

# The Contribution of C(1s) NEXAFS Spectroscopy to the Understanding of Air Pollution from Diesel Soot and Biomass Smoke

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## Introduction

Soot is a chemically and structurally very complex carbon material with adverse impact on human health and climate. Our Consortium has been looking at the carbon in soot from the environmental perspective since 2001. First experiments were done on diesel soot (DEP), where we paid also attention to the nature of extracts, atmospheric chemistry, radiation damages and to TEM-EELS [1-6]. Efforts were made to understand the influence of diesel engine operation parameters and fuel additives to soot structure [7-9]. With these fundamental studies the methodical foundations were laid to quantitatively distinguish in ambient particulate matter diesel engine soot from biomass wood smoke (WS) [10,11] and to formulate a simple semi-quantitative model for the atmospheric weathering and ageing of particulate matter (PM) [12]. The merit of this NEXAFS technique for thorough understanding of soot formation and soot interactions has now been recognized in environmental sciences [13]. Current studies include pro-inflammatory effects in human bronchial epithelial cells.

This poster summarizes C(1s) NEXAFS studies on carbonaceous ambient PM, diesel soot, and wood smoke carried out at Beamlines ALS 9.3.2 and NSLS X1A.

## Distinguish Volatiles From Particles With STXM

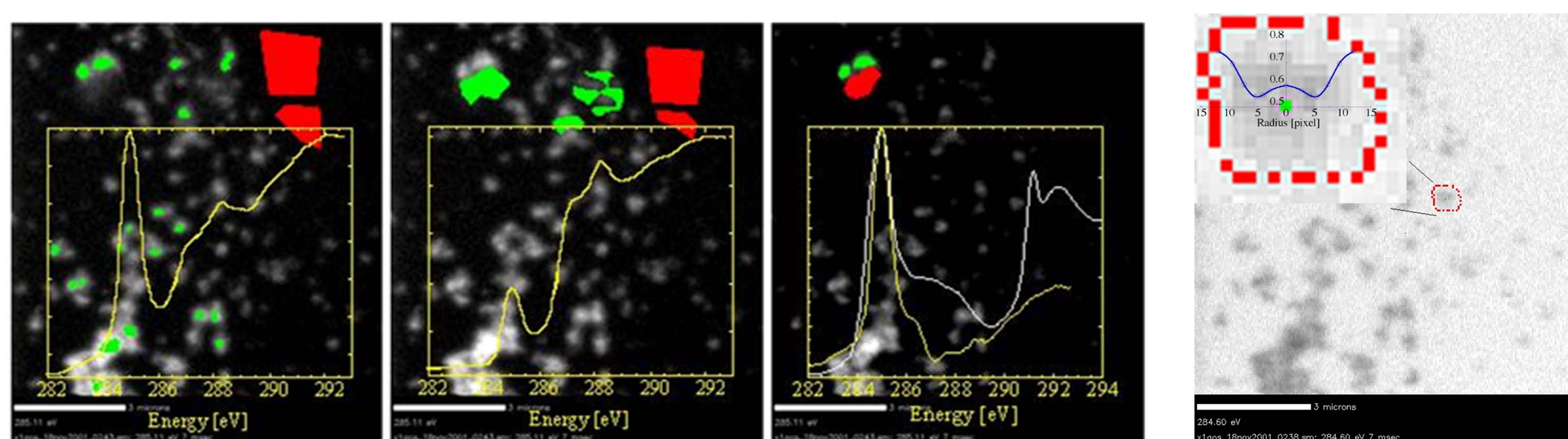
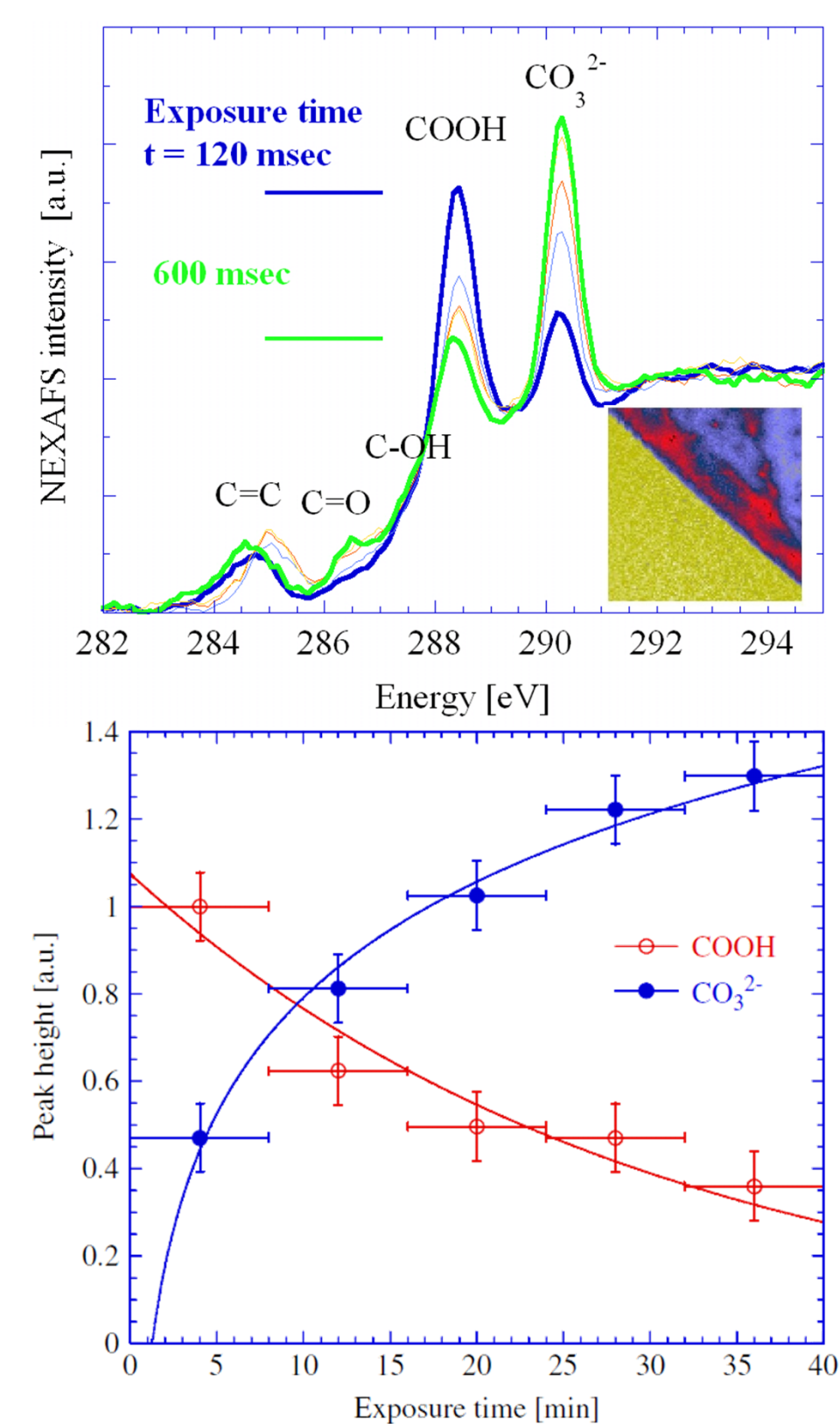


Figure: STXM images at 285.11 eV (sensitive to C=C bonds) of DEP (bright spots) after one drop of added acetone was evaporated, causing extraction of solubles. Green areas are summed up for I<sub>E</sub>(E), red areas are summed up for I<sub>O</sub>(E). Spectrum on the left is indicative of DEP. Spectrum in the center is representative of an acetone-soluble organic matter. Spectrum on the right is the difference of both spectra, highlighting the semigraphitic characteristics of the DEP. The white spectrum is from graphite. Right image: Quantitatively map the profile of an agglomerate.

## Photochemistry of Soot Extractable Volatiles



Aqueous extracts from DEP obtained by hot pressurized water extraction were subject to NEXAFS spectroscopy with STXM. The highly intense X-ray beam caused a significant decrease of the carboxyl peak intensity at 288 eV, and a newly arising carbonate peak at 291.2 eV. We were able to propose a simple photochemical reaction scenario that describes a decay path for carboxyl in soot: the radiolysis of carboxylate into carbonate in DEP during irradiation.

Figure top: Sequence of C(1s) spectra of aqueous DEP extract. Bottom: Peak heights for consumed carboxyl (red) peak and evolving carbonate (blue) resonances during irradiation for determination of the reaction rate constants.

Figure right: Drying of wood has influence on the wood chemistry and its combustion characteristic. The graph shows how well WS from well dried wood has a very small C=C peak, but a very large hydroxyl peak. Very humid wood produces soot with a high C=C peak, probably from quinones, and a smaller hydroxyl peak.

## Simple Source Apportionment by Linear Composition

Distinct signatures of wood smoke and DEP are used for source apportionment. Spectra reveal that DEP is made up from a semi-graphitic solid core and soluble organic matter, predominantly with carboxylic functional groups. Wood smoke has no or a less prevalent, graphitic signature, instead it contains carbon-hydroxyl groups. Using these features we estimate that the relative contribution of DEP to ambient PM in an urban area such as Lexington, KY and St. Louis, MO is 7% and 13.5%, respectively. Results are comparable to dispersion modeling data from non-urban and urban areas in California, and with elemental carbon measurements in urban locations such as Boston, MA Rochester, NY, and Washington, DC.

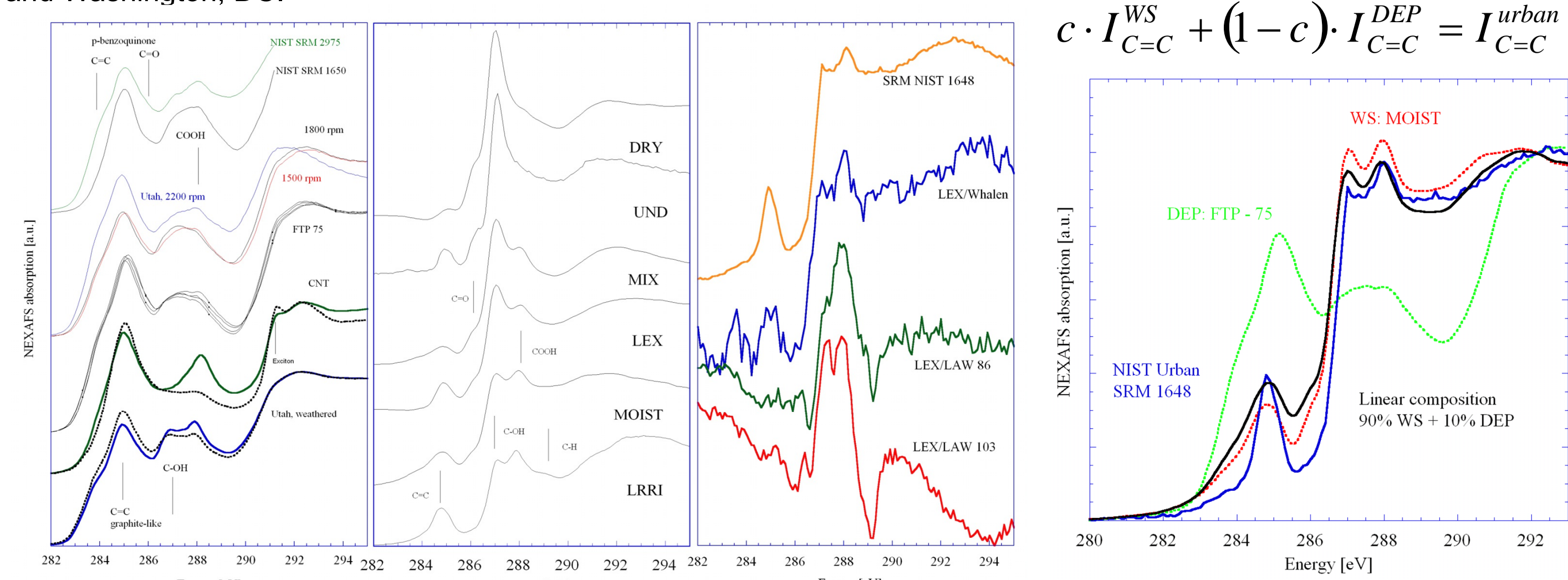
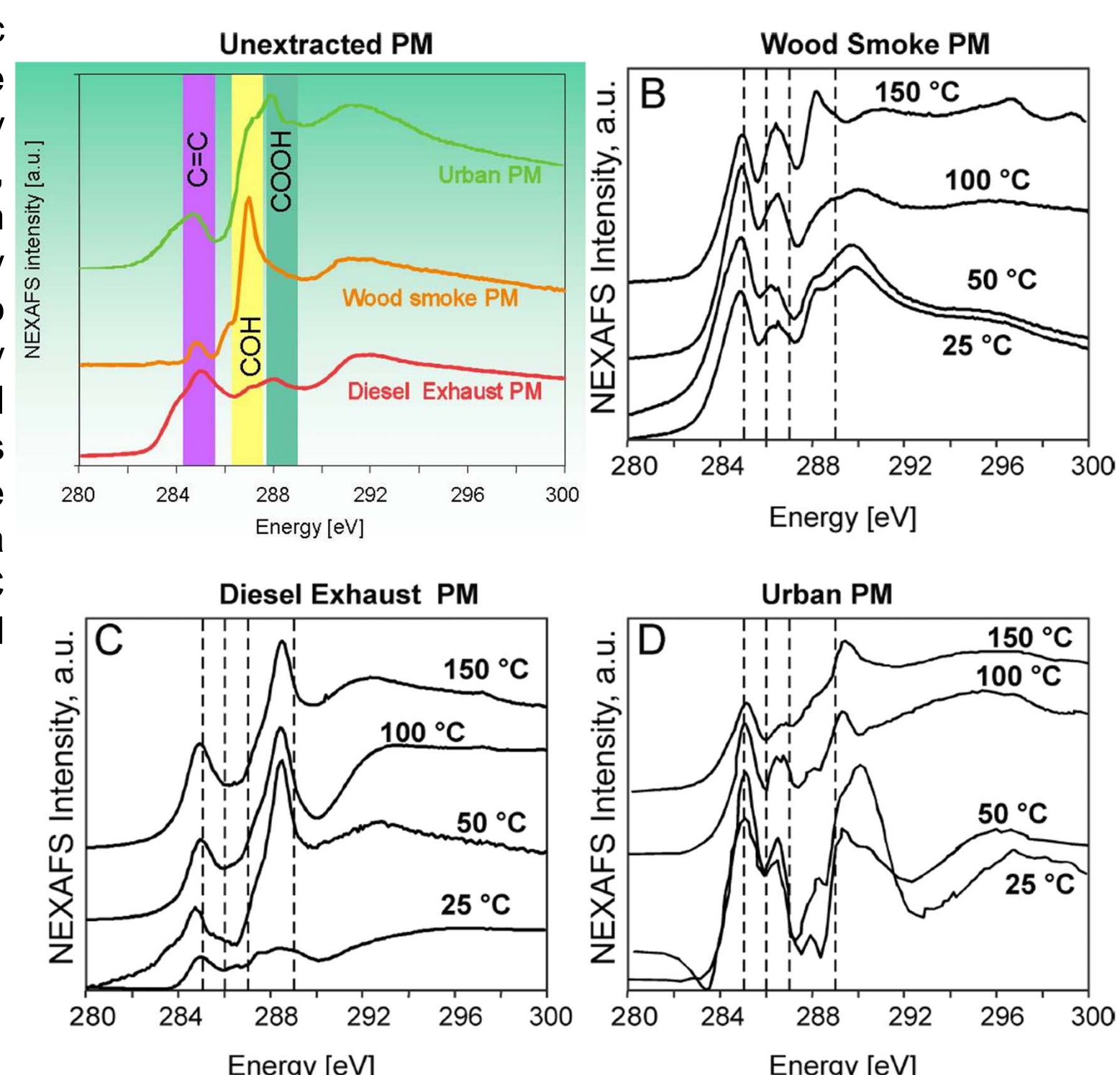
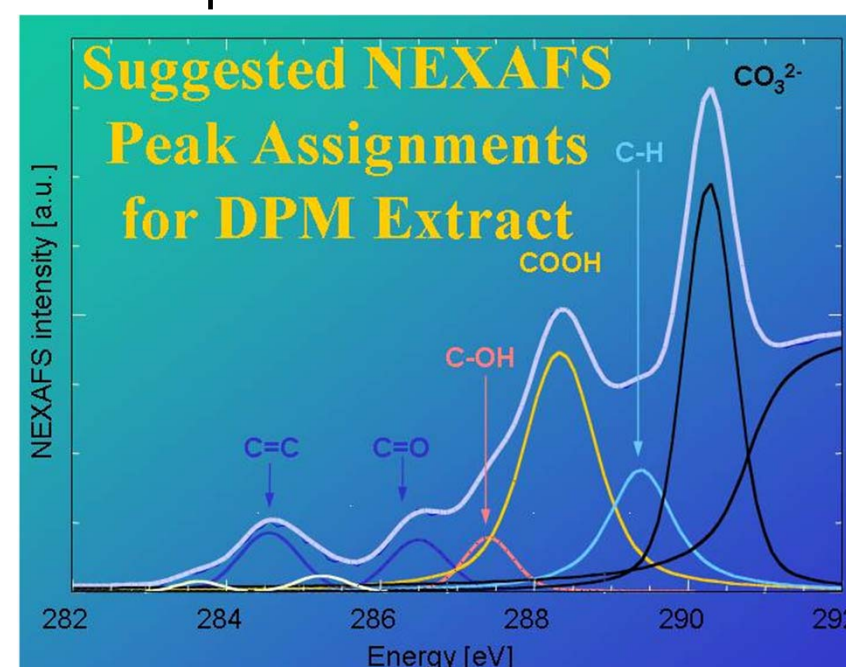


Figure -left: Spectra (from bottom to top) of DEP from Utah (solid, blue) and weathered aliquot (dashed, black); carbon nanotube (solid, green), and oxidized aliquot (dashed, black); four DEP spectra from Ford generated after FTP-75 protocol during a 10 day test; DEP from Utah generated under 3 different load conditions. For higher load and engine speed, the relative contribution of the C=C peak to the spectrum at 285 eV increases considerably; two DEP spectra from the NIST reference samples (black spectrum for heavy duty engine, green spectrum for forklift). Center: Sequence of WS spectra in the order C=C and/or C-OH peak heights. Samples UND and MIX could not unambiguously assigned the right order. LRRI has presumably the highest moisture content, and DRY presumably the lowest. Right: Summary of urban PM spectra obtained in St. Louis (SRM 1648) and two locations in Lexington KY. For SRM 1648, a peak at 285 eV can be unambiguously made out. For LEX/Whalen, intensity at 285 eV can still be distinguished from the noise in the spectra. For the LEX/LAW samples, a peak at 285 eV can be ruled out. Right: Spectra of DEP FTP-75, WS MOIST, and SRM 1648 (all thick lines). The thin line spectrum is a linear combination with 10% DEP and 90% WS.

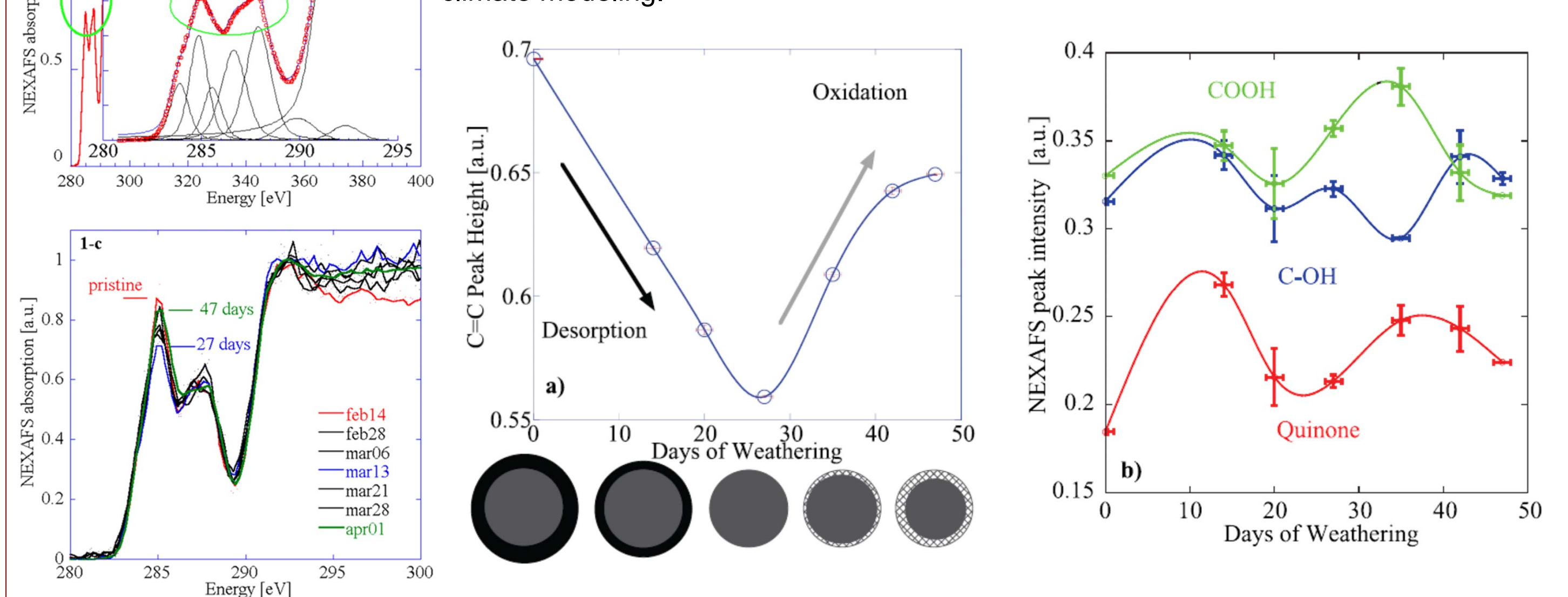
## Volatiles Extracted With Hot Pressurized Water

To determine whether characterization of organic carbon (OC) in particulate matter (PM) is limited due to extraction or analysis, we evaluated extractability from model matrices (wood smoke, diesel exhaust, urban PM). Investigation of OC distribution in different polarity fractions using spectroscopy revealed that sequential extraction may be useful to differentiate constituents attributed to primary emission sources and to secondary aerosol formation. It appears that secondary OC species (e.g., diacids) are not deeply embedded into the matrix, and thus were recovered in the solvent of a corresponding polarity. By contrast, primary OC constituents are strongly bound to the matrix and thus required harsh conditions to be recovered.



## Atmospheric Two-Process Soot Weathering Model

The weathering characteristic of diesel exhaust particulate (DEP) matter is spectroscopically obtained by an atmospheric study under realistic, ambient conditions. DEP subjected to weathering by exposure to ambient atmosphere (air, humidity, solar radiation, and temperature variation) for seven weeks shows systematic changes in C(1s) x-ray absorption spectra. Quantitative analysis suggests that volatile polycyclic aromatic hydrocarbons are released from the DEP by desorption, paralleled or followed by decomposition and reaction of the amorphous part of the solid, non-volatile carbon and potential other volatile species. The observed spectral changes are rationalized in a simple two phase model and parameterized, combining desorption of volatiles and oxidation of carbon matrix. The weathering characteristics of soot is generalized toward biomass burning products and identified as a vector quantity to be implemented for climate modeling.



## Conclusions

The use of soft x-rays for chemical speciation of carbonaceous particulate matter has turned out to be quite successful and looks promising for further development and exploitation. All work shown here is based on C(1s) data. It is likely that the oxygen and nitrogen spectra, for example, could also bear valuable information on the chemistry going on in (bulk) and on (surface) the soot. This would particularly apply to atmospheric weathering studies. Further development of in-situ methods, which to some extent is already being done at some beamlines, is definitely a "must" in order to take full advantage of synchrotron radiation.

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