

Can Sources of Single Soot Particles in Atmospheric Samples be Identified Using X-Ray Microspectroscopy?

M.G.C.Vernooij, G.Tzvetkov, V.Zelenay, M.Mohr, T.Huthwelker, R.Kaegi, R.Gehrig and B.Grobéty

Introduction

In urban areas, carbonaceous particulate matter typically accounts for 25-50% of the ambient PM 2.5 (particles with a diameter < 2.5 μm). Diesel and wood combustion related particles (size up to a few hundred nm) are a major source of these carbonaceous particles in urban and rural areas. Consequently, distinction between the particles from these two sources is very important. Recent results indicate that diesel and wood combustion particles can be distinguished based on C(1s) near edge x-ray absorption fine structure (NEXAFS) on bulk material. Characteristic resonances in the spectra allow for direct molecular speciation of the graphite-like solid core, surface functional groups, and aromatic and aliphatic components, depending on the origin of the soot. With scanning transmission x-ray microscopy (STXM), it is possible to gain more detailed information on the variation in carbon structures of single soot particles. We have investigated if it is possible to deduce the sources (diesel or wood combustion) of single particles in ambient samples from C(1s) spectral information.

Methods

We have first taken C(1s) NEXAFS spectra from individual soot particles in emission samples from test facilities (wood and diesel combustion) with STXM. Wood combustion samples were collected from the chimney of a simple wood stove in which beech wood was burned under normal and oxygen poor conditions. Diesel combustion samples were collected from a jeep (before Euro 1), a passenger car (Euro 4) and a truck engine (also Euro 4). All were operated with commercially available diesel fuel and were not equipped with particle filters. The spectra were used to find the characteristic resonances of single particles related to their source. Subsequently we have investigated the effect of particle weathering on the spectra. For several time spans, samples were kept in a glass tube through which ozone gas ($120 \mu\text{g m}^{-3}$) or nitrogen oxide ($32 \mu\text{g m}^{-3}$) flew constantly. Finally we have analysed two PM2.5 samples that were collected close to emission sources in areas where either traffic exhaust was the dominant source (arterial road in Zurich) or wood combustion was the dominant source (Roveredo, an alpine village in winter).

The morphology of the particles was analysed by TEM. STXM analyses were performed at the Pollux beam line of the Swiss Light Source (SLS). Particles were located using STXM and further characterised by C(1s) NEXAFS microspectroscopy. C(1s) spectra were gained from particles as small as 100 nm by averaging data of line scans with step size 20 nm and dwell time 10 ms. Spectra were taken between 280 and 300 eV, with a step size of 0.1 eV.

Results and discussion

Emission samples

The morphology of wood smoke and diesel soot particles is similar; both consist of fractal like chains of primary particles with sizes of ~30-40 nm. During wood combustion, soot particles develop if enough oxygen is provided. If combustion is oxygen poor, the fire is smouldering and mainly tar balls develop. Tar balls are highly spherical carbonaceous particles that have no crystallographic structure.

The dominant spectral signature of the three different vehicle engines is a strong peak at ~285 eV from C=C π -bonds and a rise in the spectra at ~291 eV from equivalent C=C σ -bonds. All C(1s)

NEXAFS spectra of car soot particles have a shoulder at $\sim 284\text{eV}$ from benzoquinone-groups. Between 285 and 290eV multiple surface functional groups can be observed. Of these, phenolic and carboxylic carbon are best developed. Small differences exist between the spectra of the different car engines.

The spectrum of soot from wood combustion is different. The aromatic peak at $\sim 285\text{eV}$ is only a shoulder of the much more pronounced phenolic carbon peak at $\sim 287\text{eV}$. The height of the aromatic, phenolic and carboxylic peaks in the tar ball spectrum are approximately the same, like in diesel soot spectra, but almost twice as high.

Altered samples

Ozone has a substantial effect on the C(1s) NEXAFS spectra of diesel soot particles. The height of the aromatic peak increases dramatically. The phenolic and carboxylic peaks also increase in height, but to a lesser extent, resulting in a steep slope dipping slope between the π -bond and σ -bond aromatic peaks. The original benzo-quinone shoulder becomes a little peak. Under the influence of nitrogen oxide, the intensity of surface functional groups has increased first, followed by a raise in intensity of the C=C π -bond peak. This finally results in similar carbon spectra as for tar balls.

Ambient samples

Most of the particles in the sample from Zurich are soot particles. Within the sample from Roveredo, only $\sim 60\%$ of the particles are soot. The rest of the particles are mainly volatile organic particles, which are not stable in the TEM. No tar balls are observed.

Three groups of particles are observed in the sample from Zurich. Particles in group 1 resemble spectra of soot particles from the passenger car and jeep. Spectra of particles from the second group have a relatively high aromatic π -bond peak. Additionally, the benzo-quinone shoulder is very pronounced, like in the spectra of ozone aged soot particles. The spectra from the third group particles do not coincide with the characteristic peaks in any of the emission samples. It is remarkable that none of the spectra in the sample from Roveredo resemble soot particle spectra from wood combustion, although wood combustion must have been the main particle source. All spectra have a dominant peak at 285eV . Particles in group 1 and 2 exhibit a steep down dipping slope between the π -bond and σ -bond aromatic peaks. Group 2 particles additionally have a little peak from benzo-quinone groups. Particles from group 3 have spectra in which the area with surface functional groups is higher than the π -bond peak.

It becomes clear from the C(1s) spectra from the particles in the ambient samples, that it is extremely difficult to identify the sources of the single particles. The similarities between the spectra of the ozone aged soot particles and the atmospheric particles are striking, even though reactions with other atmospheric gasses might have an additional effect on the carbon spectra. Although samples were collected very close to their emission sources, quick changes of the chemical structure must have already occurred. The aromatic π -bond peak of wood soot particles must have also grown under the influence of ozone. Eventually it must have even passed the intensities of the surface functional groups, thereby obliterating the key spectral signature for wood combustion at $\sim 287\text{eV}$ from phenolic carbon.

Conclusion

Particles from wood combustion cannot always be distinguished from diesel particles in emission samples using microspectroscopy. It is therefore impossible to use STXM based microspectroscopy to quantify the amount of wood smoke and diesel soot particles in atmospheric samples. Reaction with atmospheric gasses quickly changes the carbon structure of soot particles. Microspectroscopy is a powerful tool to follow these changes and study particle aging.



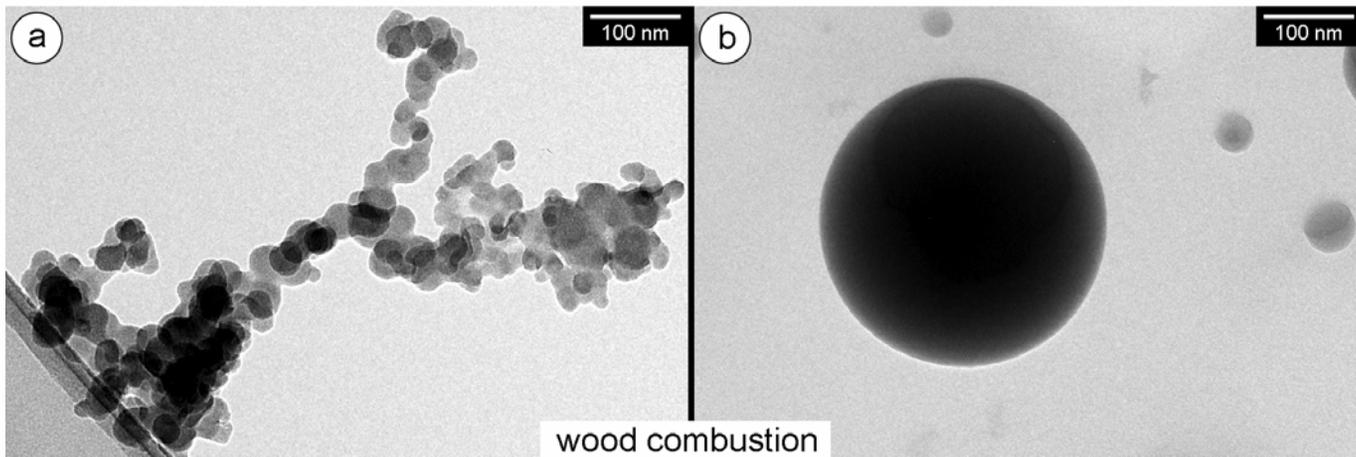
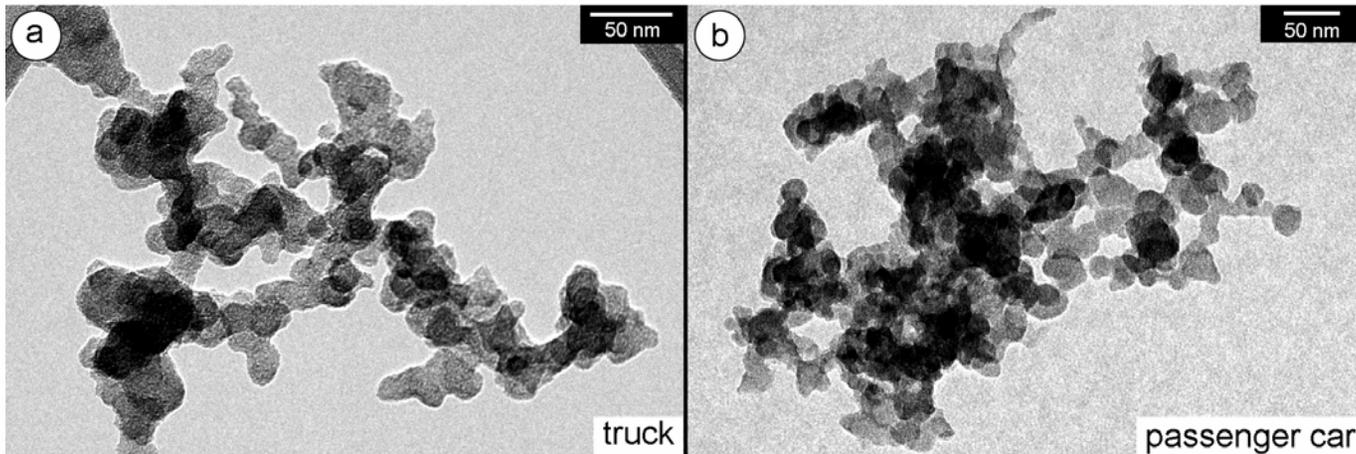
Can sources of single soot particles in atmospheric samples be identified using x-ray microspectroscopy?

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Introduction

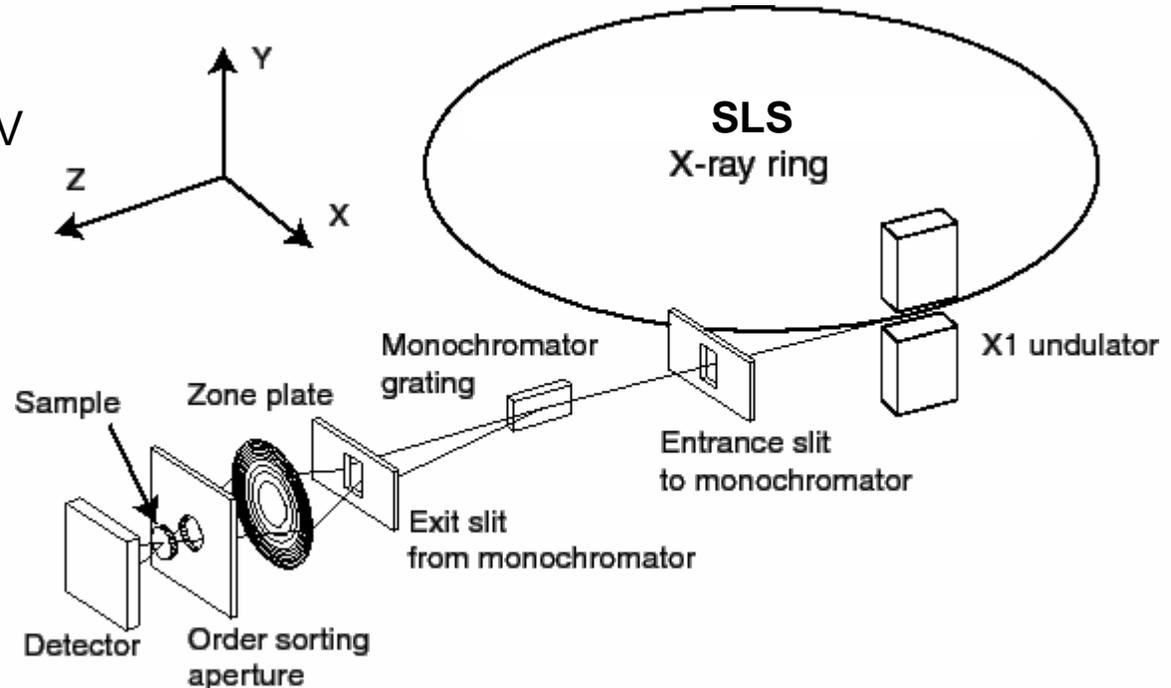


STXM

Scanning transmission x-ray microscope

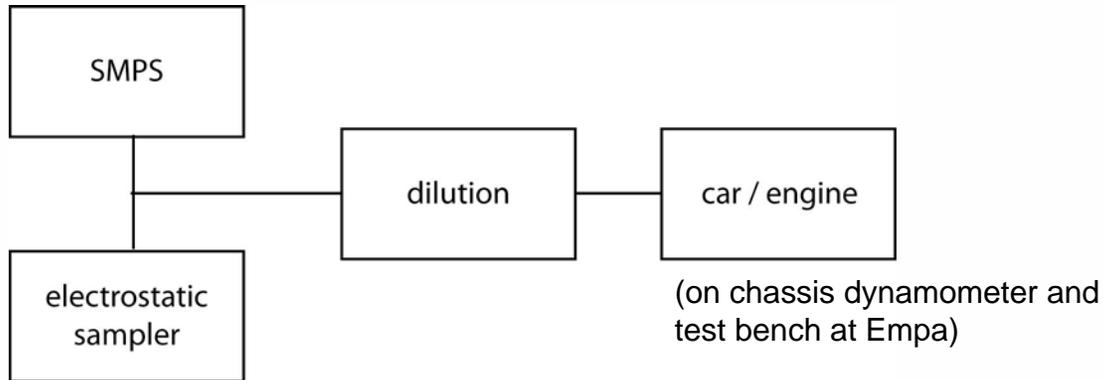
PolLux beam line
at SLS (swiss light source)

Spatial resolution ~40 nm
Energy range 200-1200 eV

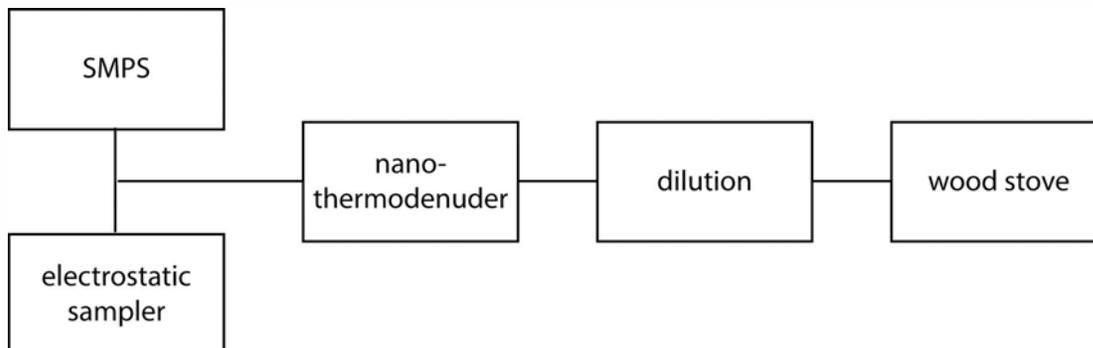


Sampling

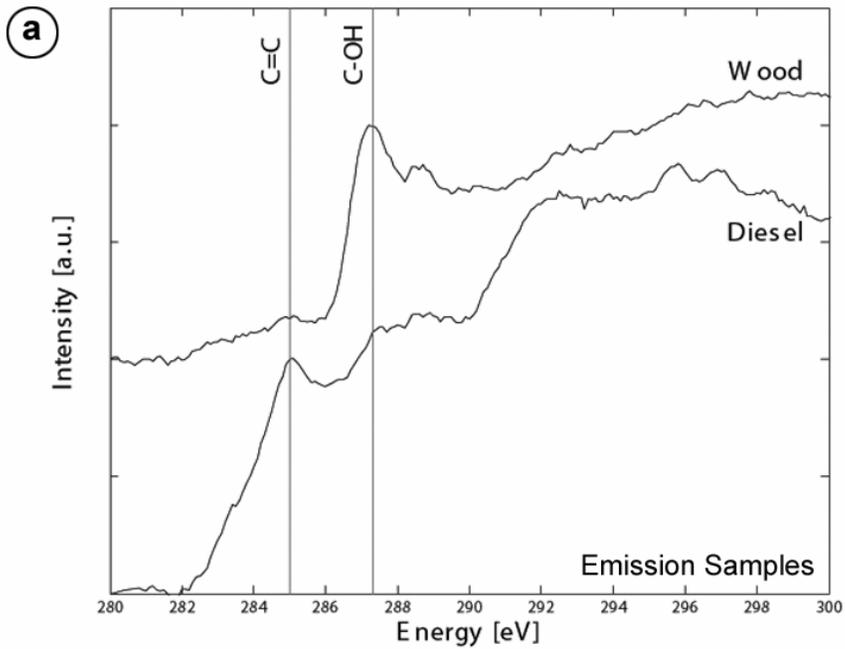
Diesel soot



Wood smoke

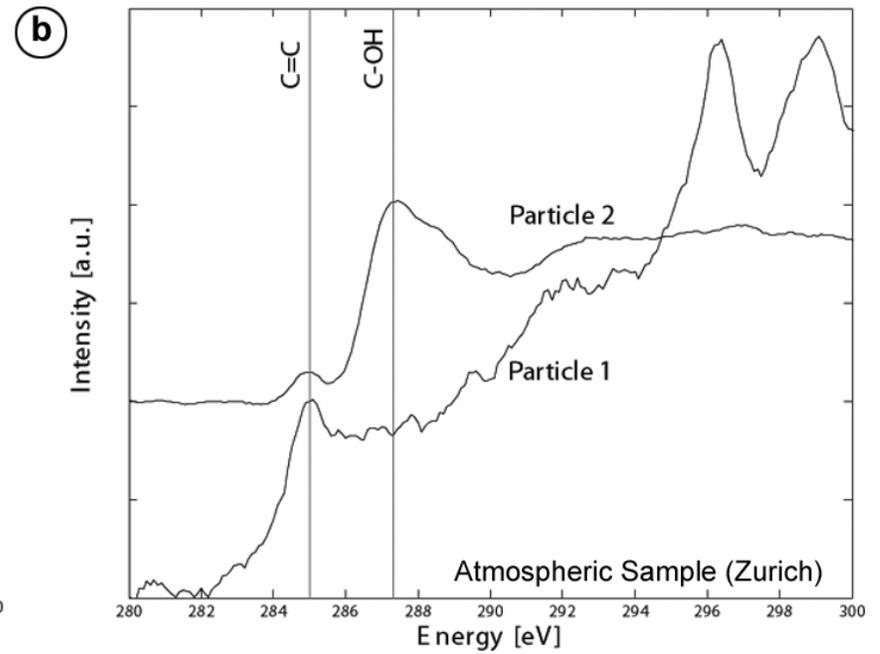
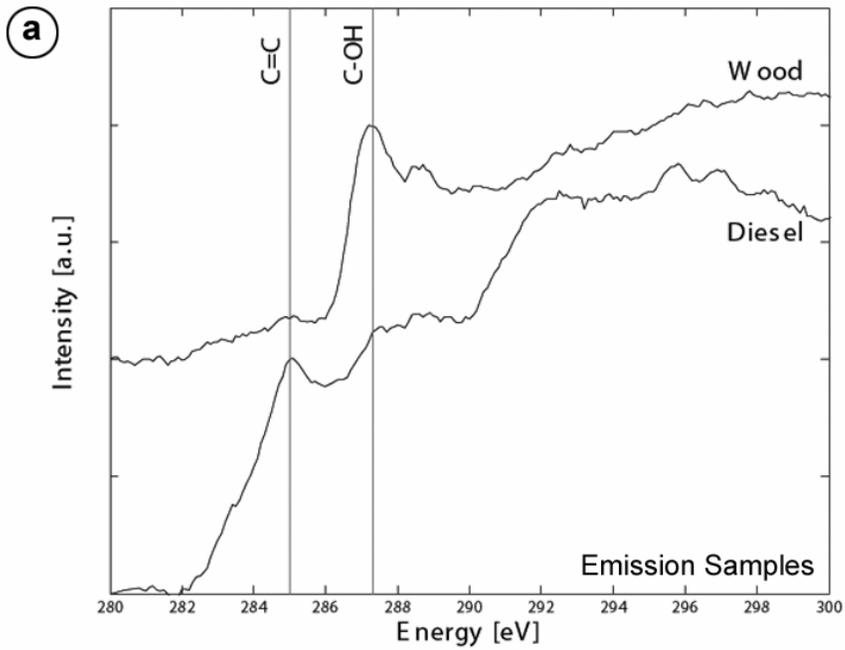


STXM



C(1s) NEXAFS spectra
(near edge absorption fine structure)

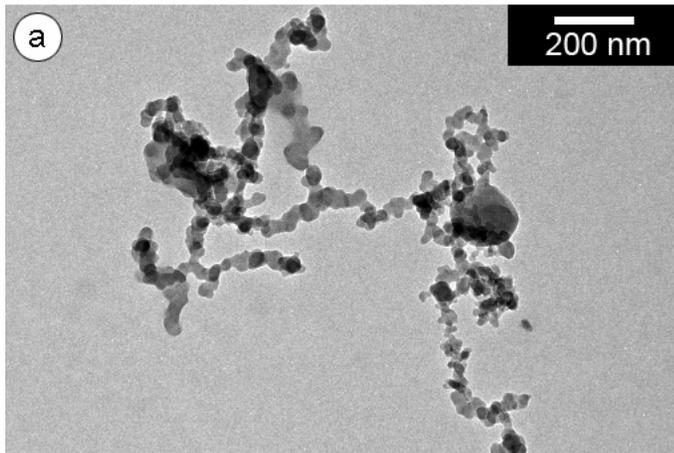
STXM



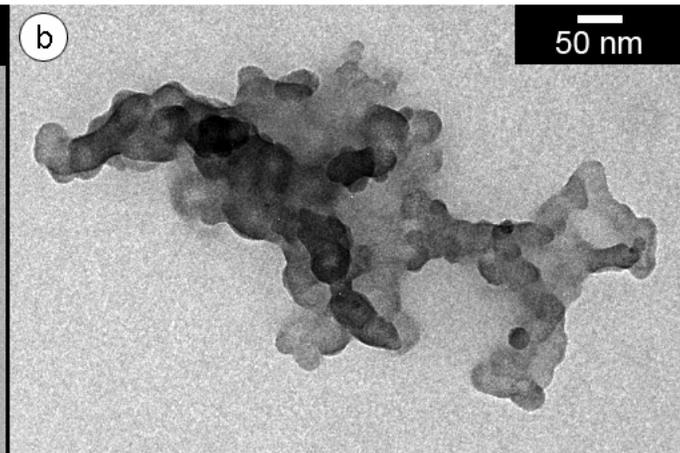
Particle aging

Aged particles

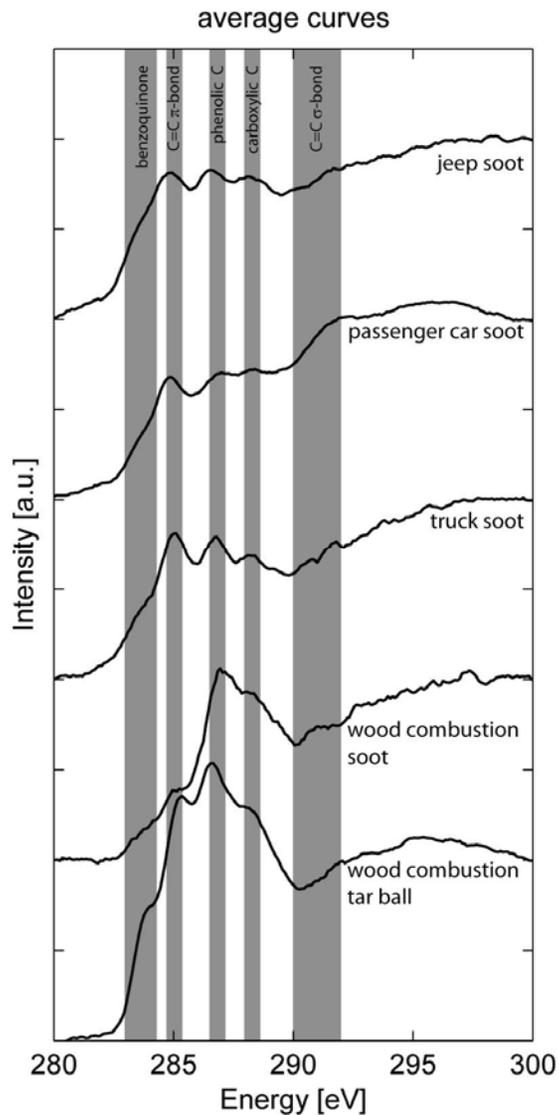
Mixed with other particles



Wrapped in other substances

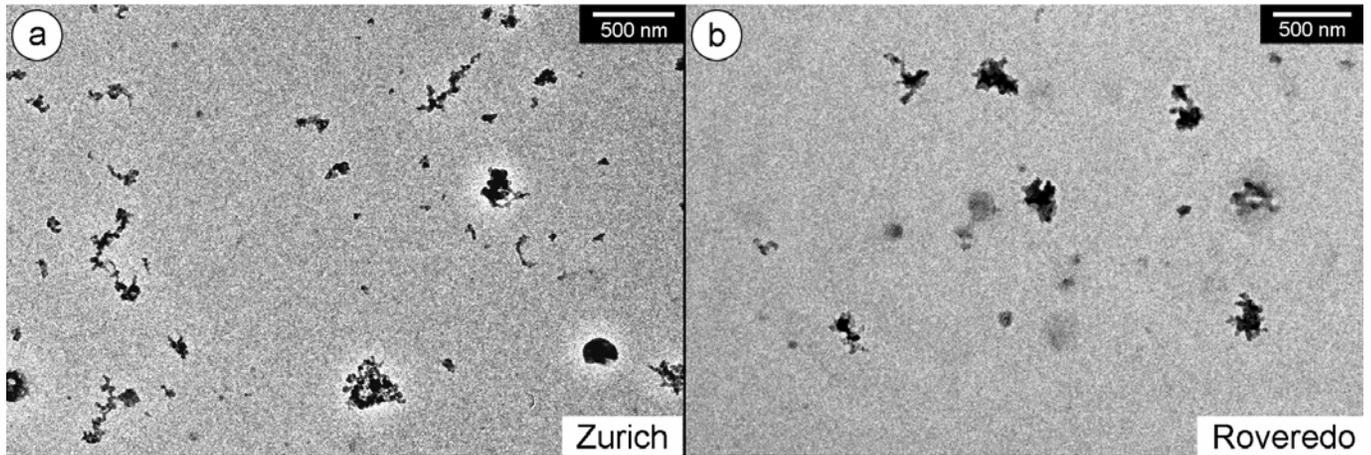


Emission samples

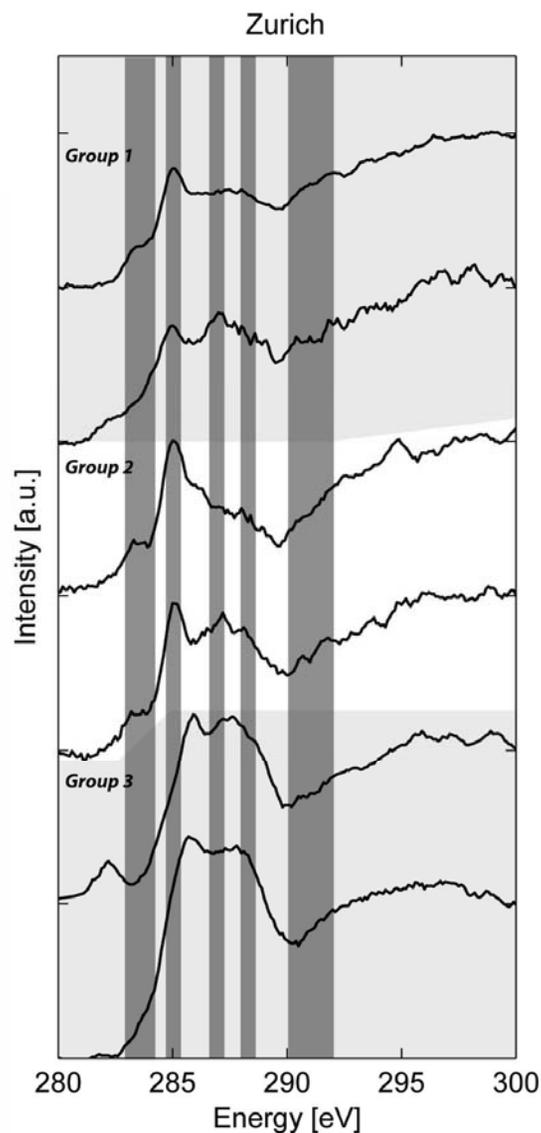


	Wood smoke		Diesel soot		
	soot	tar balls	jeep	Passenger car	truck
Shoulder at ~284eV quinone		x			
Peak at ~285eV C=C π -bond		x	x	x	x
Peak at ~287eV OH-bonds	x	x	x		x
Peak at ~288eV carboxylic	x	x	x	x	x
Shoulder at 290-292eV C=C σ -bonds	x	x	x	x	x

Ambient samples



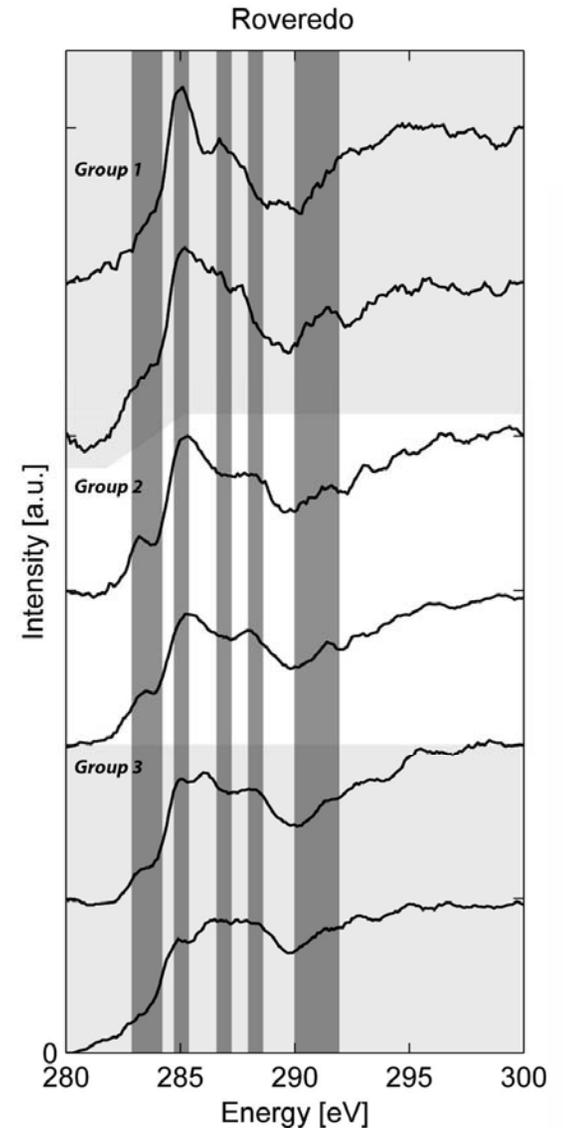
Ambient samples



	Wood smoke		Diesel soot		
	soot	tar balls	jeep	Passenger car	truck
Shoulder at ~284eV quinone		x			
Peak at ~285eV C=C π -bond		x	x	x	x
Peak at ~287eV OH-bonds	x	x	x		x
Peak at ~288eV carboxylic	x	x	x	x	x
Shoulder at 290-292eV C=C σ -bonds	x	x	x	x	x

Ambient samples

	Wood smoke		Diesel soot		
	soot	tar balls	jeep	Passenger car	truck
Shoulder at ~284eV quinone		x			
Peak at ~285eV C=C π -bond		x	x	x	x
Peak at ~287eV OH-bonds	x	x	x		x
Peak at ~288eV carboxylic	x	x	x	x	x
Shoulder at 290-292eV C=C σ -bonds	x	x	x	x	x



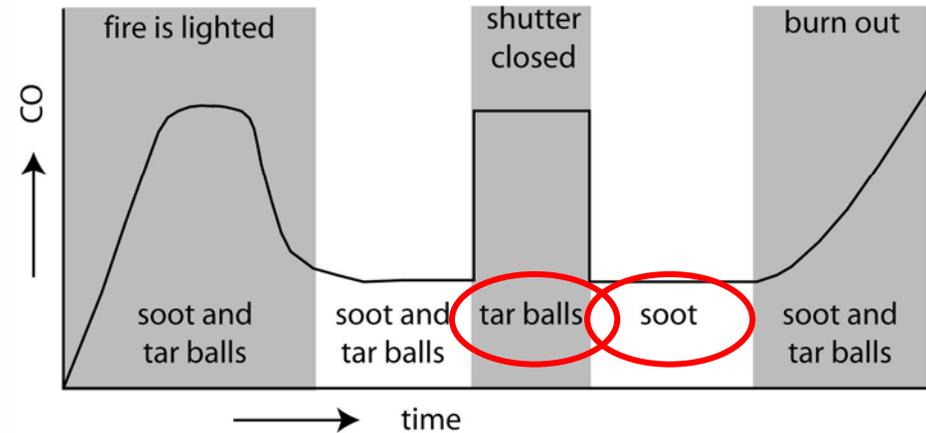
Particle aging experiments

Sample collection

Diesel combustion samples

Jeep (before Euro1) operated at 80 km/h on a chassis dynamometer

Wood combustion samples



Particle aging experiments

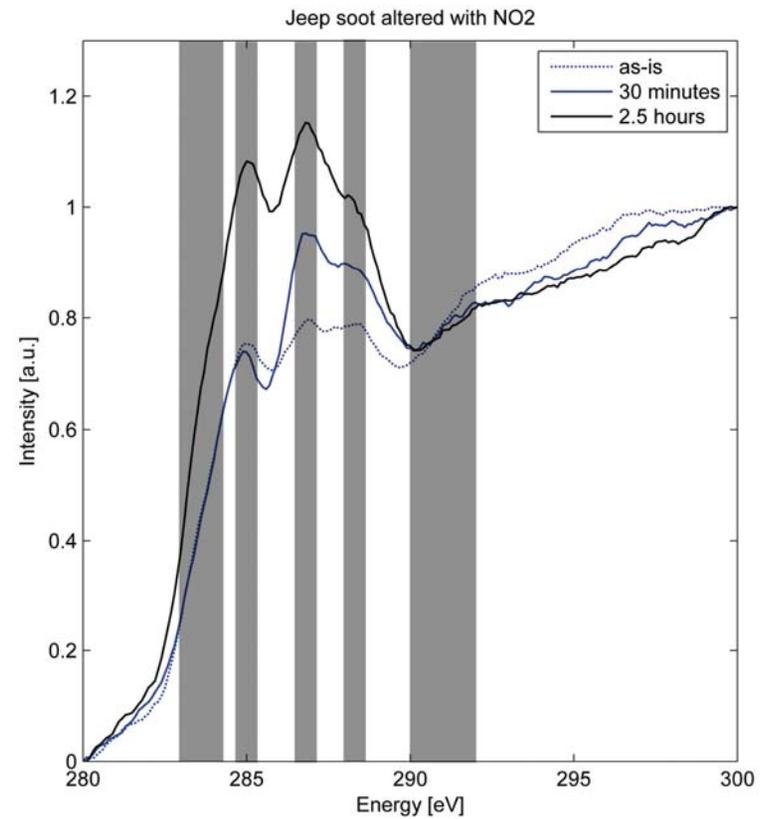
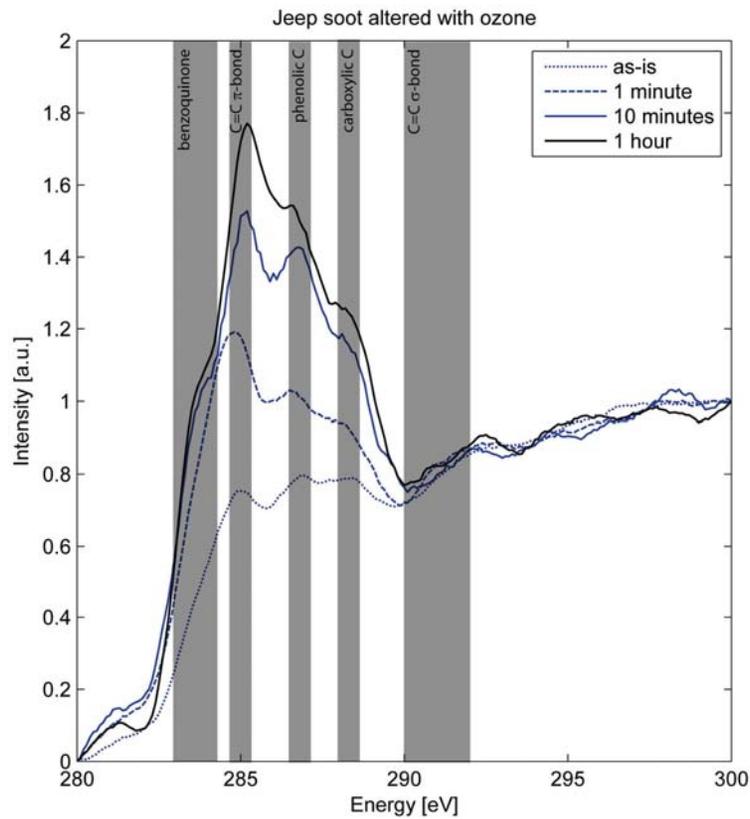
with O₃
and NO₂

120 $\mu\text{g}/\text{m}^3$
32 $\mu\text{g}/\text{m}^3$

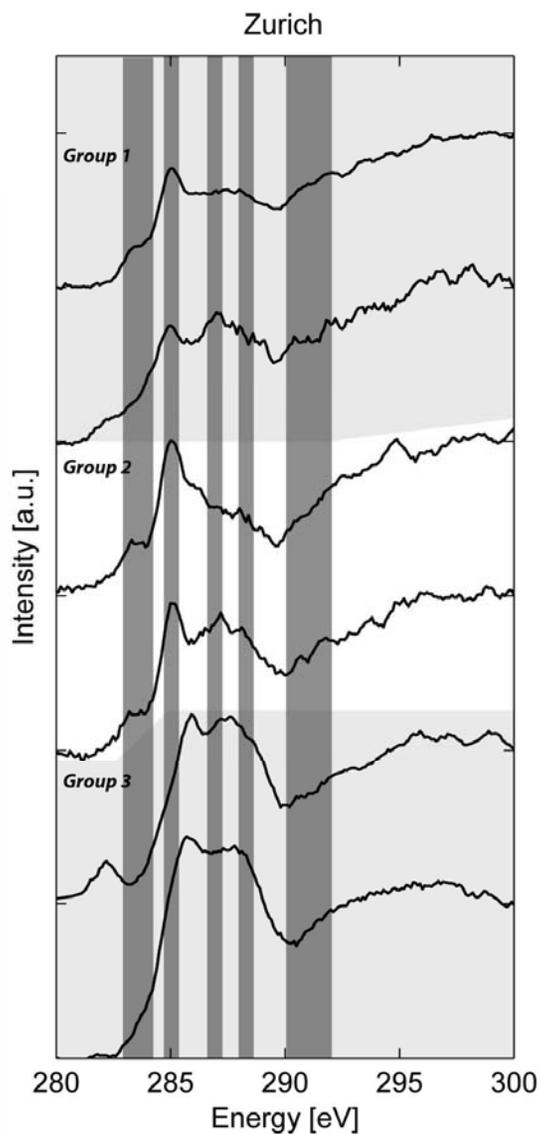
with O₃

120 $\mu\text{g}/\text{m}^3$

Aging of jeep soot



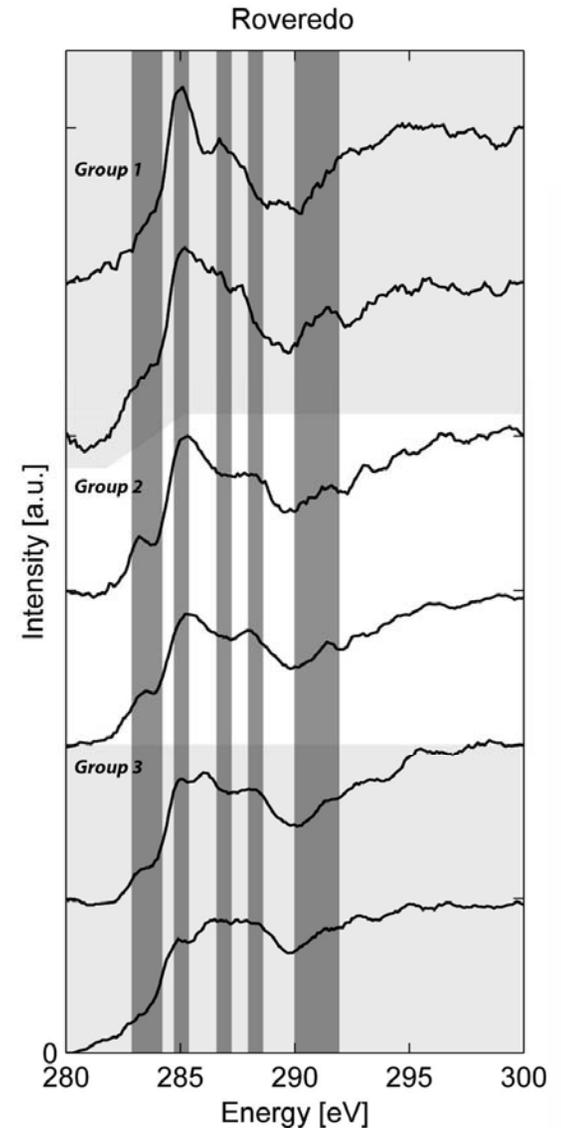
Ambient samples



	Wood smoke		Diesel soot		
	soot	tar balls	jeep	Passenger car	truck
Shoulder at ~284eV quinone		x			
Peak at ~285eV C=C π -bond		x	x	x	x
Peak at ~287eV OH-bonds	x	x	x		x
Peak at ~288eV carboxylic	x	x	x	x	x
Shoulder at 290-292eV C=C σ -bonds	x	x	x	x	x

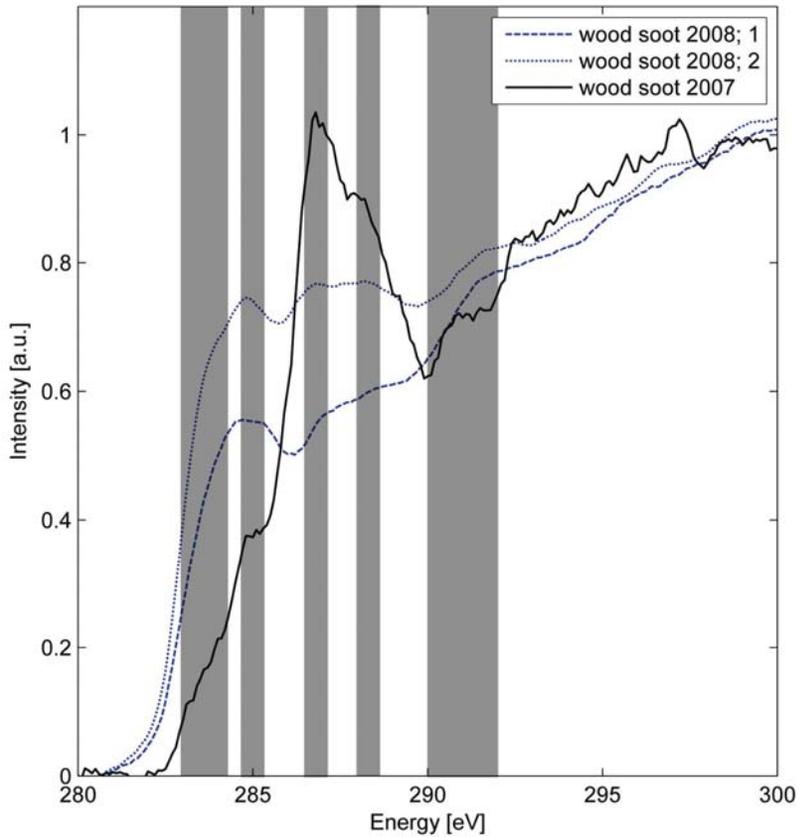
Ambient samples

	Wood smoke		Diesel soot		
	soot	tar balls	jeep	Passenger car	truck
Shoulder at ~284eV quinone		x			
Peak at ~285eV C=C π -bond		x	x	x	x
Peak at ~287eV OH-bonds	x	x	x		x
Peak at ~288eV carboxylic	x	x	x	x	x
Shoulder at 290-292eV C=C σ -bonds	x	x	x	x	x



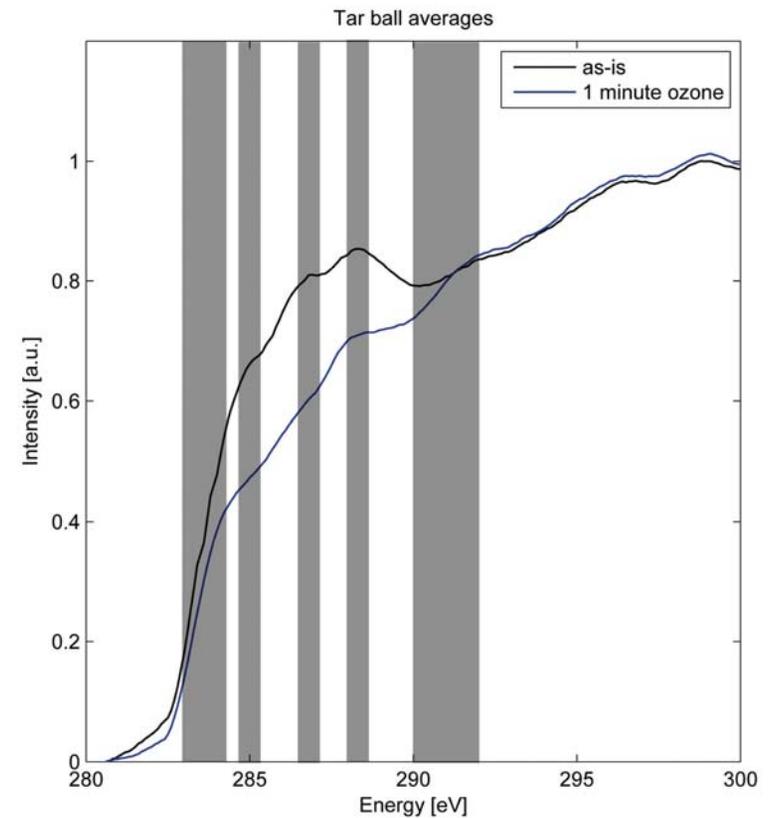
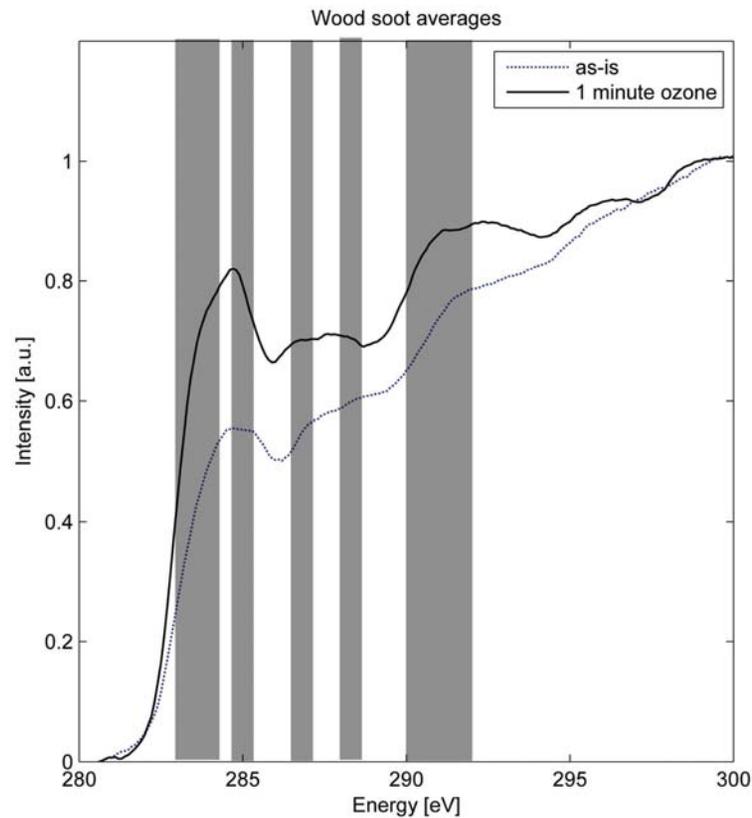
Wood smoke

variability of wood soot as-is spectra



	Wood smoke	Diesel soot		
	soot	jeep	Passenger car	truck
Shoulder at ~284eV quinone				
Peak at ~285eV C=C π -bond		X	X	X
Peak at ~287eV OH-bonds	X	x		x
Peak at ~288eV carboxylic	x	x	x	x
Shoulder at 290-292eV C=C σ -bonds	x	x	x	x

Aging of wood smoke particles



Conclusions

- Particles from wood combustion cannot always be distinguished from diesel particles in emission samples using microspectroscopy
 - It is therefore impossible to use STXM based microspectroscopy to quantify the amount of wood smoke and diesel soot particles in atmospheric samples
- Reaction with atmospheric gasses quickly changes the carbon structure of soot particles
 - Microspectroscopy is a powerful tool to study particle aging!!
 - Experiments are planned to investigate water uptake of aged soot particles with STXM based microspectroscopy

Thanks to..

- Tiba (wood smoke sampling)
- Federal offices for the environment of Zurich and Graubunden
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