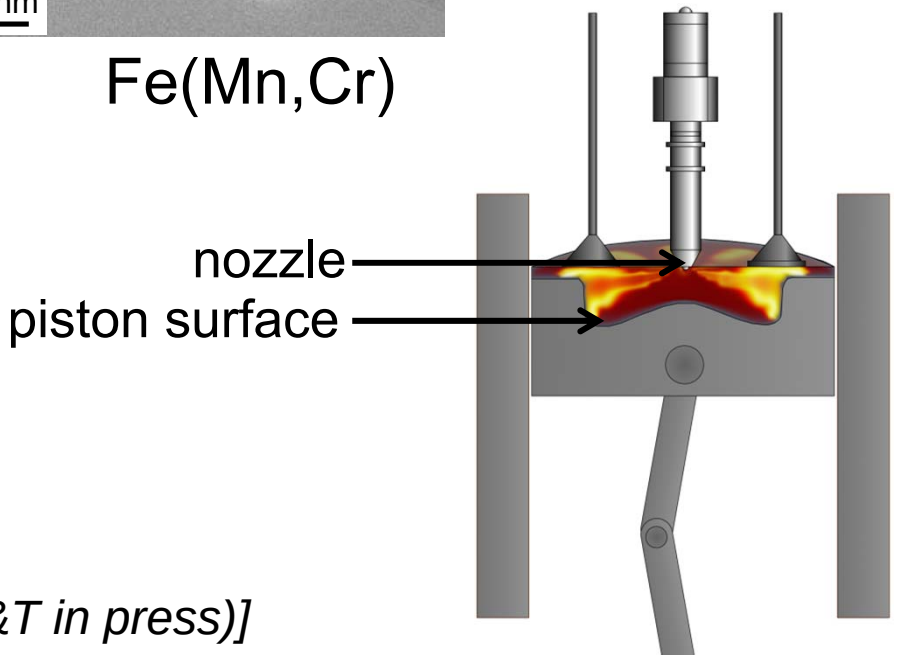




diffraction pattern



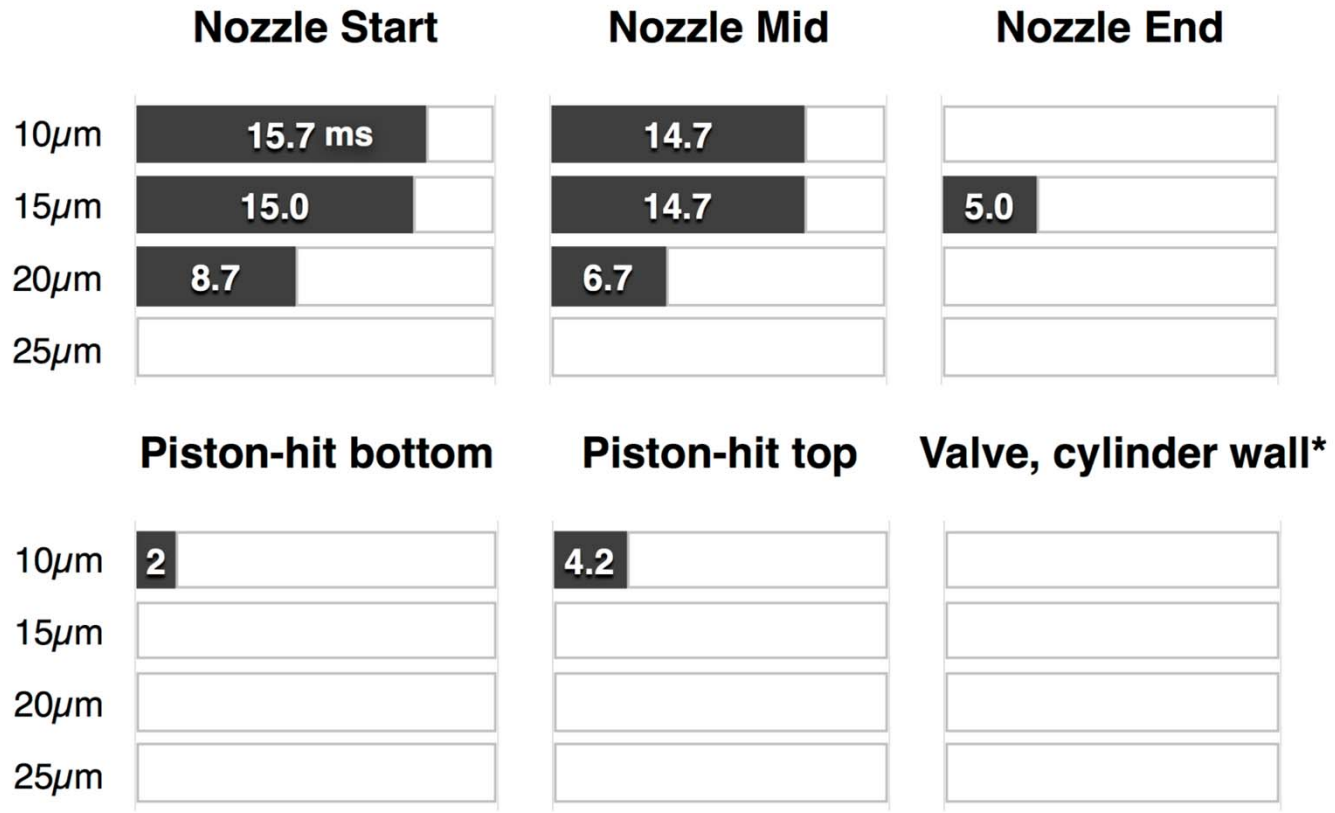
Fe(Mn,Cr)



[Liati, Pandurangi, Boulouchos et al. (ES&T in press)]

CFD simulations on steel fragment transport: steel fragments, 10-20μm in size, dislodged from the piston surface or from the fuel nozzle can be transported to hot areas of the combustion chamber where they can melt.

Time spent by the steel fragments at T≥1800 K in O-rich conditions



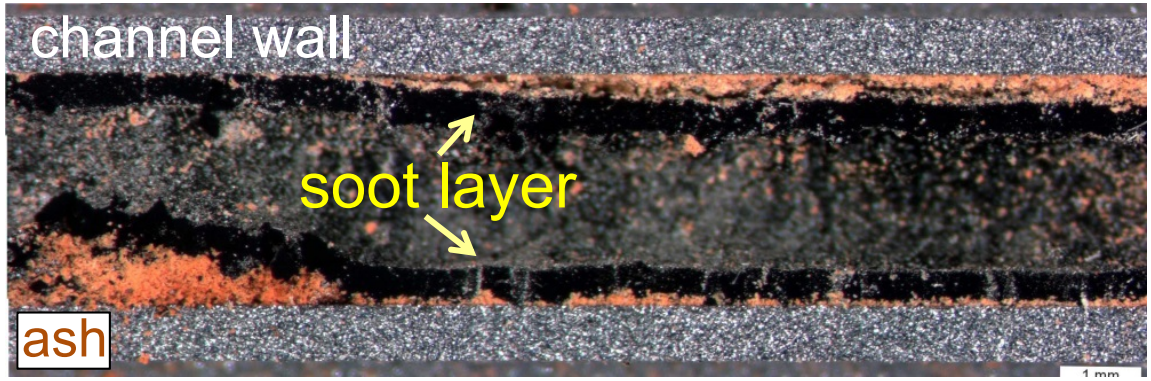
[Liati, Pandurangi, Boulouchos et al. (ES&T in press)]

Summary for ash collected directly from the exhaust stream

- Ash aggregates escape even high efficiency DPF (>99%) ; escaping ash aggregates are commonly attached onto large soot agglomerates

- Size of ash aggregates escaping filtration: 0.2-2μm; size of primary ash particles: 20-400nm.

- The DPF can promote breakout of large (ash bearing) soot agglomerates

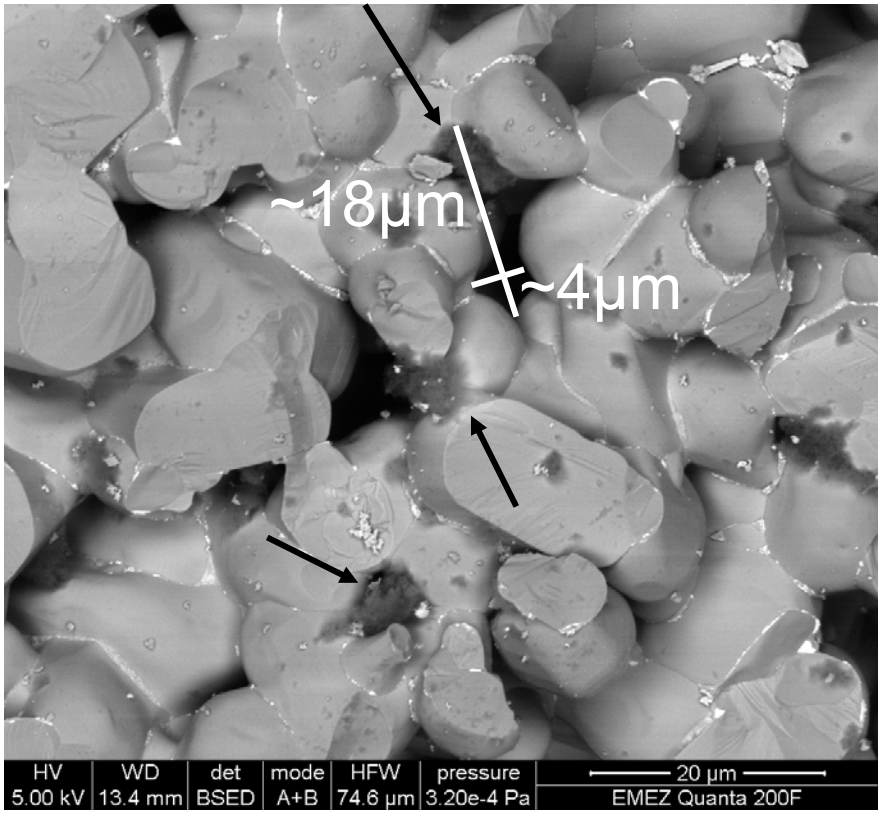

channel wall
soot layer
ash
1.5 mm
inlet channel

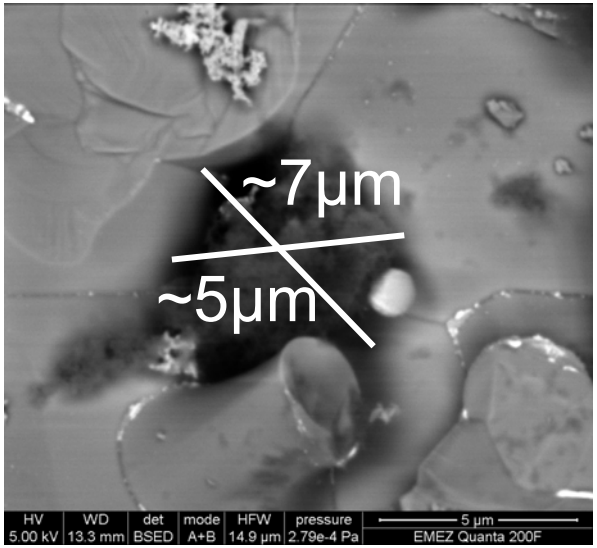
Summary for ash collected directly from the exhaust stream

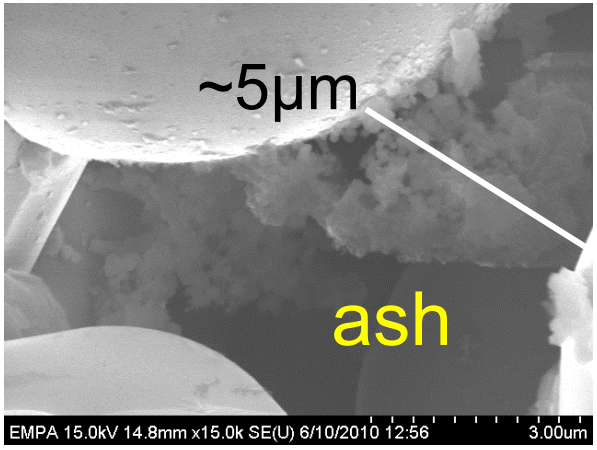
- Trace amounts of steel fragments can detach from the piston surface and/or fuel nozzle, melt and form new Fe-oxide nanoparticles.
- Environmental concern also for cars other than diesel

Thank you for listening!

Soot agglomerates may block filter wall pores and increase the ΔP between inlet and outlet channel



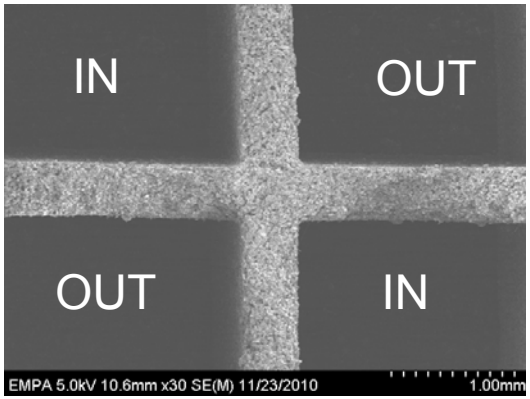




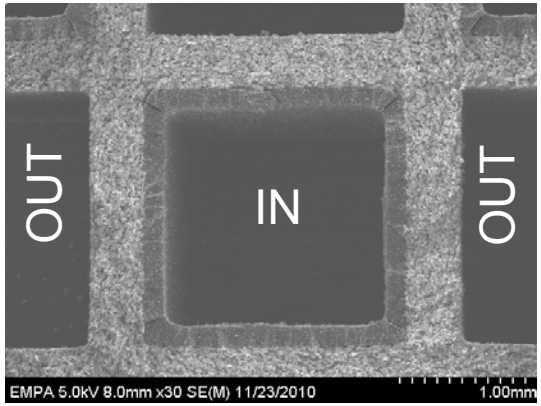
SEM – BSE images from the channel wall

Biofuel (RME) produces very little soot

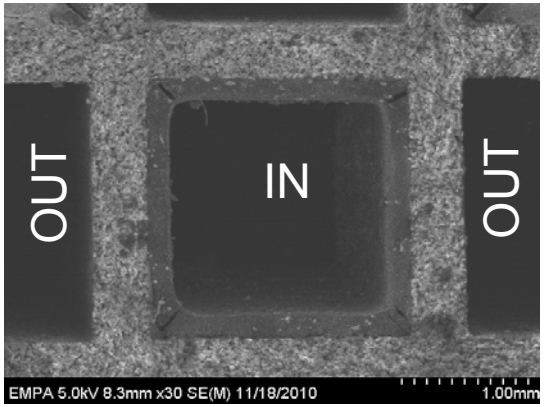
RME100



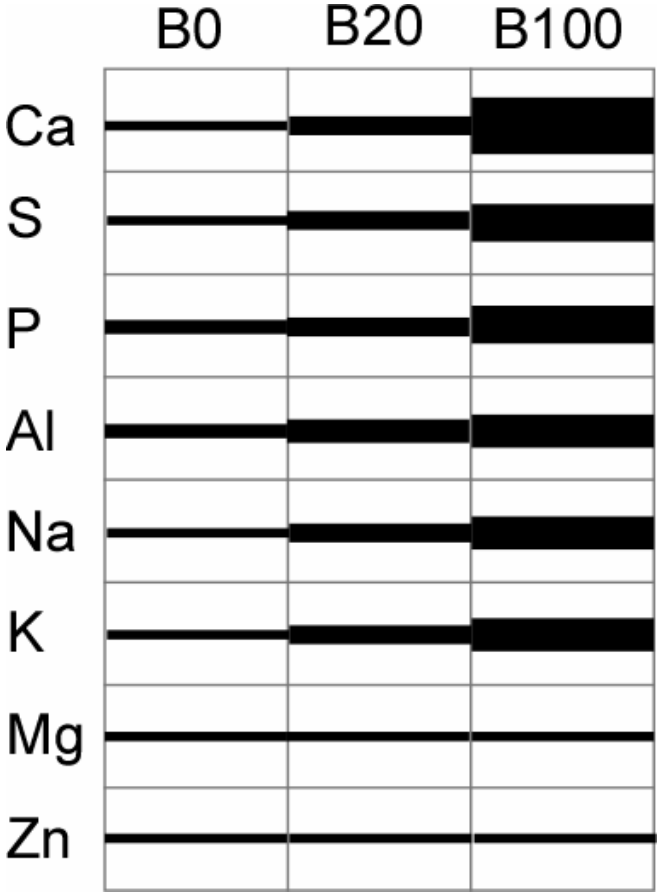
RME20



RME0



DPF operating with 100% biofuel (RME) shows most ash deposition → besides lube oil also biofuel contributes to ash production



- Mainly Ca, S and part of P derive from biofuel;
- Part of Ca,S,P, as well as Mg, Zn from lube oil;
- Na,K, part of Al from transesterification

Liati et al. (2012) J Nanopart Res 14:1224