Toward Distinguishing Woodsmoke and Diesel Exhaust in Ambient Particulate Matter

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Particulate matter (PM) from biomass burning and diesel exhaust has distinct X-ray spectroscopic, carbon specific signatures, which can be employed for source apportionment. Characterization of the functional groups of a wide selection of PM samples (woodsmoke, diesel soot, urban air PM) was carried out using the soft X-ray spectroscopy capabilities at the synchrotron radiation sources in Berkeley (ALS) and Brookhaven (NSLS). The spectra reveal that diesel exhaust particulate (DEP) matter is made up from a semigraphitic solid core and soluble organic matter, predominantly with carboxylic functional groups. Woodsmoke PM has no or a less prevalent, graphitic signature, instead it contains carbon—hydroxyl groups. Using these features to apportion the carbonaceous PM in ambient samples 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. These values are comparable to dispersion modeling data from nonurban and urban areas in California, and with elemental carbon measurements in urban locations such as Boston, MA, Rochester, NY, and Washington, DC.

Introduction

Carbonaceous airborne particulate matter (CPM), typically referred to as soot, is under scrutiny for its adverse impact on human health and climate forcing (1). Epidemiological studies worldwide have reported an association between human cardiac and respiratory morbidity and mortality from exposure to particulate matter (PM) (2). At a more detailed level, questions remain as to confounding between various components in air pollution health effects (3). PM exposure is possibly linked to inflammation through generation of reactive oxygen species and oxidative stress (2). In mice, PM was identified as a mutagen, and Mauderly et al. (4) show that rats, mice, and Syrian hamsters exhibit different pulmonary responses to inhalation exposure; thus, the question of whether a similar risk is posed to humans merits further study (5). To date, the mechanisms that cause injury in humans upon exposure to PM are not at all clear, and it remains to be established which molecular species cause health problems (6).

The potential contribution of black carbon (BC) to global warming has received considerable attention (1). Currently, the two main effects being studied are regional, in which BC can warm the atmosphere indirectly by reducing cloud coverage, and surface albedo, where BC deposits can reduce the solar radiation reflected back to space from ice and snow (7). The IPCC WGI Fourth Assessment report lists the radiative forcing of BC on snow as 0.0–0.2 W m⁻² (8), while Hansen et al. estimate an overall forcing from BC of 0.39 W m⁻² (9). BC absorbs incoming solar radiation, but has a relatively short atmospheric lifetime, and so can contribute to regional effects. For example, it has been estimated that the effect of pollution particles over the Indian Ocean on the regional atmospheric radiation balance is about 10 times the effect of greenhouse gases, leading to local cooling at the Earth’s surface and a heating of the atmosphere (10).

The advent of mass spectroscopy contributed to a paradigm shift in atmospheric science: the recognition of the global role of organic compounds (11). The highly complex organic carbon (OC) can yield 10,000 peaks eluting from a gas chromatographic column, including polycyclic aromatic hydrocarbons (PAH), redox-active quinones, organic acids, aldehydes, and alkanes, etc. The presence of so many compounds poses a conceptual difficulty, which is beyond the sole analytical challenge to deal with a complex mixture. A shorter list of key functional groups in OC could be more useful (11). Although analysis of CPM is typically performed in terms of BC, EC, and OC, such an approach is recognized as insufficient since it greatly oversimplifies the true complexity of CPM (1, 12). (Note that EC, elemental carbon, the refractory, typically sp²-bonded graphitic carbon of soot, is often equated to BC (10).) Quantity and composition of PM is highly source specific. Particularly woodsmoke samples are subject to artifacts in BC/OC determination (13). Even the range of BC/OC ratios from biofuels is deemed indistinguishable from the ratio of household coal emissions and diesel soot (11).

The apportionment of CPM as originating from diesel vehicle emissions as opposed to biomass burning is conventionally approached by chemical mass balance and
The diesel exhaust particulate matter (DEP) concentration can range from 4% to 16% of the total PM in nonurban (Fullerton, CA, Claremont, CA) and urban areas (Boston, MA, Long Beach, CA, Pasadena, CA) (1, 4 Health Assessment Document, Tables 2-24 and 2-25). CPM concentration of the total ambient PM from biomass combustion, such as woodsmoke (WS) ranks second, followed by road dust and industrial emissions. There is increasing awareness that woodsmoke or smoke from biomass combustion constitutes a significant share of air pollution, not only in South Asia (11) or Australia (16), but also in Europe (17) and the United States (18). Very recent studies suggest that biomass smoke may be an underestimated risk factor for pulmonary disease, drawing new attention to the toxicological aspects of biomass smoke components (19), but further study of this is needed.

A detailed source apportionment study on primary fine organic aerosols in several California cities (15) showed particularly high DEP and WS contributions in West LA (17.1% DEP, 28.1% WS), Pasadena (18.6%, 25.4%), Rubidoux (29.3%, 10.2%), and Downtown LA (35.9%, 16.5%), with WS contributions exceeding DEP contributions in Pasadena and West LA.

Beginning in 2001, our research consortium has addressed source apportionment by applying soft X-ray spectroscopy to CPM sampled at various combustion sources and in urban areas. Our methodological approach addresses the call for a shorter list of key functional groups, and refines the chemical description of carbon in PM beyond BC/EC/OC (1). Capable of resolving key molecular structures of the solid (EC, BC) and the volatile (OC) fractions that constitute carbonaceous aerosols, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy probes the molecular structure of CPM to a wider extent than any other nondestructive method. Specimens from sampling campaigns in the United States and Germany show that characteristic molecular signatures for CPM, like those for woodsmoke and diesel soot, can be clearly distinguished and semiquantified with NEXAFS.

Experimental Section

Samples. Standard Reference Materials (SRM) were purchased from NIST and stored in accordance with their regulations and specifications: SRM 2975 from the filtering system specifically designed for diesel-powered forklifts (20); SRM 1650 from the heat exchangers of direct-injection 4-cylinder diesel engines (21); and urban PM SRM 1648 collected over a 12-month period in the area of the city of St. Louis, Missouri (22).

Woodsmoke samples were obtained from the following sources: (1) Lovelace Respiratory Research Institute (LRRI), generated by burning a mix of uniformly split seasoned hardwood with bark and 20–25% moisture content in a wood stove (23); (2) University of North Dakota (UND), collected from the chimney that vented an airtight woodstove burning a mix of hardwoods (primarily elm, ash, and oak); the smoke was collected from the chimney outlet (24); (3) a private home in Lexington KY: creosote (LEX) was collected from the chimney damper blade of a fireplace burning wood (beech, ash, pine, oak, birch) from the Lexington ice storm (2/16/03); the split wood had dried for approximately 18 months; and (4) in-house fireplaces in a remote village in Western Germany between Zitterwald and Hohes Venn: three more creosote samples. Sample (DRY) was obtained from the interior walls of a home woodburner for central heating, fed with split beech and oak very well dried for 3 years. Sample (MOIST) was obtained from the chimney near the wood burner of a different home, fed with moist fir wood not older than 6 months. Sample (MIX) was collected from the chimney near a living room wood stove in a different home, fed with well-dried mix of fir and beech wood for about 2 years. The estimated drying times were reported by the suppliers, i.e. the home owners.

Diesel exhaust particulate matter (DEP) samples were obtained from Ford Motor Company and University of Utah. At Ford, DEP was collected on quartz filters from a 1998 diesel passenger car equipped with a 4-cylinder, turbocharged, direct-injection 1.9 L engine, and engine after-treatment unit with an oxidation catalyst. The tests were run over the 3-phase Federal Test Procedure FTP-75 transient drive cycle. Typical PM emission rates for this vehicle are 50 mg/mile, with an approximate composition of 80% soot and 20% semivolatile. Repeat tests were performed over a period of 10 (# of filters) days to collect sufficient material for detailed analyses. More details on the DEP samples from Utah generated in a 2-cylinder, direct-injection diesel model Z482B can be found in ref (25). Engine conditions were idle and 1500 rpm, 3 ft-lb load and 1800 rpm, and 6 ft-lb load and 2000 rpm.

Three urban PM samples (LEX/WHALEN, LEX/LAW) were obtained in Lexington, KY on 47 mm PTFE filters using a Rupprecht and Patashnick Partisol model 2000 FRM sampler used for gravimetric determination of PM_{2.5} mass in the ambient air. Ambient airborne PM was collected in situ, typically for 8–12 h, during day time with an ambient air flow rate of 1 m³ h⁻¹ (16.7 L min⁻¹) and preremoval of particles with aerodynamic diameters greater than 2.5 μm using a built-in WINS impactor. The three samples discussed here were collected during the 6-month period from June to December 2003, under varying meteorological conditions (temperature −4 to 27 °C, mean wind speed 4–11 mph, barometric pressure 29.8–30.5 in. of Hg).

Extraction. Aqueous extracts from Ford DEP, UND woodsmoke, and SRM 1648 urban PM (~10 mg) were obtained after a recently established procedure which allows extraction for temperatures up to 250 °C (26). We report here the 25 °C extracts, which can be considered as bioavailable. A detailed study for extracts obtained at higher temperatures is given elsewhere (27).

The extractions were performed in an apparatus previously described in detail (28). In brief, the extraction system consisted of a pump supplying water at a flow rate of 0.5 mL/min to a preheating coil and extraction cell mounted in an HP 5890 gas chromatograph oven. At the outlet of the extraction system, a pressure valve was placed to maintain the system’s pressure, ensuring that the water was in the liquid state at all temperatures. The outlet valve was heated (50–150 °C) to prevent precipitation of extracted material. The extract was transferred from the outlet valve through stainless steel tubing into 5.0 mL of water in a collection vial cooled with ice to prevent sample loss. The blank HPLC column was used as an extraction vessel. Frits were placed at the outlets of the vessel to prevent the elution of PM.

NEXAFS Spectroscopy. The NEXAFS spectroscopy technique is well described in the literature (29–31). The carbon K-shell X-ray absorption edge is located at 285 eV. The X-ray near-edge absorption fine characteristics of carbonaceous materials depend strongly on how the carbon atoms are bound to other atoms. In many cases, NEXAFS spectra can be considered fingerprints of particular carbon compounds. In this study, we have recorded spectra from PM and from their aqueous extracts. For the assignment of peaks to molecular species, we adhered to literature data (32, 33). The area under a peak is proportional to the number of absorbers and thus allows for a quantitative analysis of samples with different constituents. Deconvolution of the spectrum allows for quantitation of individual molecular species in the specimen (29).

C(ls) NEXAFS spectra of single particles were recorded at the National Synchrotron Light Source in Brookhaven National Laboratory, Upton, NY. The instrument was a
were pressed into pellets of around 250 nm, and spectra from 270 to 310 eV were acquired in 0.1 eV steps with 120 ms dwell time at each energy step. For more details see ref (35).

X-ray absorption spectra of the CPM pellets were recorded at the ultrahigh vacuum (10^-10 torr) Beamline 9.3.2 at the Advanced Light Source (ALS) in the Lawrence Berkeley National Laboratory, Berkeley, CA. The solid PM samples were pressed into pellets of around 250 µm thickness (urban PM, 100 µm thickness only) and 25 mm² area and then mounted on a sample holder. Natural graphite with a characteristically sharp π-transition at 285 eV served for the calibration of the energy axis. Further experimental details as described in ref (36) apply to these samples.

Results

Following the pioneering STXM work by Cody et al. on coal in 1995 (37), we employed STXM in 2002 on DEP (35). Figure 1 shows a STXM image of DEP after applying an extraction procedure with acetone. The image on the left shows how NEXAFS spectra are recorded from a number of particle cores, highlighted in green, along with the spectrum, which shows a strong π transition at about 285 eV due to C=C double bonds in an aromatic setting. The image in the center shows the spectrum of the leached out volatile matter, recorded from the stain around the particle cores, also highlighted in green. This spectrum has dominant relative intensity at about 287–288 eV, where carbon in aliphatic setting has typical resonances, such as from COOH or CH2, CH3 (30).

In the right image in Figure 1, the difference of both spectra is plotted, along with a separately recorded spectrum from graphite for comparison. The peak at 285 eV only when PM is generated from wood with very high moisture content. The relative intensity of this peak did not exceed 0.4 in our studies.

Woodsmoke CPM shows a very strong absorption at 287 eV, likely due to alcohol or aliphatic C–OH bonds, whereas WS extracts show a strong absorption at 285 eV due to aromatic groups (31). The wood smoke spectrum has a large peak at 285 eV only when PM is generated from wood with very high moisture content. The relative intensity of this peak did not exceed 0.4 in our studies.

Diesel Exhaust Particulate Matter. To introduce some variation into our diesel soot samples, we studied specimens generated at different facilities (NIST, University of Utah, Ford Motor Company), with different diesel engines (light duty vehicle and small generator), different diesel fuels, and different operating conditions.

Typical DEP spectra from pellets are shown in Figure 2, left. All DEP specimens exhibit a dominant spectral signature at 285 eV from unsaturated (multiple) carbon bonds in their graphitic solid core (31). A natural graphite powder pellet served as the spectral standard for diesel soot. Owing to its ordered nature, graphite displays a very sharp exciton resonance at 291.2 eV (25, 36, 43). The spectra from DEP show this feature more or less in the form of a slightly visible kink, confirming the partial graphitic nature of diesel soot. DEP generated under high engine speed and load conditions has a more pronounced exciton peak and an overall higher C=C peak at 285 eV. For higher load and engine speed, the relative contribution of the C=C peak to the spectrum at 285 eV increases considerably. Graphitization of carbon may be facilitated under such conditions due to the higher combustion temperatures of the engine under load (44).

Shoulders at 284 and 286 eV on the flanks of the peak at 285 eV are assigned to the conjugated multiple bond systems in benzoquinone and hydroquinone structures that also include the carbonyl (C=O) functionality (32, 33). Overall, the energy range from 284 to 286 eV derives from structures with aromatic unsaturated carbon bonds, including polycyclic aromatic hydrocarbons (PAHs). Model PAH compounds also have complex spectra because the resonances from excited orbitals are highly site specific in an aromatic ring (42). Aliphatic structures have resonances at energies 287 eV and above. A small peak at 287 eV is possibly from hydroxyl (C–OH) functional groups (33). Another strong spectral contribution in diesel soot, which could almost serve as a marker, arises from carboxyl groups (~COOH) at 288 eV. In aqueous extracts of DEP, this carboxyl resonance is clearly the dominant structure, followed by the resonance at around 285 eV, as shown in Figure 3, center. Since no solid DEP is
Because ambient PM has been subject to weathering (exposure to oxygen, solar radiation, humidity), the structures of its constituents, be they derived from DEP or WS, are not necessarily the same as when sampled right from the source. For instance, a recent study on ambient PM with STXM presents a quantitative analysis on atmospheric surface and bulk oxidation of the carbon (29). Peak assignment for benzoquinone after Francis, Hitchcock (29). (Center) Sequence of WS spectra in the order C–C and/or C–OH peak heights. Peak assignment according to Cody et al. (30), and Francis and Hitchcock (29). (Right) Summary of urban PM spectra obtained in St. Louis (SRM 1648) and two locations in Lexington, KY.

FIGURE 2. (Left) Spectra (from bottom to top) of DEP from Utah (solid, blue) and its weathered aliquot (dashed, black); carbon nanotube (solid, green), and its 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. Two DEP spectra from the NIST reference samples (black spectrum for heavy duty engine, green spectrum for forklift). Peak assignment for benzoquinone after Francis, Hitchcock (29). (Center) Sequence of WS spectra in the order C–C and/or C–OH peak heights. Peak assignment according to Cody et al. (30), and Francis and Hitchcock (29). (Right) Summary of urban PM spectra obtained in St. Louis (SRM 1648) and two locations in Lexington, KY.

plant in these extracts, the intensity at 284–286 eV must be assigned to organic carbon (OC) from aromatic species. Because ambient PM has been subject to weathering (exposure to oxygen, solar radiation, humidity), the structures of its constituents, be they derived from DEP or WS, are not necessarily the same as when sampled right from the source. For instance, a recent study on ambient PM with STXM presents a quantitative analysis on atmospheric surface and bulk oxidation of the carbon (29). Peak assignment for benzoquinone after Francis, Hitchcock (29). (Center) Sequence of WS spectra in the order C–C and/or C–OH peak heights. Peak assignment according to Cody et al. (30), and Francis and Hitchcock (29). (Right) Summary of urban PM spectra obtained in St. Louis (SRM 1648) and two locations in Lexington, KY.
urban sample has a high concentration in DEP. To our surprise it was the $\text{C}^-\text{OH}$ resonance that was the strongest (Figure 2, right; Figure 3, top). The aqueous extracts showed a strong $\text{C}^\text{dC}$ peak at 285 eV, possibly from PAHs, more pronounced so than in the solid urban PM. The height of the aromatic peak for $\text{C}^\text{dC}$ at 285 eV was 0.33 for SRM 1648.

Hydroxyl is obviously leached out from the urban PM, which is also characteristic of WS. The unique peak at 289.5 eV from the extract could potentially be from a hydroxylated, aliphatic carbon species ($1s$–$3p$/$\sigma^*$ (37)).

PM sampled on the roofs of two two-story buildings located along a major arterial road (less than 25 m distance) and in proximity of fast-food restaurants in the city of Lexington, KY, also showed a dominant peak at 287 eV ($\text{C}^-\text{OH}$, native to woodsmoke), but not at 285 eV ($\text{C}^\text{dC}$, native to graphitic DEP). For LEX/Whalen (sampled between the two fast food restaurants in 75 and 25 m distance), intensity at 285 eV can still be distinguished from the noise in the spectra. For the LEX/LAW samples (sampled 150 m away from the nearest fast-food restaurant), a peak at 285 eV can be ruled out.

Although noisy, we suggest the $\text{C}^\text{dC}$ relative peak height is around 0.25 for the LEX/WHALEN spectrum. Next to this peak at 283–284 eV, another peak of similar height can be made out. We can only speculate about the origin of this peak, but it should be of aromatic nature. The carbon double bonds in cholesterol, a marker for meat cooking, might be one potential source. In the two LEX/LAW samples, we cannot identify a $\text{C}^\text{dC}$ peak. However, they show strong peaks at 286 and 287 eV, possibly from phenolic structures.

Discussion

Our studies indicate that DEP and WS have distinct spectral characteristics that can be discerned in ambient samples. One interesting observation is that the spectral characteristics of WS and DEP are reversed when their aqueous, extracts are examined: solid DEP has a strong $\text{C}^\text{dC}$ peak, whereas its extracts do not. In contrast, woodsmoke PM exhibits, if any, only a minor $\text{C}^\text{dC}$ peak, whereas its extracts have a much more significant peak. This result parallels those of the recent study by Kocbach et al. who found that WS has twice as much OC than DEP, and 150 times more PAH than DEP (17).

Therefore, combining NEXAFS spectroscopy with extraction, we can distinguish between graphitic solid material and PAHs in PM samples. We neglect here the case that high molecular weight hydrocarbons, which do not dissolve easily, might be in the PM as well.

In Lexington, we know that people in the city operate residential fireplaces fed with wood. Obviously, firewood burning in residential urban areas finds its manifestation in woodsmoke-typical resonances in urban PM. In Lexington, the diesel soot emitted by trucks and public busses does not add a major part to the overall PM structure, whereas measurements near a railway track and highway in LA revealed relative DEP concentrations of almost 36% of primary fine organic aerosol (15). It is known that air quality in St. Louis is affected by heavy industry (14, Air Quality Document). The spectra of St. Louis’ urban PM do not grossly deviate from the spectrum in Lexington (LEX/WHALEN).
In our considerations we neglect any other carbonaceous contributions to urban or ambient PM, seasonal concentration variations, and assume that it is only WS and DEP that constitutes the majority of carbon in these urban PM samples. Additional sources can be nearby restaurants, gasoline PM, road dust, and regional coal power plants.

We briefly want to address the error sources in our method. Reproducibility of spectra is demonstrated best by the four DEP spectra obtained from FTP-75 protocol, which was repeated during 10 days. The variation of the relevant peak is smaller than 4%. The peak height difference of as-received repeated during 10 days. The variation of the relevant peak road dust, and regional coal power plants. constitutes the majority of carbon in these urban PM samples.

We recall that we consider in this study only DEP characteristic signatures, particularly when we allow for the effect of changes in DEP spectra upon weathering. Instead, structures that are typical to woodsmoke can be clearly identified.

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Literature Cited


(20) Standard Reference Material 2975, Diesel Particulate Mater (Industrial Forklift), Certificate of Analysis, National Institute of Standards & Technology, Gaithersburg, MD 20899, 07 November 2000.


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