Light absorption of organic aerosol from pyrolysis of corn stalk

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ABSTRACT

Organic aerosol (OA) can absorb solar radiation in the low-visible and ultra-violet wavelengths thereby modifying radiative forcing. Agricultural waste burning emits a large quantity of organic carbon in many developing countries. In this work, we improved the extraction and analysis method developed by Chen and Bond, and extended the spectral range of OC absorption. We examined light absorbing properties of primary OA from pyrolysis of corn stalk, which is a major type of agricultural wastes. Light absorption of bulk liquid extracts of OA was measured using a UV-vis recording spectrophotometer. OA can be extracted by methanol at 95%, close to full extent, and shows polar character. Light absorption of organic aerosol has strong spectral dependence (Absorption Ångström exponent = 7.7) and is not negligible at ultra-violet and low-visible regions. Higher pyrolysis temperature produced OA with higher absorption. Imaginary refractive index of organic aerosol (k_{OA}) is 0.041 at 400nm wavelength and 0.005 at 550nm wavelength, respectively.

Keywords: organic aerosol, light absorption, corn stalk, pyrolysis, spectral dependence

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1. Introduction

Organic aerosol (OA) is ubiquitous, comprising a major fraction (20-90%) of the atmospheric fine aerosol mass (Kanakidou et al., 2005; Zhang et al., 2007) around the world, and has important effects on regional and global climate, air quality visibility, and human health. OA mainly scatters incoming solar radiation and many climate models treat it as a purely cooling agent (Chung and Seinfeld, 2002; Ming et al., 2005; Myhre et al., 2007). However, there is a growing body of evidence that OA can absorb radiation in the low-visible (blue) and ultra-violet (UV) wavelengths thereby modifying radiative forcing (Kirchstetter et al., 2004; Alexander et al., 2008; Chen and Bond, 2010; Chakrabarty et al., 2010; Lack, et al., 2012; Saleh et al., 2013, 2014). Such OA is referred to as brown carbon (BrC) (Andreae and Gelencser, 2006). A few recent climate modeling studies demonstrated that BrC was an important atmospheric absorber, globally and regionally (Park et al., 2010; Feng et al., 2013; Lin et al., 2014; Lu et al., 2015). Due to lack of available measurement data on BrC's light absorbing properties, its absorbing effect was simplified in models, which couldn't reflect its absorptive behavior varieties from different sources.

The complex refractive index ($m=n-ik$) is the fundamental parameter to determine the particle's optical properties. BrC's light absorption is often quantified by mass absorption cross section (MAC, m^2g^{-1}), and its spectral dependence is described by Absorption Ångström Exponent (AAE). MAC can be calculated using Mie theory if m and particle size are known.

Because BrC is a complex mixture containing a large group of organic compounds with various absorptivities and lacking a formal analytical definition, many methods have been used to determine its light absorbing properties. Kirchstetter et al. (2004) extracted organic carbon (OC) with acetone from the loaded filters and used optical transmission method to determine the difference in the light transmission of the filters before and after extraction, and then estimated optical constants for OC from biomass smoke and motor vehicle. Chen and Bond (2010) extracted OC with different solvents and measured light absorption of bulk liquid extract, and then derived light absorbing properties of

45 OC from wood pyrolysis. Alexander et al. (2008) applied the electron energy-loss spectrum in the
46 transmission electron microscope and quantified the optical properties of individual amorphous
47 carbon spherical particles in East Asia outflow. Yang et al. (2009) used a multi-wavelength
48 aethalometer to measure atmospheric aerosol light absorption, assumed that black carbon (BC)
49 followed an inverse-wavelength relationship from 370 to 950 nm, BC was the only significant light
50 absorber at 950nm, i.e. light absorption effect of BrC and dust was negligible at this wavelength, and
51 then derived BrC light absorbing properties. Favez et al. (2009) applied the same method to quantify
52 light absorption of organic aerosol from agricultural waste burning. Several studies employed
53 optical closure methods (Chakrabarty et al., 2010; Lack et al., 2012; Saleh et al., 2013; 2014),
54 namely, the complex refractive index of the particles were retrieved from Mie closure calculation
55 based on particle size, scattering and absorption measurement. Lu et al. (2015) reviewed available
56 measurements of the light-absorption properties of primary OA from various combustion sources.

57 Since biofuel combustion and biomass open burning contributes about 90% of the total primary
58 OC (Bond et al., 2004), investigation of the light absorbing properties of primary OC has been
59 focused on this type of source. However, most of them concern wood combustion, savanna and
60 forest fire, duff combustion (Kirchstetter et al. 2004; Chen and Bond 2010; Chakrabarty et al., 2010;
61 Lack et al., 2012; Saleh et al., 2013; 2014). Agricultural wastes are often burned in the field after
62 harvesting and used as fuel for cooking and heating in developing countries (Li et al, 2007, 2009).
63 These emissions contribute 9% to global annual OC emission and 27.5% to its emission in China
64 (Bond et al., 2004; Cao et al., 2006). Only two studies have examined light absorption of OA from
65 burning of rice straw (Favez et al., 2009; Saleh et al., 2014), and it is not known whether OA from
66 waste of other crops, which is structurally different, has similar properties.

67 In this work, we explored light absorbing properties of primary OA from combustion of corn
68 stalk, which is a major type of agricultural waste. The experiments were designed to generate OA
69 under the pyrolysis combustion phase only, since approximately 80% of OC is emitted in this

70 combustion phase (Einfeld et al., 1991). Roden et al. (2006) used real-time emission measurements
71 to demonstrate that solid-fuel combustion occurs in distinct phases, with black and brown carbon
72 emitted separately. Real-time measurements (Chen et al., 2011) also show that about half of organic
73 carbon mass is emitted in the rapid ejection that occurs after fuel addition. Therefore, separating
74 combustion by phase, rather than separating particles physically, allows exploration of different
75 realistic aerosol types.

76 We put the corn stalk into an electrically-heated and temperature-controlled pyrolysis reactor,
77 with nitrogen (N₂) as carrier gas, and organic aerosol was generated at three temperatures. We used
78 the improved extraction method and extracted organic aerosol samples with methanol and employed
79 a UV-vis spectrophotometer to measure light absorption of the extracts. We derived absorption per
80 mass of organic aerosol (α/ρ), a parameter related to MAC of OC. We also reported imaginary
81 refractive index of organic aerosol (k_{OA}) and its absorption Ångström exponent (AAE).

82 **2. Method**

83 **2.1 Generation and collection of organic aerosol**

84 Corn stalks were collected from a field, near University of Illinois at Urbana-Champaign
85 (Illinois, USA), after the corn was harvested. The corn stalks were dried in the lab for over a week
86 and then cut into pieces with about 4 cm in length.

87 Organic aerosol was generated by pyrolyzing pieces of corn stalks in a temperature-controlled
88 pyrolysis reactor. The reactor consisted of a resistive heating cylinder and a heater with 120 volt, 650
89 watt (Watlow VC403A06A). A proportional integral differential (PID) controller was used to control
90 the reactor temperature fluctuation due to the pyrolysis process within 10°C. Corn stalk pieces were
91 placed on a stand, 3cm above the bottom center of the pyrolysis reactor. In order to prevent flame
92 and thus the production of BC, N₂ was used as the carrier gas and injected at the bottom of the
93 reactor with a flow rate at 6 L min⁻¹, which kept the reactor at a slightly positive pressure and
94 prevented oxygen from entering. The reactor was previously used to generate organic aerosol from

wood pyrolysis by Chen and Bond (2010) and Brem et al. (2012). Moreover, before pyrolysis, corn stalk pieces were purged with N₂ and vacuumized, and then soaked into N₂ for over one day, which removed oxygen within the corn stalk and prevent BC production during the pyrolysis. In order to investigate the effect of pyrolysis temperature on OC absorption, the experiments were carried out under three temperatures: 210 °C, 270 °C, 360 °C. These temperatures were chosen, based on biomass thermal degradation behavior (White and Dietenberger, 2001), to span the range of conditions where pyrolysis occurs. In each run, three pieces of corn stalk were pyrolyzed sequentially and the pyrolysis lasted for about 10 minutes. The pyrolysis procedure was designed to simulate the release of organic aerosol from corn stalk combustion under normal combustion temperatures. Pyrolysis product was released from the corn stalk, escaped from the reactor and then formed organic aerosol through partial condensation in the cooling plume.

The aerosol generated by the pyrolysis of corn stalk pieces was sampled 4cm above the reactor chimney at a flow rate of 3.75 L min⁻¹. The sampling air was then diluted with particle-free dry air with 7:1 dilution ratio. After dilution, the sample temperature was about 30 °C. Before collection, particles larger than 1 μm was removed by a two-stage Berner type impactor.

Aerosol was collected by four parallel sampling branches (Fig. 1). The first branch and second branch collected primary OA on 47mm quartz fiber filters (Tissuquartz 2500, Pall Inc.), under high (20 L min⁻¹) and low (2 L min⁻¹) flow rates, respectively. The purpose of collecting samples at two flow rates will be discussed in Section 2.2. However, quartz filters may also collect adsorbed organic vapors. A Teflon-quartz filter combination has been recommended to estimate this artifact (Turpin et al., 1994), with a front Teflon filter (Millipore, Fluoropore™ Membrane Filters, FALP04700) removing particles from the gas stream, and a backup quartz filter estimating the gaseous adsorption. The third branch contained this combination. The sampling flow rate in this branch was set to 2L min⁻¹, same as the second branch. The rest of the dilution aerosol flow was bypassed through the fourth branch.

Prior to sampling, quartz filters were baked in a muffle furnace at 550°C for at least 4 hours to reduce blank carbon levels and then stored individually in Petri dishes lined with aluminum foil. At the end of the sampling, the filters were returned to the dishes immediately and stored in a freezer until further analysis.

Fig. 1 Schematic of generation and collection system of organic aerosol

2.2 Analysis method

We used the method developed by Chen and Bond (2010) to extract and characterize the spectral light absorption by organic aerosol samples. It involves extracting samples with a solvent, measuring light absorption of the extracts, and determining OC concentrations in the extracts where absorption is measured. However, due to the limit of instrument detection range, the valid range of OC absorption reported in previous study are from 360 nm and ends around 500nm. Lack of OC absorption at longer wavelength is not conducive to estimate brown carbon total radiative forcing.

To extend the spectral range of OC absorption, the method has been improved by 1) extracting samples both under high and low flow rates, measuring light absorption of the extracts, combining

136 those two sets of data to obtain valid absorbance values across wavelength spectra ranging from
 137 360nm to around 600nm; 2) analyzing OC in samples under the low flow rate directly, measuring
 138 OC content in the extracts under the high flow rate by pipetting a droplet of extracts on the blank
 139 filter and then analyzing OC after drying, thus determining OC concentrations in the extracts from
 140 samples both under high and low flow rate. Analysis procedures of samples collected at three
 141 sampling branches are shown in Fig. 2.

142

143

(a)

144

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(b)

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(c)

148 Fig.2 Analysis procedures of samples collected at three sampling branches (a) high flow rate branch,
 149 (b) low flow rate branch, (c) backup filter branch.

150 2.2.1 Filter extraction

151 The loaded quartz filters in the high and low flow rate branches, and backup quartz filters were
 152 extracted with methanol (Fisher Scientific, A.C.S. certified), which was found previously to extract
 153 organic mass from wood pyrolysis efficiently. Chen and Bond (2010) reported that the fraction of
 154 total OC extracted by methanol was from 92% to 98%. A punch of quartz filter with 3 ml methanol
 155 was sonicated for 1h in an ultrasonic bath (Model 8892, Cole Parmer, Inc), kept at room temperature
 156 for 20h to let the solution reach equilibrium, and sonicated for an additional hour. After sonication,
 157 all the extracts were filtered by a 25mm diameter syringe filter with 0.2 μm pore size (Whatman,
 158 Anotop@ disposable syringe filter) to remove impurities and undissolved materials for further
 159 absorption analysis by UV-vis spectrophotometer. Prior to the filtration, the syringe filter was pre-
 160 washed with 20 ml methanol to remove impurities which could have an effect on further absorption
 161 analysis.

After extraction, residual filters were taken out of the solutions and dried in a fume hood and then kept in dishes immediately and stored in a freezer for post-extraction OC analysis. This analysis determined the amount of unextracted OC.

2.2.2 Absorbance measurement

Light absorption of bulk liquid extracts was measured using a UV-vis recording spectrophotometer (Shimadzu, UV-2401) for wavelength spectra ranging from 250nm to 750nm. The instrument was operated in spectrum mode at a wavelength resolution of 1 nm. Each spectrum was determined relative to the extraction solvent, methanol, as reference. According to Chen and Bond (2010), valid absorbance (A) values from the spectrophotometer should be in the range of 0.05 and 1. The lower limit, $A=0.05$, is the instrument detection limit. While A values exceed the upper limit, $A=1$, the Beer-Lambert law is not valid. In previous work (Chen and Bond, 2010), the valid range of OC absorption ended around 500nm, and absorption measured at longer wavelength was usually below the lower limit. In order to meet the requirement, we measured both absorbance of extracts from quartz filters in the high and low flow rate branches. For the former, the absorbance values were often in the valid range in the visible region, but often exceeded the upper limit in the ultraviolet region. Meanwhile, for the latter, its absorbance values were often in the valid range in the ultraviolet region, however often below the lower limit in the visible region. Hence, we combined those two sets of data to obtain valid absorbance values across wavelength spectra ranging from 360nm to around 600nm.

In order to investigate absorbance property of organic vapors adsorbed on the quartz filters, we also measured absorbance of extracts from backup quartz filters.

2.2.3 Determination of OC concentrations in the extracts

OC concentrations in the extracts where absorption is measured were derived by 1) difference of OC loading on the quartz filters before and after extraction divided by extraction volume; 2) OC

mass in the volume of extract. OC concentrations in the extracts could not be analyzed by total carbon analyzer because of the organic solvent.

For quartz filters in the low flow rate branch and backup quartz filters, OC content on the filters before and after extraction was determined by a thermal-optical OC/EC analyzer (Sunset Laboratory, Tigard, OR) using the NIOSH protocol (2003). The choice of temperature protocol can affect the division between OC and EC (Chow et al., 2004), but the aerosol generated in this work was entirely OC, so the protocol used does not affect the findings.

OC loading on the quartz filters in the high flow rate branch before extraction was above the valid range of the OC/EC analyzer. The exact OC content could not be obtained by direct analysis of quartz filters. Instead, 30 μ l of extract was pipetted onto a blank 1 cm² quartz filter punch and then the punch with the extract was dried for 30 minutes in a fume hood. After drying, OC on the filter punch was measured by the thermal-optical OC/EC analyzer and the concentration in the extracts was calculated by dividing OC mass with pipetted extraction volume. Some extracted organic materials may evaporate with methanol during drying in the fume hood, which results in underestimation of OC content. The organic materials which may co-evaporate should have very high volatility. Since the filters were heated at 170°C to remove SVOC (including the organic materials with high volatility), the amount of organic materials which co-evaporate should be negligible. In order to determine fraction of total OC extracted by methanol, OC content on the quartz filter after methanol extraction was also analyzed by OC/EC analyzer. OC loading for methane residual on the filter after drying was negligible compared with OC samples.

2.2.4 Semi-volatile organic carbon (SVOC)

In the sampling gas, fresh OC concentrations were a few orders of magnitude higher than that diluted to ambient condition, which leads to a substantial part of SVOC partition to the particle phase. Some of the SVOC could be in the gaseous phase under ambient condition (Donahue, et al., 2006). In order to investigate mass and absorption of SVOC and non-volatile organic carbon (NVOC)

separately, we removed SVOC in low flow rate samples by heating the sampled quartz filters at 170°C at the helium mode in the OC/EC analyzer. This temperature roughly reproduced atmospheric partitioning but did not cause charring of OC. This method was previously used by Chen and Bond (2010). We analyzed OC concentration and its absorbance in methanol extract for both original filters (representing total organic carbon, TOC) and heated filter (representing NVOC). The difference between those two is the contribution of SVOC.

2.3 Data analysis

The main values reported in this paper are absorption per mass of organic aerosol (α/ρ), imaginary refractive index of organic aerosol (k_{OA}) and absorption Ångström exponent (AAE). We describe how these values are deduced as follows:

2.3.1 Absorption per mass

Absorption per mass (α/ρ) reported in this paper is absorption cross-sections divided by organic compound density in the unit of m²/g. Here α is the absorption coefficient in liquid, and ρ is the density of dissolved organic compounds. The α/ρ values can be derived from Equation 1.

$$\frac{\alpha}{\rho}(\lambda) = \frac{A(\lambda)}{c \times L} \times \ln(10) \quad (1)$$

Where A is the absorbance value measured by the spectrophotometer at the wavelength λ , L is the optical path length and equal to 1 cm, and c is the concentration of the organic carbon in the extract determined by the OC/EC analysis as described in 2.2.3. A similar approach has been used by Chen and Bond (2010). The α/ρ has the same unit (m²/g) as MAC, which is a fundamental input to radiative transfer models. However, the two describe different properties and should not be confused. The α/ρ in our study is bulk absorption by liquid extract, however, MAC is value of absorption by particles. MAC can be compared with α/ρ only after considering the particulate effect, ζ (Sun et al., 2007).

$$MAC = \frac{\alpha}{\rho} \varepsilon \quad (2)$$

Where ξ is a function of n and k :

$$\varepsilon = \frac{9n}{(n^2 - k^2 + 2)^2 + 4n^2k^2} \quad (3)$$

2.3.2 Imaginary refractive index (k_{OA})

The complex refractive index ($m=n-ik$) is the fundamental parameter in Mie theory to calculate mass scattering and absorption cross section (MSC and MAC). The values n and k , i.e., real and imaginary part of the complex refractive index, are mainly associated with the scattering and absorption, respectively. This paper focuses on absorption, so we report values of k . The k_{OA} can be derived from Equation 4.

$$\alpha = 4\pi k / \lambda \quad (4)$$

Here α was calculated from the determined α/ρ values with Equation 1 by assuming an organic compound density (ρ) of 1.2, which is a commonly used density for OC (*Turpin and Lim, 2001*).

2.3.3 Absorption Ångström exponent

Absorption Ångström exponent (AAE), a parameter used to describe the spectral dependence of aerosol light absorption, is defined as:

$$AAE = \frac{-\ln\left(\frac{\alpha(\lambda_1)}{\alpha(\lambda_2)}\right)}{\ln\left(\frac{\lambda_1}{\lambda_2}\right)} \quad (5)$$

The AAE values were determined by means of linear regression of $\ln(\alpha/\rho)$ versus $\ln(\lambda)$.

3. Results and discussion

3.1 Fraction of total OC extracted by methanol

The fraction of OC extracted by methanol at three pyrolysis temperatures ranged from 90.6% to 98.2%. Average fractions are $95.3 \pm 1.8\%$, $96.1 \pm 1.4\%$ and $93.7 \pm 2.3\%$ at 210 °C, 270 °C and 360 °C,

respectively. Our results for aerosol from pyrolysis of corn stalk are consistent with previous results from wood pyrolysis (Chen and Bond, 2010). The high extraction fraction by methanol indicated that absorption by methanol extraction could represent the behavior of the total OC. No obvious difference was found in OC extraction fraction by methanol at different pyrolysis temperatures.

3.2 Effect of organic vapors adsorbed on the quartz filters

Adsorbed organic vapors on the backup quartz filters contributes only a small fraction to the total OC mass. Its average percentages are 4.0%, 4.7% and 7.5% at 210 °C, 270 °C, 360 °C pyrolysis temperatures, respectively. Its contribution to total OC increases with pyrolysis temperature increasing.

Absorbance values of extracts from adsorbed organic vapors are much less than those from low flow rate branch (representing TOC). Even in the ultraviolet region, the values are lower than the instrument detection limit.

3.3 SVOC effect

SVOC, determined by heating samples to 170 °C, contributes significantly to the total OC mass, with average percentages of 51.1%, 52.8% and 52.7% at 210 °C, 270 °C, 360 °C pyrolysis temperatures, respectively. When heated at 170 °C, adsorbed organic vapors are also released, so SVOC in our study also includes adsorbed organic vapors.

The curves in Figure 3 indicate the ratio of absorbance by NVOC over that by TOC for samples generated at different temperatures. NVOC contributes 56.8%, 58.4% and 65.8% of the absorbance at 360nm at 210 °C, 270 °C, 360 °C pyrolysis temperatures, respectively. This indicates that the removed SVOC does contribute to the light absorption in the ultraviolet region, and we need to account for this effect when estimating the absorption of NVOC. Increased absorbances after removal of SVOC are observed in the visible range, and it could have several causes. One is chemical changes of organics when heated, and the other is measurement error because the measured absorbance values in the visible range were below the instrument detection limit. We have not

280 conducted further study since OC absorption in the visible range is negligible, so we assume that
 281 SVOC will not contribute to the light absorption in the visible range.

282 As discussed in Section 2.2.4, SVOC should be in the gaseous phase when organic aerosol
 283 generated by the pyrolysis process was diluted to ambient condition. To provide data suitable for
 284 radiative-transfer models, SVOC should be separated from NVOC. In the following section, we only
 285 provide data for optical properties for NVOC.

286
 287 Fig.3 Ratio of absorbance of NVOC and TOC (Dashed lines indicates the measured absorbance
 288 values are below the instrument detection limit).

289 3.4 Absorption per mass of organic carbon

290 In this study, we investigated three different pyrolysis temperatures: 210 °C, 270 °C, 360 °C. Actual
 291 temperature varied 10 °C from the nominal temperature. Figure 4 shows average and standard
 292 deviation of absorption per mass of organic carbon (α/ρ) at three pyrolysis temperatures. It illustrates
 293 that α/ρ increases with increasing pyrolysis temperatures across the investigated temperature range.
 294 An increase from 210 °C to 270 °C and 210 °C to 360 °C results in approximately 20% and 50%
 295 increase of α/ρ (average in ultraviolet range), respectively. Chen and Bond (2010) also observed the
 296 similar results for wood pyrolysis. High temperature favors polymerization of volatile matter before

297 it exits the fuel, which results in greater absorption per mass. However, the degree of α/ρ increase
 298 with temperature is much lower than that of wood pyrolysis (Chen and Bond, 2010). Difference in
 299 α/ρ for wood pyrolysis at 210 °C and 360 °C was observed for a few times. The discrepancy may be
 300 due to the difference in fuel structure. Corn stalk has a looser fiber structure relative to wood. During
 301 the pyrolysis of the corn stalk, OC precursors are released more easily, and hence have less
 302 residence time. This weakens the polymerization and results less increase of α/ρ than in the wood
 303 pyrolysis.

304
 305 Fig.4 Average absorption per mass of organic carbon (α/ρ) at three pyrolysis temperatures. Dashed
 306 lines with the same color indicate upper and lower range.

307 We list α/ρ at different wavelengths from this study and along with similar values in our prior
 308 works in Table 1. Values of α/ρ for corn stalk pyrolysis are comparable with those for wood
 309 pyrolysis. In general, values of α/ρ for corn stalk are higher than wood at 210°C and 270°C pyrolysis
 310 temperatures. However, the situation is the opposite at 360°C pyrolysis temperature, possibly
 311 because of greater polymerization in wood at this temperature. It may also relate to difference on
 312 biomass constituents. Wood has a higher lignin content relative to corn stalk (McKendry, 2002).

313 Lignin, an essential and major biopolymer of biomass tissue, is derived primarily from aromatics
 314 alcohols (Simoneit, 2002). Pyrolyzed at 360°C, a large amount of lignin decomposes (Collard and
 315 Blin, 2014), polymerizes, and releases the aerosol enriched of aromatic moiety (Simoneit, 2002),
 316 which is thought as high absorption (Chen and Bond, 2010).

317 Table 1. Average absorption per mass (α/ρ) at different wavelength from this study and literature
 318 values (unit: m²/g)

λ (nm)	corn stalk pyrolysis			wood pyrolysis ^a		
	210°C	270°C	360°C	210°C	270°C	360°C
360	1.53	1.80	2.07	1.55	1.79	3.06
400	0.66	0.76	1.06	0.50	0.68	1.66
450	0.29	0.33	0.48	0.15	0.24	0.68
500	0.14	0.16	0.20	0.07	0.10	0.27
550	0.07	0.09	0.09	0.03	0.05	0.11

319 ^a derived from Fig.11 in Chen and Bond (2010).

320 3.5 Imaginary refractive index

321 Figure 5 shows the average and standard deviation of imaginary part of refractive index (k) at
 322 three pyrolysis temperatures. As with α/ρ , k_{OA} increases with increasing pyrolysis temperatures.

Fig.5 Average imaginary part of refractive index (k_{OA}) at three pyrolysis temperatures. Dashed lines with the same color indicate upper and lower range.

Since k_{OA} is an intrinsic property, we now compare our k_{OA} values with other values found in the literature. Table 2 shows a summary of k_{OA} obtained using various methods for various types of biomass burning aerosols. We choose only k values for primary organic aerosol (POA) from biomass burning excluding other emission sources, secondary organic aerosol (SOA) and HULIS. As with α/ρ , our k_{OA} values for corn stalk pyrolysis are comparable with those for wood pyrolysis (Chen and Bond, 2010). However, our k values are a few times lower than those reported by Kirchstetter et al. (2004). Kirchstetter et al. (2004) used filter-based optical transmission method to determine difference in light transmission of the loaded filters before and after extraction with acetone (aerosols mixed with organic and black carbon), and then calculated optical constants including k_{OA} . They admitted this method may overestimated absorption due to multiple scattering by the filter medium. Other possible reasons for the discrepancy are particle light scattering effect, and liquid organic material coating the filter fiber (Bond et al., 1999; Subramanian et al., 2007).

Our k_{OA} values are much higher than the two studies that used optical closure methods (Chakrabarty et al., 2010; Lack et al., 2012). Chakrabarty et al. (2010) used a photoacoustic

340 spectrometer to determine scattering and absorption coefficients of particles emitted from smoldering
341 combustion of two commonly occurring dry mid-latitude fuels, and then retrieved the complex
342 refractive indices of the particles by adjusting the refractive index used as input in the Mie theory to
343 match the measured scattering and absorption data. In their study, no detectable elemental carbon
344 was found in the particles, so particle light absorption can be considered to be from organic carbon.
345 Lack et al. (2012) used multi-wavelength photoacoustic aerosol absorption spectrometer to measure
346 absorption coefficients of mixed particles emitted from ponderosa pine forest fire, and applied Mie
347 Theory modelling to calculate BC, internal mixing and OC contribution to the absorption, and
348 retrieved k_{OA} at 404nm. These values of k_{OA} would be an average over all OC, including semi-
349 volatile material.

350 Saleh et al. (2013, 2014) also determined refractive index by optical closure methods. Their
351 work indicates that almost all of the OA absorption was associated with extremely low-volatile
352 organic compounds (ELVOCs). They obtained values of k_{OA} using several assumptions (see table
353 footnotes). Our values from extracts are in the lower bound of their results for total OA, and are an
354 order of magnitude lower than their results for ELVOCs.

355 The optical closure method requires the assumption that 1) the particles are spherical in shape, 2)
356 particle size distribution can be represented by a log-normal function, 3) particles are externally or
357 internally mixed. Moreover, the densities of particles were chosen from previous study, not from the
358 direct measurement. Above assumption may not satisfy the case and can cause uncertainties to the
359 calculated results. Other source of uncertainty are the assumption of m_{BC} and n_{OA} during Mie Theory
360 modelling. Given the variation in k_{OA} induced by the above assumptions, one should remain cautious
361 about drawing conclusions based on comparison of refractive indices of OC obtained using different
362 closure methods.

363 Measuring absorption for suspended particles with in-situ methods such as photoacoustic
364 spectrometer along with filter-based optical transmission measurement and extraction methods are

encouraged in the future. This effort will be helpful to explain the discrepancy among different methods. Our improved extraction method extends OC absorption measurement to around 600nm in this study, and longer wavelength could be achieved if more careful experiments are designed. The improvement makes the comparison between extraction methods and the multi-wavelength in-situ methods (such as PASS-3, a commercialized photoacoustic spectrometer, is operated at 405nm, 532nm and 781nm) possible.

Table 2. Summary of k and AAE of OC obtained using various methods for various types of biomass burning aerosols.

Aerosol source	λ (nm)	k	AAE	Method	Reference
Pyrolysis of corn stalk ^a	400	0.041 ^b	7.7	Extract bulk light	This study
	550	0.005		absorbance measurement	
Pyrolysis of wood ^a	400	0.063 ^b	6.9-7.8	Same as before	Chen and Bond,
	550	0.006			2010
Firewood smoke and savanna fires ^c	400	0.11	1.2-2.2 ^d	Filter-based optical	Kirchstetter et al.,
	550	0.03		transmission measurement ^e	2004
Smoldering biomass combustion ^a	405	0.0076~0.015	4.2~6.4 ^f	Optical closure ^g	Chakrabarty et al.,
	532	0.002~0.008	2.3~2.4		2010
Ponderosa pine forest fire ^c	404	0.009	2.3 ^d	Optical closure ^g	Lack et al., 2012
Biomass burning ^c	550	0.0055~0.02 ^h	3.2~3.9 ^h	Optical closure ^g	Saleh et al., 2013
		0.022~0.06 ⁱ	3.1~4.2 ⁱ		
Biomass burning ^c	550	0.006~0.035 ^j	1.5~5.4 ^j	Optical closure ^g	Saleh et al., 2014
		0.007~0.037 ^k	1.4~5.3 ^k		
		0.07~0.22 ^l	2.1~2.4 ^l		
		0.09~0.24 ^m	1.9~2 ^m		

- 373 ^a Organic carbon, no black carbon.
- 374 ^b Values at pyrolysis temperature 360°C.
- 375 ^c Mixed aerosol, including OC and BC.
- 376 ^d Values for mixed aerosol
- 377 ^e Measure difference in light transmission of the loaded filters before and after extraction with
- 378 acetone.
- 379 ^f AAE values at 4.2-6.4 are for wavelength between 405 and 532nm; those at 2.3-2.4 are for
- 380 wavelength between 532-780nm.
- 381 ^g The complex refractive indices of the particles were retrieved from Mie “closure” calculations
- 382 based on particle size, extinction and absorption measurements.
- 383 ^h Assuming BC and OA are externally-mixed.
- 384 ⁱ Assuming BC are internally-mixed with OA.
- 385 ^j Assuming BC are internally-mixed with total OA.
- 386 ^k Assuming BC and OA are externally-mixed with total OA.
- 387 ^l Assuming BC are internally-mixed with ELVOCs.
- 388 ^m Assuming BC and OA are externally-mixed with ELVOCs.

389 3.6 Absorption Ångström exponent (AAE)

390 Values of AAE for OC extracted by methanol at three pyrolysis temperatures are shown in

391 Table 2. The values range from 7.0 to 7.7 in the whole investigated range, showing strong spectral

392 dependence. Those are similar to the data reported by Chen and Bond (2010) for organic carbon from

393 wood pyrolysis (6.9-11.4), but much higher than the values derived from aerosols mixed with

394 organic and black carbon from biomass burning emissions (1.2-5.4) (Saleh et al., 2013; 2014;

395 Kirchstetter et al., 2004; Lack et al., 2012), and also higher than those of OC from smoldering

396 biomass burning (Chakrabarty et al., 2010).

397 4. Summary and conclusions

With the improved the extraction method and extended the spectral range of OC absorption, we investigated light absorption of organic aerosol from pyrolysis of corn stalks at different temperatures. The absorption shows strong spectral dependence ($AAE=7.7$) and is not be negligible at shorter wavelengths. Absorption per mass of organic carbon increases with increasing pyrolysis temperatures in the range of temperatures we investigated (210 °C to 360 °C). Imaginary refractive index of organic aerosol (k_{OA}) were determined and compared with other values found in the literature.

Measured absorption in extracted OA appears to have some consistency, regardless of whether the OA is generated from wood or from agricultural waste, although the effect of pyrolysis temperature depends on the biomass type. We confirm the finding that semi-volatile organic carbon adsorbs primarily at ultraviolet wavelengths, and including it in measurements reduces the apparent imaginary refractive index at visible wavelengths. However, imaginary refractive index values inferred from optical closure depend upon a few assumptions about particle properties.

In order to gain a more fundamental understanding of factors affecting the absorptive properties of isolated organic aerosol and aerosol mixed with other compounds, an inter-comparison study of different methods to determine light absorbing properties of OC should be conducted in the future. This effort will be helpful to explain the discrepancy among different methods.

Acknowledgements

This work is supported by the U.S. DOE research grant: “Isolating Weakly and Strongly-Absorbing Classes of Carbonaceous Aerosol: Optical Properties, Abundance and Wet Removal” (Grant No.A0871 DOE DE-SC0006689). Xinghua Li was partly supported by National Natural Science Foundation of China (Grant No. 41275121 and 41575119) and Chinese National Foundation for Studying Abroad (China Scholarship Council).

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525 **Graphical abstract**

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