Light-absorbing organic carbon from prescribed and laboratory biomass burning and gasoline vehicle emissions

Mingjie Xie, Michael D. Hays, Amara L. Holder

U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, 109 T.W. Alexander Drive, Research Triangle Park, NC 27711, USA

Introduction and Goals

Carbonaceous aerosols are ubiquitous in the atmosphere and can directly affect Earth's climate by absorbing and scattering incoming solar radiation. Both field and laboratory measurements have confirmed that biomass burning (BB) is an important primary source of light absorbing organic carbon (OC), also termed as "BrC", which is also clearly observed in BB-impacted atmospheres. However, chemical and optical information about the BrC emitted from prescribed or controlled burning is scant. Prescribed burning is a less intensive fire technique used in forest and agricultural land management, or for land restoration objectives. Prescribed agricultural burns prepare fields for planting, stimulate plant growth and yields, and control pests, whereas prescribed forest burning is used to abate aggressive wildfire and promote ecological succession and sustainability. In addition, motor vehicles are also a primary source of PM2.5 emissions to urban atmospheres. While direct measurements of BrC from primary vehicle emissions are still lacking.

This study attempts to address limitations in understanding BrC as it relates to primary source combustion emissions. In that vein, UV-Vis spectrometry was applied to measure the light-absorbing properties of OC in methanol extracts of prescribed and laboratory BB and gasoline vehicle aerosol emissions. The gasoline vehicle emissions were sampled during different seasons (winter and summer) while also examining vehicle class (truck and car) and model year variables.

Sample Collection

1. Biomass burning emission sampling

Location	Fuel type	Field sample No.	Laboratory sample No.[d]
Agriculture Field			
Nez Perce, ID	Kentucky Bluegrass ("KBG")	6[a]	3
Nez Perce, ID	Wheat stubble ("Wheat")	2[a]	3
Walla Walla, WA	Chemically fallowed wheat stubble ("Wheat + Herbicide")	6[a]	3
Forest Field[b]			
Eglin Air Force Base, FL	Grass/forb/shrub/wood debris ("Forest burn")	4[c]	9
Eglin Air Force Base, FL	Grass/forb/shrub ("Grass burn")	2[a]	0

[a] Contain equal numbers of ground and aerostat samples;
[b] Aurell et al., 2015; Holder et al., 2016;
[c] Contain 3 ground and 1 aerostat samples;
[d] Collected in the open burn test facility (OBTF) of EPA at RTP.

2. Motor vehicle emission sampling

$PM_{2.5}$ samples collected from gasoline vehicle exhaust were selected from the Kansas City Light-Duty Vehicle Emissions Study (KCVES) filter archive (Fulper et al., 2010; Nam et al., 2010; Sonntag, et al., 2012).

Exhaust emissions from 496 vehicles recruited from the Kansas City metropolitan area were measured in two rounds: round 1 summer (261 vehicles), and round 2 winter (235 vehicles). Vehicles were tested on a portable chassis dynamometer in a warehouse at ambient temperature using the LA92 Unified Driving Cycle. The LA92 cycle is 15.7 km and consists of three operating phases, including "cold start" (phase 1), "hot running" (phase 2) and "hot start" (phase 3). Vehicle exhaust was cooled and diluted and drawn through a $PM_{2.5}$ cyclone, followed by 47 mm Teflon[TM] and quartz-fiber (QF) filters. $PM_{2.5}$ samples were collected for each of the three phases of the LA92 cycle. In the present study, $PM_{2.5}$ QF samples were selected from both rounds of emissions testing.

	Sample No.[a]	Vehicle Year Range	OC (μg m^{-3})	EC (μg m^{-3})
Winter	30	1978-2004	302 ± 183	79 ± 54
Summer	28	1985-2002	225 ± 158	56 ± 48

[a] Each sample represents a whole LA92 cycles, including three QF filters collected during the three phases, respectively.

Analysis Method

1. UV/Vis analysis

Methanol was used for sample extractions. A punch area (1.5 cm^2) of each sample was extracted with 5 mL methanol (HPLC grade) in a tightly closed amber vial, sonicated for 15 min, and then filtered (National Scientific Company, 30 mm diameter. × 0.2 μm pore size, polytetrafluoroethylene (PTFE)) using a glass syringe. The light absorption of filtered extracts was measured with a UV-Vis spectrometer at λ = 200-900 nm and a resolution of 0.2 nm (V660, Jasco Incorporated, Easton MD). This study focused on λ = 300 – 550 nm, where most of the BrC absorption has been observed (Chen and Bond, 2010).

2. OC-EC analysis.

All QF samples were analyzed for OC and elemental carbon (EC) content using a thermal-optical instrument (Sunset Laboratory, Portland, OR) and modified National Institute of Occupational Safety and Health (NIOSH), Method 5040 (NIOSH, 5040). The amount of OC extracted was calculated as the difference between OC on the un-extracted QF and OC in the air-dried residual QF following extraction. The OC extraction efficiency was calculated as the ratio of extracted OC to OC on the un-extracted filter multiplied by 100%.

1. Light absorption coefficient (Abs_λ, Mm^{-1})

Light absorbance at a given wavelength (A_λ) is converted to a light absorption coefficient (Abs_λ, Mm^{-1}) by (Hecobian et al., 2010):

$$Abs_\lambda = (Abs_\lambda - Abs_\lambda) \times \frac{v_l}{v_a \times L} \times \ln(10)$$

where A_{700} is referenced to account for systematic baseline drift, v_l (m^3) is the volume of methanol (5 mL) used for extraction, v_a (m^3) is the volume of the sampled air represented by the extracted filter punches, and L (0.01 m) is the optical path length of the quartz cuvette in the UV-vis spectrometer.

2. Mass absorption coefficient (MAC_λ, m^2 g^{-1}C)

The bulk mass absorption coefficient (MAC_λ, m^2 g^{-1}C) could be used to describe the absorption efficiency of extracted OC and the value at 365 nm was typically used as a measure of BrC.

The MAC_λ was calculated as:

$$MAC_\lambda = \frac{Abs_\lambda}{C_{oc}}$$

where C_{OC} is the mass concentration of extracted OC in PM (μg m^{-3}). The absorption Ångström exponent ($Å_{abs}$), a measure of the λ dependence of aerosol light absorption, is determined by the linear regression of $\log_{10}(Abs_\lambda)$ vs. $\log_{10}(\lambda)$ over the λ range of 300 and 550 nm.

Results

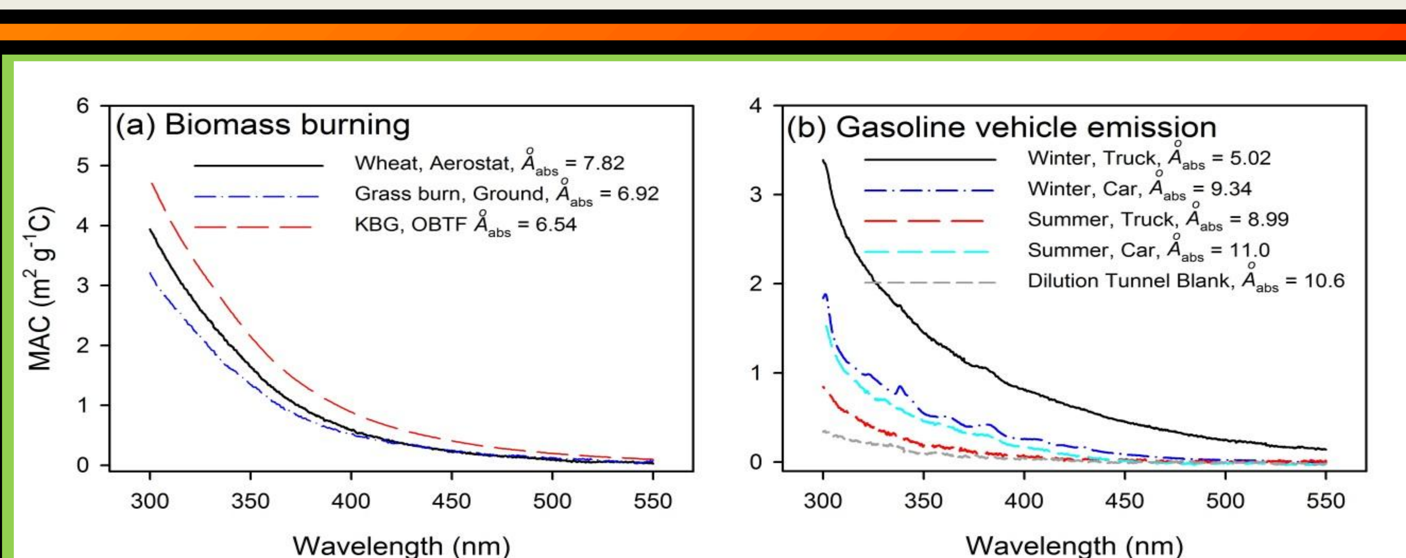

Figure 1. Representative MAC spectra for $PM_{2.5}$ samples from (a) Biomass burning and (b) gasoline vehicle emissions.

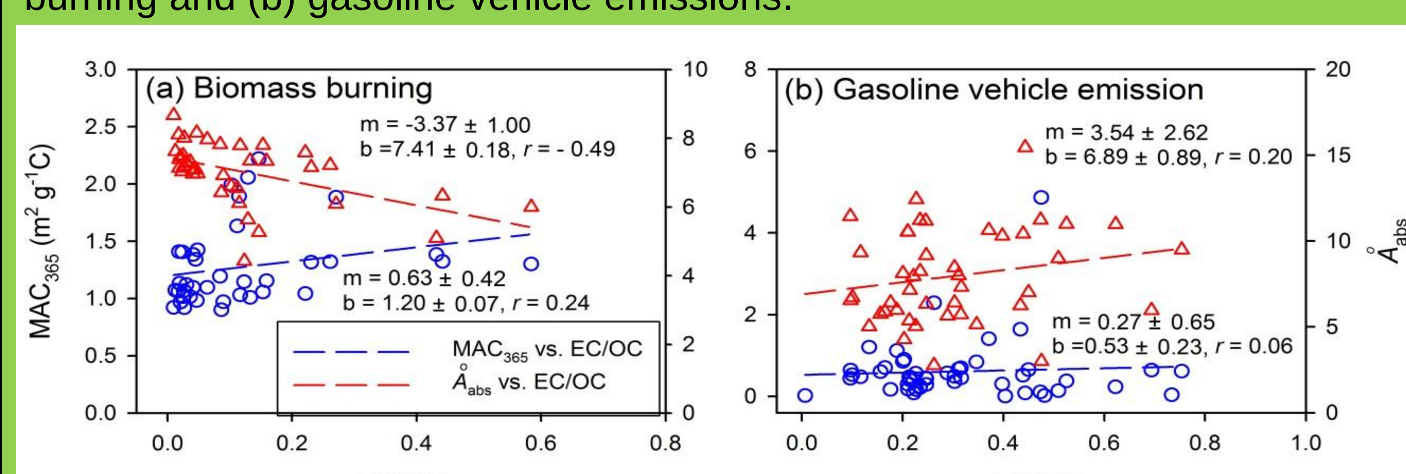

Figure 2. Linear regressions of MAC_{365} vs. EC/OC, and $Å_{abs}$ vs. EC/OC for (a) prescribed and laboratory biomass burning and (b) gasoline vehicle emissions. In each plot, m and b represent regression slope and intercept, respectively, with one standard error.

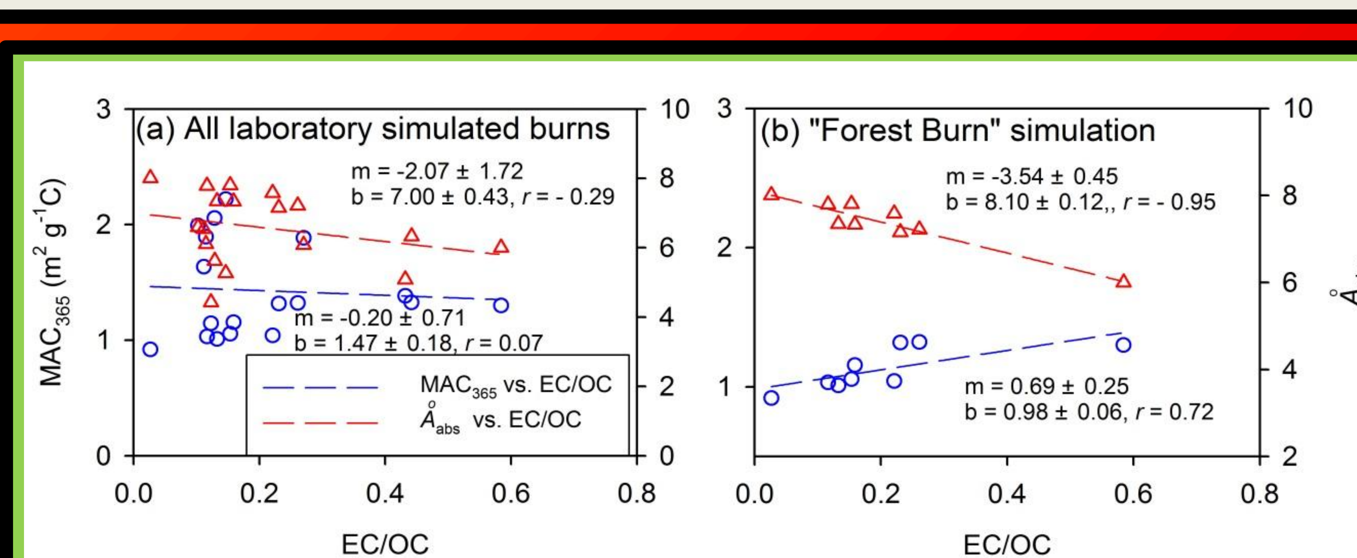

Figure 3. Linear regressions of MAC_{365} vs. EC/OC, and $Å_{abs}$ vs. EC/OC for (a) all laboratory simulated burns (OBTF) and (b) laboratory simulations for "Forest burn". In each plot, m and b represent regression slope and intercept, respectively, with one standard error.

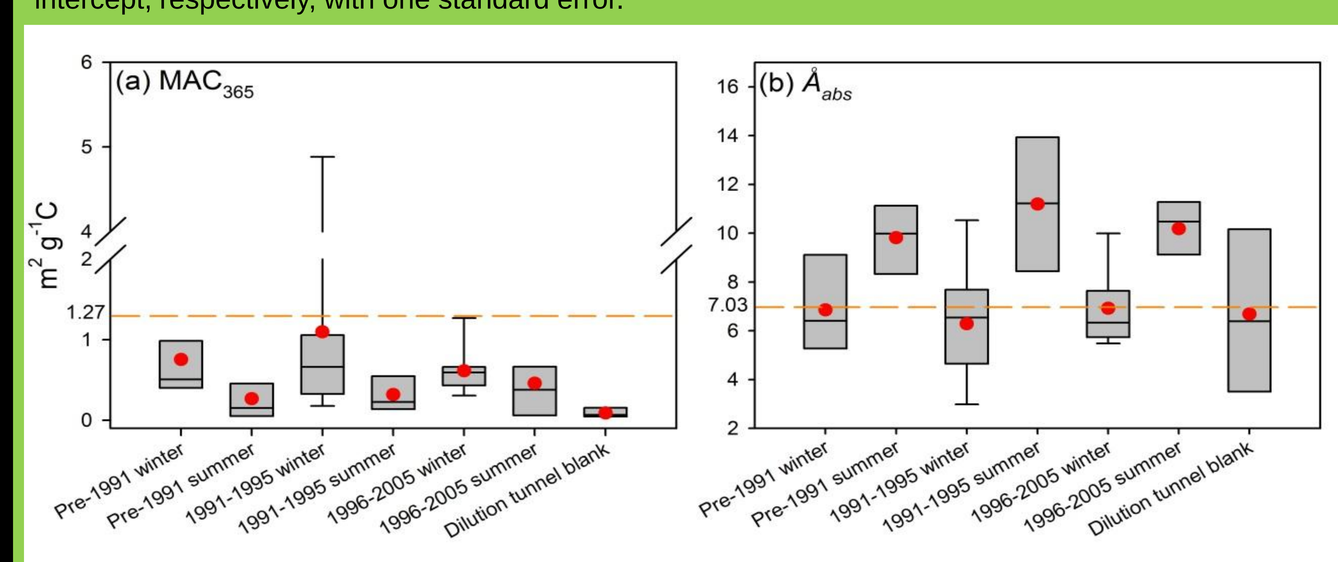

Figure 4. Seasonal box plots for (a) MAC_{365} and (b) $Å_{abs}$ for different model year vehicles emissions. The boxes depict the median (dark line in the box), inner quartile range (gray box), 10[th] and 90[th] percentiles (whiskers) and the average (red circle). The orange dash lines represent the average MAC_{365} and $Å_{abs}$ for biomass burning samples.

Conclusions and Future Work

1. The OC generated from BB or gasoline vehicle emissions shows strong light absorption and wavelength dependence; the biomass fuel type may also play a role in the light-absorbing properties of OC generated from BB.
2. How biomass fuel type affects the light absorption of OC from BB is uncertain and merits further study.
3. Gasoline vehicles tend to emit stronger light-absorbing OC in winter than in summer.
4. Compared to BB, the light absorption of OC from gasoline vehicle emissions was of the same magnitude but weaker, suggesting the importance of gasoline vehicle emissions as a BrC source in urban regions.

References

Aurell, J., Gullett, B. K. & Tabor, D. Emissions from southeastern U.S. Grasslands and pine savannas: Comparison of aerial and ground field measurements with laboratory burns. *Atmos. Environ.* **111**, 170-178, doi:http://dx.doi.org/10.1016/j.atmosenv.2015.03.001 (2015).

Holder, A. L., Hagler, G. S. W., Aurell, J., Hays, M. D. & Gullett, B. K. Particulate matter and black carbon optical properties and emission factors from prescribed fires in the southeastern United States. *J. Geophys. Res.* **121**, 3465-3483, doi:10.1002/2015jd024321 (2016).

Fulper, C. R. *et al.* Methods of characterizing the distribution of exhaust emissions from light-duty, gasoline-powered motor vehicles in the U.S. fleet. *J. Air Waste Manage.* **60**, 1376-1387, doi:10.3155/1047-3289.60.11.1376 (2010).

Nam, E. *et al.* Temperature effects on particulate matter emissions from light-duty, gasoline-powered motor vehicles. *Environ. Sci. Technol.* **44**, 4672-4677, doi:10.1021/es100219q (2010).

Sonntag, D. B., Bailey, C. R., Fulper, C. R. & Baldauf, R. W. Contribution of lubricating oil to particulate matter emissions from light-duty gasoline vehicles in Kansas City. *Environ. Sci. Technol.* **46**, 4191-4199, doi:10.1021/es203747f (2012).

NIOSH, 1999. National Institute of Occupational Safety and Health. Elemental carbon (diesel particulate): Method 5040, *Rep.* https://www.cdc.gov/niosh/docs/2003-154/pdfs/5040f3.pdf (1999), last accessed December, 2016.

Hecobian, A. *et al.* Water-Soluble Organic Aerosol material and the light-absorption characteristics of aqueous extracts measured over the Southeastern United States. *Atmos. Chem. Phys.* **10**, 5965-5977, doi:10.5194/acp-10-5965-2010 (2010).