Air Pollution And Climate Change - Who Takes The Blame ?
C(1s) NEXAFS spectroscopy on fine particulates *"Feinstaub"* could provide answers

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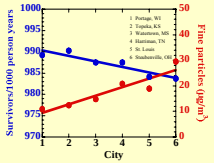
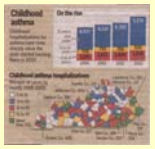
Airborne fine particulate matter, in particular solid combustion products like soot from fossil fuel and biomass burning, is increasingly under scrutiny for its adverse impacts on human health and climate change. As a matter of fact, quite recently have some governments in Europe have imposed restrictions 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. Some of the data shown in this poster support this alternative view. This poster summarizes 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 the four major synchrotron radiation centers in the U.S.A (SSRL, ALS, APS, NSLS).

Objective

Who contributes (most) to urban and rural air pollution with carbonaceous airborne particulate matter (PM) ?
Identification of source specific signatures of utmost importance for subsequent source attribution and apportionment. Signatures not easy to obtain for carbonaceous PM. Classification often only in terms of elemental and organic carbon: EC and OC. Scheme too primitive for source apportionment. We propose use of 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. We also present SAXS and WAXS ("diffuse XRD") data on diesel exhaust PM (DPM) and believe that these relatively old and simple techniques are quite useful and underestimated for carbonaceous PM characterization.

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

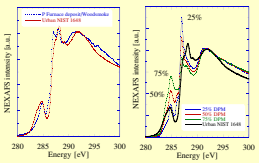




Left: Correlation between mortality and PM concentration [6 cities study; 1]. **Right:** Coal electric power plants in Kentucky/USA blamed for poor air quality and childhood asthma.

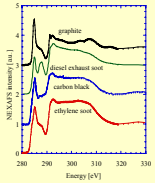
Major Conclusions

- Diesel PM not necessarily major contributor to Urban PM
- TEM-EELS performs poor for molecular carbon speciation
- NEXAFS performs very well for carbon speciation and can provide characteristic source signatures.
- WAXS, SAXS quite helpful for characterization of carbon-rich PM
- Be aware of radiation damages, in particular in STXM.

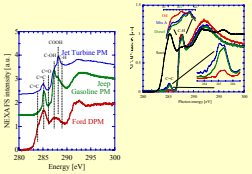


Attempted modelling of urban PM (NIST 1648 Standard collected in St. Louis MO, USA) by linear combination of spectra from diesel exhaust PM and woodsmoke. It doesn't work without adding at least one 3rd. component.

Carbon C(1s) NEXAFS or reference materials



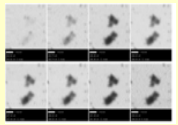
Left: Comparison of spectra from graphite, diesel exhaust, carbon black, and ethylene soot reveals their graphitic nature due to the aromatic setting of carbon atoms in double bonds: C=C. The corresponding π resonance is found at 285 eV. The plateau from 292 to 310 eV is typical for electronically well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



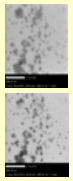
Right: NEXAFS spectra of Diesel, Oxygenated Diesel, Motor Oil, and Soot, all obtained with STXM. C=C bonds are found at 285 eV, C=H at 287 eV. Center: Peak assignment for Jet, Gasoline enegine and diesel engine PM.

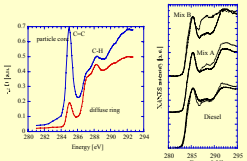
Carbon-NEXAFS of Single Diesel-PM Particles with STXM

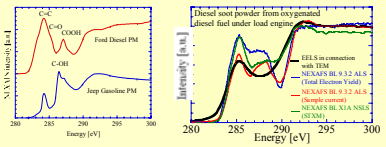
Spectro-microscopy with the Scanning Transmission X-ray Microscope (STXM) allows for chemical contrast variation on sub-micrometer scale. Every pixel on a STXM image can be assigned a NEXAFS spectrum, and every energy can be assigned one image. Image on the right shows the STXM microscope at beamline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

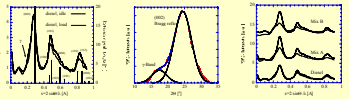






Wide and Small Angle X-ray Scattering

Quantitative analysis of diffuse XRD diffractograms (WAXS) provides information on aromaticity (area under γ-band peak vs. the entire peak area, including (002) peak), ratio of crystalline/amorphous carbon (background scattering), and crystallite sizes (Scherrer Formula).

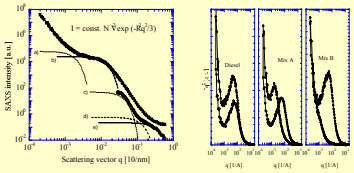


Left: X-ray diffractograms from load/idle soot, and reference Bragg peaks of graphite (2H Graphite PDF 26-1079). **Center**: Deconvolution of Peak into (002) and γ-sideband for determination of aromaticity. **Right**: Comparison of load/idle soot XRD from Diesel and oxygenated Diesel Mix A, Mix B.

Aromaticity f of diesel soot			
	diesel	diesel Mix A	diesel Mix B
Idle	0.15	0.34	0.31
load	0.22	0.15	0.08

Aromaticiy of oxygenated and non-oxygenated diesel exhaust PM for idle and load engine conditions.

Idle soot particles have smaller crystallites than load soot. Aromaticity higher for idle soot from oxygenated Diesel (Mix A, Mix B). Idle soot contains more amorphous carbon than crystalline carbon. Adding oxygenates to fuel causes bigger differences in the structure between idle and load soot, in line with NEXAFS and TGA.



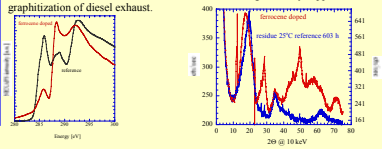
Left: Log-log plot of small angle scattering curves reveal at least 5 size ranges in Diesel PM, with size L=2π/q. Curve with open symbols was obtained after subtraction of Porod- and constant background scattering. Exponent of decay allows determination of fractal dimension, and was close to –4 for high q range and thus indicates smooth surfaces of primary particles and sub-units. For low q, exponents of decay are close to –3. **Right**: Maxima in Kratky plots of scattering curves provide information about compactness of soot particles and size of agglomerates: L=π/q.

Soot	Elementary units D[nm]	Sub units D [nm]	Primary Particles D [nm]	high q exponent	Fractal dimension	low q exponent	Fractal dimension
Diesel, idle	1.5	17.4	49.16	3.99	2.01	3.28	2.72
Diesel, load	1.6	14.5	41.50	3.86	2.14	3.12	2.88
Mix A, idle	1.9	21.1 (14.2	78.29	3.97	2.03	3.02	2.98
Mix A, load	1.4	13.8 (12)	36.78	3.96	2.04	3.09	2.91
Mix B, idle	2.0	14.3 (14.5	83.85	3.92	2.08	2.96	2.96
Mix B, load	1.4	22.0 (18.6	48.73	3.98	2.02	2.75	2.75

Elementary particles sizes 1-2 nm range. Form compact cluster to built subunits of 15-20 nm size. These build up larger structures (primary particles) of 40-80 nm, which form aggregates. Aggregates are found at q-values of 0.001 1/A, though harder to resolve in the SAXS curves. Idle soot has generally larger particles than load soot.

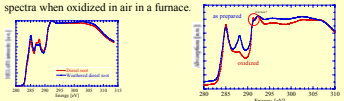
Soot from ferrocene doped diesel fuel

NEXAFS and WAXS data reveal that ferrocene can significantly suppress graphitization of diesel exhaust.



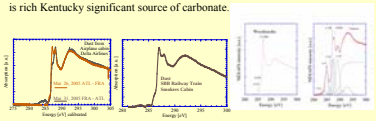
Oxidation & Weathering Studies

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.

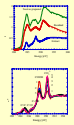


Indoor and Urban PM

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.



Atmospheric Chemistry on Aqueous Extracts

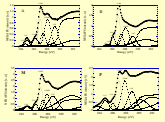


Extraction of volatiles from DPM with subcritical water. Exposure to soft X-rays causes decarboxylation and generation of a carbonate resonance. Quantitative kinetic studies on photolysis possible.

Left, above: C(1s) spectra of DPM residuals look quite similar to spectra from unextracted DPM.

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 !**



Toxicological Studies

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

References

[1] D.W. Dockery et al., New Engl. J. of Medicine (1993):329/24 1753-1759. Diesel Exhaust in the United States, U.S. EPA Publication EPA 420-F-02-048 September 2002.
[2] A. Braun, S. Wirick, A. Kubátová, F. E. Huggins, G.P. Huffman. Atmospheric Environment, in review.
[3] A. Braun, N. Shah, F.E. Huggins, G.P. Huffman, K.E. Kelly, A. Sarofim, S.B. Mun, S.N. Ehrlich, Carbon, in review.
[4] S. di Stasio, A. Braun. Energy & Fuels 2006, 20(1), 187-194.
[5] A. Braun, Review on C(1s) NEXAFS, J. Env. Monitoring, 2005, 7(11), 1059-1065.
[6] A. Braun, N. Shah, F.E. Huggins, K.E. Kelly, A. Sarofim, C. Jacobsen, S. Wirick, et al, Carbon 43, (12), 2431-2642 (2005).
[7] A. Braun, N. Shah, Y. Chen, F. Huggins, S. Wirick, S.B. Mun, C. Jacobsen, G.P. (J. Electron Spectroscopy & Related Phenomena, in press).
[8] A. Braun, S. Wirick, C. Jacobsen, F.E. Huggins, S.B. Mun, N. Shah, Y. Chen, G.P. Huffmann. Carbon 43 (2005) 117-124.
[9] A. Braun, J. Ilavsky, S. Seifert, P. R. Jemian. J. Appl. Phys. 98, 073513 (2005).
[10] A. Braun, F. E. Huggins, S. Seifert, J. Ilavsky, N. Shah, K. Kelly, A. Sarofim, G. P. Huffman Combustion & Flame 137 (1/2) pp. 63-72 (2004).
[11] A. Braun, N. Shah, F.E. Huggins, C. Jacobsen, S. Wirick, K. Kelly, A. Sarofim, G.P. Huffman. Fuel (2004) 10 7/8 997-1000.

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