Air Pollution And Climate Change - Who Takes The Blame ?

C(1s) NEXAFS spectroscopy on fine particulates *"Feinstaub"* could provide answers

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Airborne fine particulate matter, in particular solid combustion products like soot from fossil fuel and biomass burning, is increasingly under scrutiny for its adverse impacts on human health and climate change. As a matter of fact, quite recently have some governments in Europe have imposed restrictions on public traffic in order to curb emission of fine particulate matter (Feinstaub) from vehicles. In particular are diesel engines blamed for such pollution, but very recent studies press releases in Switzerland, for instance, point to potential other sources for pollution from carbonaceous particulate matter, for instance emissions from "cheminee" wood in domestic furnaces. Data shown in this poster support this alternative view. This poster summarizes our NEXAFS research activities on this important topic that have been carried out by the Consortium for Fossil Fuel Sciences at the University of Kentucky in the past four years, involving some major synchrotron radiation centers in the USA (ALS, NSLS).

Who contributes (most) to urban and rural air pollution with carbonaceous airborne particulate matter (PM) ?

Identification of source specific signatures is of utmost importance for subsequent source attribution and apportionment. Signatures are not easy to obtain for carbonaceous PM. Classification typically exists in terms of elemental and organic carbon only: EC and OC. This distinction appears too primitive for source apportionment. We propose use of soft X-ray techniques for characterization and molecular speciation of carbonaceous PM. Emphasized are recent results on diesel exhaust, wood smoke, urban PM and others with C(1s) NEXAFS spectroscopy, which appears superior to IR and TEM-EELS, and GC-MS.

Recent and current research activities on the chemical characterization of carbon in airborne carbonaceous particulate matter with near-edge X-ray absorption fine structure (NEXAFS) spectroscopy are reviewed. This relatively novel technique is often superior to TEM-EELS and FTIR spectroscopy. In the extreme case, one single PM particle is sufficient for characterization. Liquids, extracts, solid core and surface functional groups can be quantified. Preliminary data on combustion derived PM such as diesel soot, wood smoke and tobacco smoke are compared with ambient samples. Scanning transmission X-ray micro-spectroscopy and conventional C(1s) NEXAFS data of diesel particulate matter, and aqueous extracts thereof are presented. A significantly better spectral resolution of molecular species than with TEM-EELS is obtained and allows for source signature attribution. Noteworthy observations are the absence of graphitic structures in woodsmoke. Graphitization of diesel soot can strongly depend on engine operation conditions and fuel doping; surprisingly, ferrocene prevents soot from graphitization. Preliminary results on combined toxicological bio-assay and NEXAFS studies on extracts are also shown.

C(1s) NEXAFS for environmental applications is still in its infancy but has a good potential to become a useful analytical technique for atmospheric and environmental scientists and combustion engineers, who need to address carbon relevant issues like global climate change or human health impact of PM. This concerns in particular soot, and similar combustion derived carbonaceous matter. The conjugated surface and bulk sensitivity of NEXAFS is superior to any of the aforementioned techniques and invaluable to researchers who have to tackle with a broad range of chemically and structurally complex carbonaceous PM. Extracts and solid residuals can be studied. Radiation damages are less significant than in TEM-EELS but harder than in IR spectroscopy. Intense probe techniques like STXM bear the risk of considerable radiation damages and hence alteration of the sample, as previously observed, but also the potential for atmospheric in situ studies. A disadvantage is that NEXAFS studies require access to synchrotron facilities, but more and more such facilities are built and equipped for soft X-ray experiments. Radiation damages might be useful for the simulation of weathering of PM, for instance. STXM, the microscopy variant of NEXAFS, lacks in resolution as far as the finest tail in size distribution of the ultra-fine PM is concerned. A potentially interesting near-future application of STXM will be the study of the interaction between PM and biological cells. Biological cells are large enough for STXM to give high resolution, better than the IR microscope in terms of spatial resolution, and better than TEM-EELS in terms of chemical sensitivity with respect to carbon. Biofilms have already been studied with NEXAFS and STXM. Several research groups have mastered the problems that result from bringing samples in aqueous environment into the STXM. Mechanisms that govern adverse health effects when humans are exposed to PM are more likely to be elucidated with such experiments. This review was about carbon NEXAFS spectroscopy. The same technique applies to oxygen as well.

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C(1s) NEXAFS spectroscopy on fine particulates *"Feinstaub"* could provide answers

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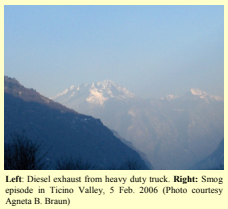
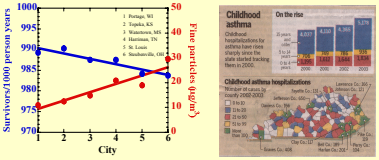
Objective

Who contributes (most) to urban and rural air pollution with carbonaceous airborne particulate matter (PM) ?
Identification of source specific signatures is of utmost importance for subsequent source attribution and apportionment. Signatures are not easy to obtain for carbonaceous PM. Classification typically exists in terms of elemental and organic carbon only: EC and OC. This distinction appears too primitive for source apportionment. We propose use of soft X-ray techniques for characterization and molecular speciation of carbonaceous PM. Emphasized are recent results on diesel exhaust, wood smoke, urban PM and others with C(1s) NEXAFS spectroscopy, which appears superior to IR and TEM-EELS, and GC-MS.



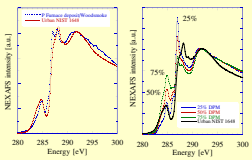
Left: Diesel exhaust from heavy duty truck. **Right:** Smog episode in Ticino Valley, 5 Feb. 2006 (Photo courtesy Agneta B. Braun)



Left: Correlation between mortality and particulate concentration [6 cities study; 1].
Right: Coal electric power plants in Kentucky/USA blamed for poor air quality and childhood asthma.

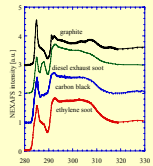
Major Conclusions

- Diesel PM *not necessarily* a major contributor to Urban PM
- TEM-EELS performs poorly in molecular carbon speciation
- NEXAFS spectroscopy performs well for carbon speciation and can provide characteristic source signatures.
- Be aware of radiation damages, in particular in STXM.

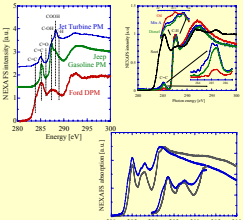


Attempted modelling of urban PM (NIST 1648 Standard collected in St. Louis MO, USA) by linear combination of spectra from diesel exhaust PM and woodsmoke. It doesn't work without adding at least one 3rd. component.

Carbon C(1s) NEXAFS or reference materials



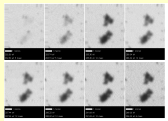
Left: Comparison of spectra from graphite, diesel exhaust, carbon black, and ethylene soot reveals their graphitic nature due to the aromatic setting of carbon atoms in double bonds: C=C. The corresponding π resonance is found at 285 eV. The plateau from 292 to 310 eV is typical for electronically well conducting soot and graphite samples.

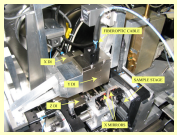


Right: Spectra of Diesel, Oxygenated Diesel, Motor Oil, and Soot, all obtained with STXM. C=C bonds are found at 285 eV, C–H at 287 eV.
Left: Peak assignment for Jet, Gasoline engine and diesel engine PM. **Bottom**: NIST diesel heavy duty (SRM 1650) and forklift (SRM 2975) reference material soot.

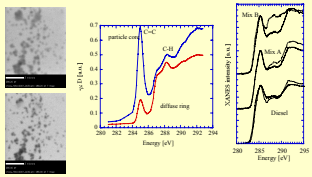
Carbon-NEXAFS of Single Diesel-PM Particles with STXM

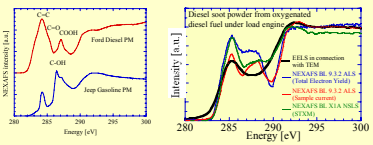
Spectro-microscopy with the Scanning Transmission X-ray Microscope (STXM) allows for chemical contrast variation on sub-micrometer scale. Every pixel on a STXM image can be assigned a NEXAFS spectrum, and every energy can be assigned one image. Image on the right shows the STXM microscope at beamline X1A in Brookhaven National Lab (NSLS).





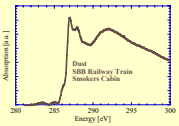
Left: Series of Scanning Transmission X-ray Microscopy (STXM) images of load soot particles, for energies from 282.5 eV to 296.0 eV. Due to X-ray optical contrast, spatial chemical variations allow to assign specific absorption spectra to single particles or even particular sample regions. **Right**: NEXAFS of single (load idle ---) soot particles from Diesel and oxygenated Diesel, as obtained with STXM.

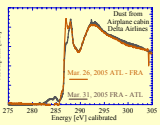


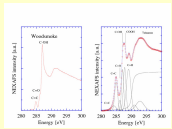


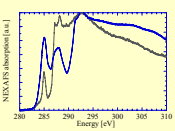
Indoor and Urban PM

Indoor PM not necessarily rich in carbon. Data acquisition and processing need care and caution. Don't take these data literally. Dust samples collected in 1) *Delta Airlines* passenger air plane cabin, 2) *SBB* smokers railway cabin. Not shown here, dust from home in Limestone is rich Kentucky significant source of carbonate.





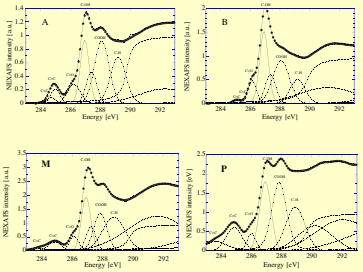




Right: NIST SRM reference materials.Spectra of urban particulate matter SRM 1648 (solid, black) and diesel exhaust SRM 1650.

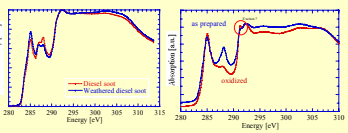
Woodsmoke from dry and humid wood

Woodsmoke PM C(1s) NEXAFS spectra show significant C-OH resonance at 287 eV. PM from wet wood shows strong response from quinone and carboxyl groups, while dry wood doesn't. **Chimney of sample P eventually caught fire !**

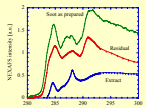


Oxidation & Weathering Studies

Diesel PM exposed to air, sunlight and humidity for 7 days shows less surface functional groups and appears "more graphitic" than unexposed DPM. Important finding for conclusion whether urban PM is dominated by DPM. Interestingly, single wall carbon nanotubes exhibit a similar change of spectra when oxidized in air in a furnace.

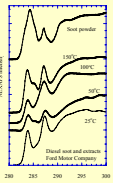


Aqueous Extracts



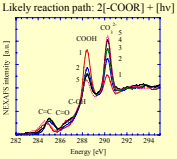
C(1s) spectra of DPM residuals look quite similar to spectra from unextracted DPM. Spectra of extracts, volatiles may look entirely different from original PM material. Extraction a good step for further analysis with NEXAFS spectroscopy.

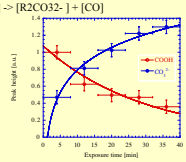
Sequence of C(1s) NEXAFS spectra from from DPM and volatiles, extracted with subcritical water at various temperatures. Significant changes in peak positions and peak heights indicate that particular molecular species, including polycyclic aromatic hydrocarbons, are selectively extracted at particular temperatures.



Atmospheric chemistry

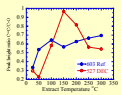
Extraction of volatiles from DPM with subcritical water. Exposure to soft X-rays causes decarboxylation and generation of a carbonate resonance. Quantitative kinetic studies on photolysis possible.
Likely reaction path: 2[-COOR] + [hv] -> [R2O32-] + [CO]

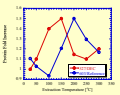




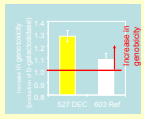
Toxicological Studies

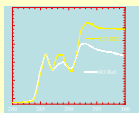
Correlation of C (1s) NEXAFS peak heights and protein fold increase indicate toxicity and toxic surface functional groups in diesel exhaust PM.





Diesel exhaust PM generated with oxidizer has higher genotoxicity.





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