Traffic exhaust or wood smoke?

Source specification of ambient samples with TEM and C(1s) NEXAFS spectroscopy

M.G.C. Vernooij, R. Kägi, A. Braun, M. Mohr, R. Gehrig and B. S. Mun

INTRODUCTION

High concentrations of particulate matter (PM) in Switzerland's main cities in the winter of 2006 brought up a vivid debate about particle sources. Major constituents of urban PM are assumed to be soot particles from diesel and wood combustion and it is important to quantify their abundances in ambient air. Recent investigations have shown that diesel PM samples can be clearly distinguished from wood combustion PM samples (both from test facilities) based on carbon near-edge X-ray absorption fine structure (NEXAFS) spectroscopy (Braun 2005). Carbonaceous soot particles constitute a major part of the PM of these samples. 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 (di Stasio and Braun, 2006). Such detailed analyses can only be attained with NEXAFS. Other techniques like TEM_EELS for example fail to detect surface functional groups (Braun et al. 2005).

METHOD

Ambient air samples were collected in winter next to an arterial road in Zurich (CH) and in Roveredo (CH), a small village in an alpine valley. The main source of soot particles in the sample from Zurich is the local car traffic (i.e. diesel soot); the main sources of soot particles in the winter sample from Roveredo are combustion particles from wood stoves that are used to warm the houses (Prévôt et al. 2006). Samples were collected on Nuclepore and Teflon filters and on TEM-grids with an especially designed electrostatic sampler. Soot particles on TEM grids were analysed with a Phillips CM30 TEM operating at 300 kV. The loaded filters were immersed in ethanol and ultra-sonicated to become a PM-ethanol solution. Drops of this solution were put on clean gold foils and measured with the NEXAFS beam line (9.3.2) at the ALS in Berkeley (USA). To characterise the bulk structure of the particles in each sample, absorbance spectra were collected between 275 and 320 eV. The NEXAFS spectra were background corrected. Peaks can be observed within the measured range that are related to the gold foil on which the samples have been deposited. To exclude these gold peaks, the background corrected samples were divided by the spectrum of a clean gold foil.

RESULTS AND DISCUSSION

The morphology of diesel and wood smoke soot particles is very similar. Both consist of chains of primary particles with a graphitic structure. However, the average diameter of primary particles of diesel soot (27±7 nm) is generally smaller than the average diameter of primary particles of wood smoke soot (38±11 nm, Kocbach et al. 2005). The average diameter of primary particles in ambient samples from Zurich (26±9 nm) are approximately the same as those from diesel exhaust, the average diameter of primary particles in ambient samples from Roveredo in winter (36±11 nm) are only slightly smaller than those from wood smoke.

The NEXAFS spectra from the samples from the traffic dominated location in Zurich have a clear peak at 285 eV. This peak is very pronounced in spectra of diesel PM samples and of graphite samples as well and referred to as the C=C π–bond peak (Braun et al. 2004). Within the spectra from the wood smoke dominated sample from Roveredo, this peak is not very distinct. These spectra, though, have a firm peak at 287 eV, which is also prominent in spectra from samples from different fireplaces (and referred to as C-OH, Braun 2005). The clear differences between the spectra from the locations in Zurich and Roveredo indicate that it is possible to distinguish the dominant source of soot particles with this technique.

OUTLOOK

We assume that the C-OH peak in the spectrum of the ambient winter sample from Roveredo is characteristic for wood smoke. To prove this statement, samples were collected in Roveredo in summer for NEXAFS measurements. During the summer season, a minimum contribution of wood combustion is expected (because houses do not need to be warmed) and diesel combustion from the local car traffic will be the dominant source of soot particles (average diameter of primary particles in the collected sample is now 28±8 nm). Consequently, the C-OH peak at 287 eV in the spectra from the summer samples is expected to be smaller or not existent and the C=C peak at 285 eV is expected to be more pronounced.

STXM measurents are planned at the Swiss Light Source (SLS) to quantify the relative abundance of soot particles from wood combustion (classified with C-OH peak at 287 eV) and from diesel combustion (classified with relatively firm C=C peak at 285 eV) in ambient samples.

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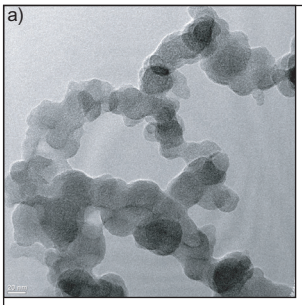
Introduction

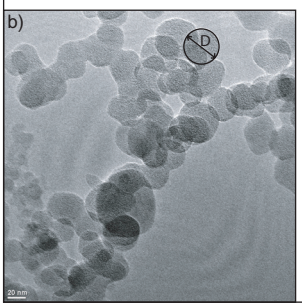
High concentrations of particulate matter (PM) in Switzerland's main cities in the winter of 2006 brought up a vivid debate about particle sources. Major constituents of urban carbonaceous PM are soot particles from diesel and wood combustion and it is important to quantify their abundances in ambient air. However, differentiating between the two sources using bulk analytical techniques is difficult. In this project we investigate the feasibility of transmission electron microscopy (TEM) analysis and carbon near edge x-ray absorption fine structure (NEXAFS) spectroscopy to discriminate between the two sources.

Reference samples were collected from wood and diesel combustion test facilities. Ambient samples were collected in winter next to an arterial road in Zurich and in Roveredo, a small village in an alpine valley (on occasion of the AEROWOOD-project). The filter from Zurich is expected to be predominantly burdened with traffic exhaust particles and the filter from Roveredo with wood combustion particles.

TEM Analysis

Particles were collected on TEM grids with an especially designed electrostatic sampling device.The morphology of diesel and wood smoke soot particles is very similar (Fig.1). Both consist of chains of primary particles with a graphitic structure.





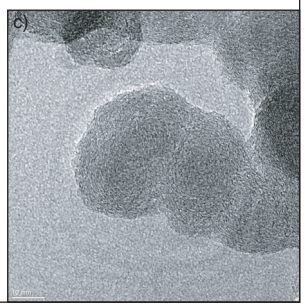


Figure 1: Comparison of the morphologies of diesel soot (a,c) and soot from wood smoke (b). Both show chain-like branching structures. The primary particles in both aggregates consist of concentrically stacked graphitic layers (c). TEM bright field images from samples from test facilities.

The average diameter of primary particles (D) from diesel exhaust vehicles is smaller than the average D from wood smoke (Table 1). The average D from ambient samples from Zurich and from Roveredo in summer are approximately the same as those from diesel exhaust, the average D from ambient samples from Roveredo in winter are slightly smaller than those from wood smoke.

Sample	Number ofparticles	Primary particle diameter [nm]	Standard deviation [nm]
Vehicle (Kocbach et al.)	-	27	7
Ford cold idle	242	29	9
Wood smoke (Kocbach et al.)	-	38	11
Zürich, arterial road	210	26	9
Roveredo winter	566	36	11
Roveredo summer	243	28	8

Table 1: Primary particle sizes. Vehicle and Ford are diesel combustion.

C1s NEXAFS spectroscopy

PM10 samples were collected on nuclepore and teflon filters, immersed in ethanol and ultra-sonicated to obtain a PM10-ethanol solution. Drops of this solution were put on clean gold foils. The bulk structure of the samples was measured with C1s NEXAFS spectroscopy (Fig. 2).

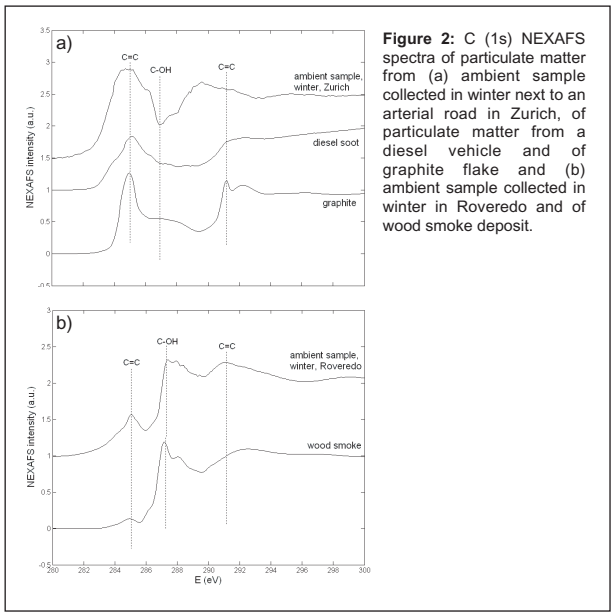


Figure 2: C (1s) NEXAFS spectra of particulate matter from (a) ambient sample collected in winter next to an arterial road in Zurich, of particulate matter from a diesel vehicle and of graphite flake and (b) ambient sample collected in winter in Roveredo and of wood smoke deposit.

The spectra from the samples from the traffic dominated location in Zurich have a clear peak at 285 eV (Fig. 2a). This peak is very pronounced in spectra of diesel PM samples and of graphite samples as well and referred to as the C=C bond peak (Braun 2005). Within the spectra from the wood smoke dominated sample from Roveredo, this peak is not very distinct (Fig. 2b). These spectra, though, have a firm peak at 287 eV, which is also prominent in spectra from samples from different fireplaces (and referred to as C-OH, Braun 2005).

Conclusions

1. The average diameter of primary particles of soot might give an indication for the dominant source of soot particles from ambient samples (i.e. diesel combustion or wood combustion) .

2. Dominant sources of PM10 in ambient air samples can be distinguished with NEXAFS spectroscopy.

Future perspectives

1. NEXAFS spectra of samples from Zurich and Roveredo in summer are being measured to investigate seasonal changes.

2. STXM measurents are planned at the Swiss Light Source to quantify the relative abundance of soot particles from wood combustion (classified with C-OH peak at 287 eV) and from diesel combustion (classified with relatively firm C=C peak at 285 eV) in ambient samples.

References

Braun 2005. Carbon speciation in airborne particulate matter with C (1s) NEXAFS spectroscopy. J. Environ. Monit. 7: 1059-1065.

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