

2015

Determination of the Optical Properties of Secondary Organic Aerosol Particles

Matthew E. Wise

Concordia University - Portland, mawise@cu-portland.edu

John Shilling

Pacific Northwest National Laboratory

Felisha Imholt

Concordia University - Portland

Ryan Caylor

Concordia University - Portland

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Recommended Citation

Wise, Matthew E.; Shilling, John; Imholt, Felisha; and Caylor, Ryan, "Determination of the Optical Properties of Secondary Organic Aerosol Particles" (2015). *Faculty Research*. 2.

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Determination of the optical properties of secondary organic aerosol particles

Abstract

The enhanced greenhouse effect is currently considered to be our most important global environmental problem. While the magnitude of radiation absorbed by greenhouse gases is known to a high certainty, the absorption of radiation by atmospheric aerosol particles is not. In the initial Visiting Faculty Program application, we proposed the use of an ultraviolet-visible (UV/Vis) spectrometer equipped with a liquid waveguide capillary flow cell to determine the extent to which secondary organic aerosol particles (SOA) absorb visible light. Early in the research period, the UV/Vis technique was optimized for three solvent systems (methanol, water and 0.1 M hydrochloric acid). Using the optimized UV/Vis technique optical properties such as mass specific absorption cross-section and imaginary refractive index were determined for SOA dissolved in different solvent systems. The end result of the UV/Vis studies is the inclusion of SOA optical properties into climate models developed at the Pacific Northwest National Laboratory (PNNL). This knowledge will help to improve climate models, which currently do not include the effect of SOA. We also utilized Fourier Transform Infrared Spectroscopy to help elucidate the chemical composition of SOA. Finally, an experimental method was developed to determine the peroxide content of SOA. It is expected that these studies will connect the chemical composition of SOA to their optical properties. The research carried out at PNNL will be included in two undergraduate senior theses at Concordia University - Portland (CU). It is also expected that this research will be included in a peer-reviewed journal article. It is our hope that success of our work will result in future collaborations between PNNL and CU students.

1. Introduction - Background and Research Objectives

The enhanced greenhouse effect is a phenomenon resulting from an increase in the abundance of carbon dioxide and other infrared radiation absorbing gases in the atmosphere. Currently the magnitude of future temperature increases is not known with high certainty. However, if atmospheric models are correct, a significant warming of the atmosphere will occur in the near future. The radiative forcing due to long-lived greenhouse gases is now well established. However, the level of scientific understanding of the radiative forcing due to atmospheric aerosol particles remains low [1]. It is crucial to understand the microphysical properties of aerosol particles if their influence is to be constrained in climate models.

One chemical classification of atmospheric aerosol particles is carbon containing aerosols. These particles account for 40 – 90% of the total fine particle mass and most particles in the atmosphere contain at least some carbonaceous material. They originate from a variety of sources including biomass burning, fossil fuel combustion, and in-situ formation from more volatile organic precursors. Bond and Bergstrom [2] coined the term “light absorbing carbon (LAC)” particles for those containing black carbon (BC). The optical properties of LAC particles are difficult to constrain because they do not all have a single chemical composition with consistent physical properties. It is known that BC absorbs light at wavelengths greater than 500 nm which is important in the context of the enhanced greenhouse effect [2]. However, the climactic effect due to the combination of light absorption by BC and the light scattering properties of organic carbon (OC) is unknown.

A second type of LAC that has recently been gathering attention is “brown” carbon (BrC). BrC is a subset of OC and is commonly referred to as the light absorbing part of organic aerosol particles [3]. It is clear that BrC has different optical properties and different sources/sinks compared to BC. However, the effect of BrC on climate change is poorly constrained. Kirchstetter and Thatcher [4] calculated that 14 % of the solar radiation (300-2500 nm) absorbed by wood smoke was attributed to BrC and 86 % was attributed to BC. Furthermore, Kirchstetter and Thatcher [4] calculated that at wavelengths below 400 nm, the radiation absorbed by BrC increased to 49%. In most modeling studies, organic compounds are treated as purely scattering (i.e. non-absorbing). These studies have not included the absorption of radiation due to BrC which challenges the notion that the combination of BC and OC in aerosol particles leads to a cooling effect in the Earth’s atmosphere.

BrC can originate from several sources including biomass burning, humic-like substances from soils and biogenic emissions. Additionally, BrC can be formed in atmospheric chemical reactions. Secondary organic aerosol particles (SOA) are particles formed in the atmosphere from the oxidation of gas phase organic compounds emitted from either natural or anthropogenic sources. When the gas phase compounds are oxidized, their vapor pressures decrease thus transferring the compounds from the gas phase to the particle phase. Therefore it is reasonable to assume that BrC is a component of SOA.

Lambe et al. [5] studied the relationship between the level of oxidation and the optical properties of different types of SOA. The various types of SOA were created in a flow reactor by the OH oxidation of gas phase precursors mimicking anthropogenic (naphthalene and tricyclodecane), biomass burning (guaiaicol) and biogenic (α -pinene) volatile organic compounds (VOC). The resulting SOA were analyzed to determine their mass specific absorption cross-

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section (MAC) and imaginary refractive index (k) at 405 and 532 nm. MAC and k values are used to determine how much light is being absorbed by the particles. Numerically, higher values of MAC and k indicate greater absorption. It was found that the SOA created in the Lambe et al. [5] study could contribute significantly to the amount of BrC in the atmosphere. This result lends experimental credibility to the notion that BrC is a component of SOA. Therefore, climate models that do not include the influence of SOA in their calculations could be drastically underestimating their warming potential.

A research team led by Dr. John Shilling (Co-PI) at the Pacific Northwest National Laboratory (PNNL) studied the hydrolysis of organonitrate functional groups in SOA [6]. The SOA was generated in a temperature controlled reaction chamber using UV lights and differing concentrations of 1,2,4-trimethylbenzene (anthropogenic VOC), water vapor and NO_x . They found that the SOA formed under high (~225 ppb) and low (~30 ppb) NO_x conditions absorbed light differently. The experimentally determined MAC at 467 nm under high NO_x conditions was more than three times higher than that at low NO_x conditions. Lui et al. [6] theorized that nitroaromatic groups in the SOA absorb light. It is these experiments that give rise to the study conducted for the VFP appointment.

In the summer of 2013, Dr. Matthew Wise (Associate Professor of Chemistry, Co-PI) and Vanessa Selimovic an undergraduate chemistry student at Concordia University – Portland (CU) worked with Dr. Shilling to determine the optical properties of SOA produced in his lab at PNNL. The research was conducted over a period of two weeks and was funded by a faculty research grant from CU. The experiments conducted for the VFP extended the work Vanessa and Dr. Wise started in 2013.

The key deliverables for the work proposed in the 2014 VFP application were:

- 1) the optimization of the ultraviolet-visible (UV/Vis) technique for the study of the optical properties of SOA
- 2) the determination of MAC and k values for different types of SOA generated at PNNL
- 3) the inclusion of the optical properties of SOA into climate models developed at PNNL

During the VFP appointment, we have succeeded in accomplishing two of the three key deliverables. We optimized the UV/Vis technique for the study of optical properties of SOA and determined the MAC and k values for different types of SOA. Data from these experiments will be implemented in the CAM5 global model by Phil Rasch and co-workers as part of an ongoing research project. Currently, CAM5 runs have been completed using fulvic acid optical constants for SOA and indicate that climate forcing from brown SOA could be significant.

In addition to the three key deliverables listed above, we added and completed two other objectives during the course of the project. The objectives were:

- 1) the determination of SOA composition using Fourier Transform Infrared Spectroscopy (FTIR)
- 2) the determination of organic peroxide content in SOA via a wet chemical analysis

2. Progress: Scientific Approach, Impacts and Accomplishments

2.1 Optimization of the UV/Vis technique

The experiments carried out during the VFP at PNNL utilized an UV/Vis spectrometer and a 100-cm liquid waveguide capillary flow cell (LWCC) to determine the extent to which SOA particles absorb visible light (~280-700 nm). Because this type of experiment had not been previously performed at PNNL, the experimental procedure had to first be validated. In order to validate the experimental procedure, the absorption of visible light by various concentrations of Suwannee River fulvic acid (FA) in water was studied. FA was used to characterize the instrument because its light absorption properties in water are well known (e.g., Ghabbour and Davies [7]). Methanol was chosen as a second solvent to elucidate the effect of a different solvent on the optical properties of SOA. The third solvent, 0.1 M hydrochloric acid (HCl), was chosen because experiments characterizing the peroxide content of SOA required 0.1 M HCl as a solvent.

The following is a condensed experimental procedure for the analysis of FA using the UV/Vis technique. First, stock solutions of FA were made by adding ~0.0060 g of Suwannee River FA to 50.0 mL of each solvent. This produced three ~120 mg/L solutions that were diluted to various concentrations using their corresponding pure solvent. Next, the FA solutions were placed in a 10-mL syringe and injected into the 100-cm path length LWCC (World Precision Instruments model LWCC-3100) at 3 mL/hr using a syringe pump (New Era Pump Systems Inc., model NE-300). The absorbance of the solutions, at wavelengths ranging from 250-700 nm, was measured using a high resolution UV/Vis spectrometer (Ocean Optics, Inc. Jaz model UX-83500-20) coupled with a miniature Deuterium-Tungsten Halogen light source (Ocean Optics Inc. model DT-MINI-2-GS).

Figure 1 shows the data generated from the FA absorption experiments. The data points represent the absorbance (at 405 nm) of various concentrations of FA in methanol (filled circles), water (open squares) and 0.1 M HCl (filled triangles). The lines represent linear fits through each data set. Each solution absorbs strongly

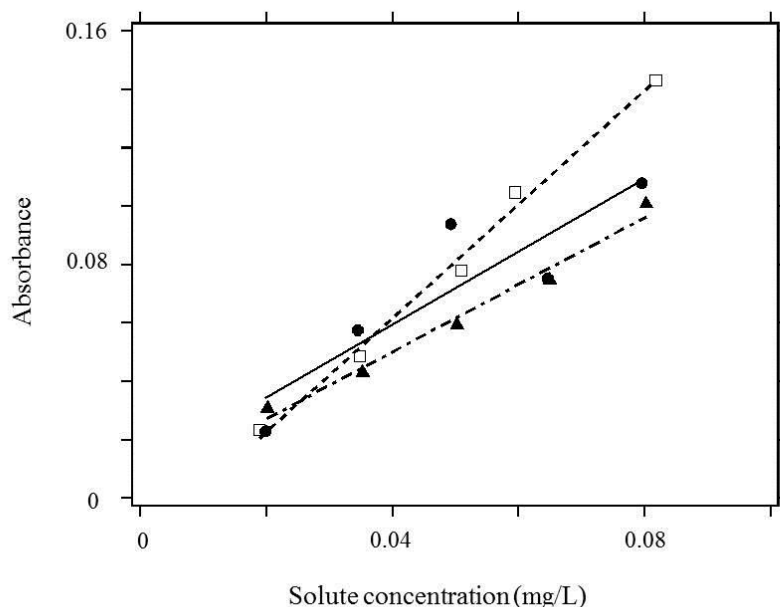


Figure 1. Absorbance by fulvic acid in methanol (filled circles), water (open squares) and 0.1 M HCl (filled triangles). The solid line, dashed line, and dash-dotted line represent straight line fits to the methanol, water and HCl data respectively.

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at 405 nm and, as expected, absorbance increases with increasing solute concentration.

Furthermore, the absorbance values increase in a

linear fashion. In theory, the MAC values (in units of m^2/g) for each system should be independent of solute concentration. This was found to be the case. Table 1 lists the average MAC and k values at 405 nm values for each solvent system.

The MAC values here are a significant improvement from the values generated in 2013. The MAC value for the FA/water solutions in 2013 was 0.28 ± 0.08 . Not only did we determine the MAC value for two more solvent systems but we also reduced the standard deviation in the data by more than 50%. Furthermore, the MAC value reported by Ghabbour and Davies [7] was 0.17. The MAC values here are now consistent with those in the literature. It is also interesting to note that the MAC values for FA each solvent are the same within error. We are now confident that the experimental procedure used to determine the optical properties of SOA is valid in methanol, water and 0.1 M HCl.

Solvent	MAC	k
methanol	0.14 ± 0.03	0.0036 ± 0.0008
water	0.15 ± 0.03	0.0048 ± 0.0010
0.1 M HCl	0.13 ± 0.02	0.0042 ± 0.0006

Table 1. MAC and k values for fulvic acid in various solvents.

2.2 Determination of MAC and k values for SOA

SOA particles were generated in the PNNL environmental chamber as part of ongoing research under the Atmospheric Systems Research (ASR) program. The PNNL chamber design and general experimental method are provided in Liu et al. [6]. Briefly, the chamber consisted of two 10' x 5' x 7' Teflon reaction bags enclosed in a single temperature controlled room (15 – 45 °C). Both chambers were operated independently and could operate either in the traditional batch mode or in a continuous-flow mode (Shilling et al. [8]). Constant light flux was provided by 110 UVA-340 fluorescent lamps which surrounded the chamber. Volatile organic compounds (VOC) were typically injected into the chamber by pipetting the VOC into a gently heated glass bulb with a syringe. Vapors were transferred to the chamber via a flow of pure air. A variety of oxidants were used to initiate SOA formation from the vapors. OH was generated by photolysis of either H_2O_2 or HONO (depending on whether experiments were run under high- NO_x or low- NO_x conditions). Additional NO was sometimes injected from a pre-mixed gas cylinder to further control the NO_x concentrations, which determined the fate of generated organic peroxy radicals. A suite of analytical instrumentation analyzed the particle and gas phases in real time including an Aerodyne HR-ToF-AMS, an Ionicon PTR-MS, and a TSI SMPS.

SOA samples (generated using the procedure outlined above) were collected on 47-mm Teflon filters. Collection times ranged from 2 to 6 hours. After collection, the filters were cut in half with a razor blade, and the SOA was extracted from the filter via ultrasonication in 15-mL of methanol, water or 0.1 M HCl. After sonicating one side of the filter for 5 minutes, the filter was flipped and sonicated for another 5 minutes. The absorbance of the resulting SOA solution was measured using the UV/Vis procedure outlined above for the FA solutions.

Figure 2 is an example of light absorbance by 0.596 mg/L SOA dissolved in water (solid line). The SOA was generated from the photolysis of toluene under high-NO_x conditions. For comparison, the light absorbance by 0.510 mg/L FA in water is shown (dotted line). The SOA solution absorbs most strongly between 280 and 400 nm. At wavelengths greater than 340 nm the SOA absorbs more strongly than FA.

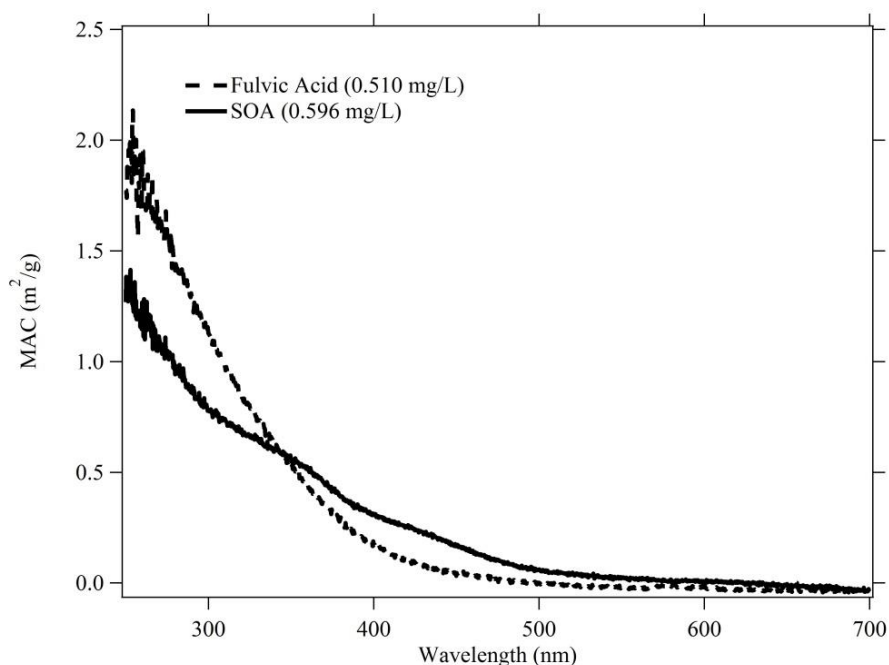


Figure 2. Absorbance spectrum of 0.596 mg/L SOA in water compared to the absorbance by FA in water.

This result is surprising because it has been assumed that FA is a better absorber of radiation in

the UV/Vis than SOA. However, this finding is not true of all SOA generated at PNNL.

Therefore, the chemical identity of the SOA is strongly coupled to its light absorbing properties.

Lambe et al. [5] found MAC values for SOA generated in their laboratory ranged from 0.001 to 0.088 at 405 nm. Additionally, Lambe et al. [5] calculated *k* values between 0.0001 and 0.025 for SOA. Using the absorbance spectrum in Figure 2, the MAC value at 405 nm for the SOA particles generated at PNNL was approximately 0.291. Using a MAC value of 0.291, the SOA had an imaginary refractive index of 0.013. The difference in chemical composition of the SOA generated at PNNL and those studied in Lambe et al. [5] most likely accounts for the difference in MAC values.

3. Future Work

The research described here is not sufficient to fully understand the optical and chemical properties of SOA. More UV/Vis absorbance and FTIR compositional measurements must be collected using SOA generated under different conditions. Once a complete data set is generated, it is expected that it will be used in climate models (developed at PNNL) to constrain the effect of SOA on the Earth's radiation budget. The data collection portion of this work will be carried out by researchers in Dr. Shilling's group. This modeling portion of the project will be conducted by Dr. Phil Rasch and co-workers at PNNL and is currently in progress. In order to achieve these project deliverables, resources must be allocated to fully analyze the SOA, process the data and calculate the full wavelength dependent optical constants. During the collection of the compositional data, an interesting phenomenon was observed. The IR spectrum of the SOA changed over the course of a week. Therefore, either the SOA reacted with the air or a portion of

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the SOA vaporized during storage. A systematic study of the aging process of SOA should be carried out in the future. In order to complete this study, additional personnel and financial resources must be allocated in Dr. Shilling's lab.

4. Impact on Laboratory or National Missions

There have been few studies that have quantitatively determined the optical properties of SOA. Therefore the influence SOA has on climate forcing remains poorly understood. This large gap in the current state of knowledge is the impetus for this work. Climate change science is a key research area for both PNNL and for the Department of Energy's (DOE) Office of Science programs. SOA is regularly produced in the environmental chamber at PNNL as part of ongoing research sponsored by DOE's Biological and Environmental Research (BER) division. Several programs funded by DOE's Climate and Environmental Sciences Division have a strong need and interest in wavelength-dependent aerosol optical constants.

Regional WRF-CHEM modeling funded by the ASR program and global climate models funded by the Earth System Modeling (ESM) program are prepared to utilize SOA optical constants. The models can then be run to predict the effect of brown carbon on the Earth's radiation balance. The Environmental Molecular Science Laboratory (EMSL) has recently placed stronger emphasis on aerosol science and is beginning a program on understanding BrC chemistry. Finally, a joint Laboratory Directed Research and Development (LDRD) project funded by PNNL has the goal of bringing together scientists from different directorates at PNNL, including Atmospheric Sciences and Global Change, EMSL and Physical Sciences to understand the chemistry and climate effects of BrC. This work ties in with all of these ongoing research efforts at PNNL by measuring wavelength-dependent BrC optical constants across the entire UV-VIS spectrum, which underlie the ultimate climate effects of SOA.

5. Conclusions

The UV/Vis technique, used to measure the optical properties of SOA, was optimized for three solvent systems: methanol, water and 0.1 M HCl. The MAC and k values determined during the optimization process agreed well with values found in the literature. SOA particles were then analyzed to determine their optical properties. It was found that the SOA particles absorb radiation most strongly between 280 and 400 nm. Their MAC and k values fell into a range reported in the literature. The optical properties determined here will be included in climate models developed at PNNL. Additional analytical techniques were used to study different properties of SOA. FTIR was used to obtain the chemical composition of SOA. Furthermore, an experimental technique was developed to determine the peroxide content of SOA. These studies were developed to connect chemical composition of SOA to their optical properties.

Without the VFP, the undergraduate students working on this project (Ryan Caylor and Felisha Imholt), would not have the ability to work in a cutting edge research environment. Furthermore, they would not have the ability collect the data needed to complete their senior research theses. We are very grateful to DOE, PNNL, VFP administrators and Dr. Shilling for the opportunity to conduct this research. It is our hope that future collaborations between PNNL and Concordia University students will occur.

6. References

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Appendix

Participants

Name	Institution	Email	Role
Dr. John Shilling	PNNL	john.shilling@PNNL.gov	Co-PI
Dr. Matthew Wise	Concordia University- Portland	mawise@cu-portland.edu	Co-PI
Felisha Imholt	Concordia University- Portland	f_imholt@yahoo.com	Student
Ryan Caylor	Concordia University- Portland	rcaylor@livecom	Student

Dr. Shilling was a co-PI on the project and the contact person for our work at PNNL. He dictated the SOA generation procedures and conditions in the aerosol chamber. We sampled and analyzed the particles created in the chamber. Dr. Wise was a co-PI on the project and oversaw data generation and collection by the two undergraduate students: Felisha Imholt and Ryan Caylor. Felisha was responsible for the data generated by the UV/Vis instrument. Ryan was responsible for the data generated by the FTIR instrument. Although it seems like each person had separate responsibilities, it was a team effort. Each participant helped with all facets of data generation and collection at some point during the 10-weeks.

Scientific Facilities: No scientific user facilities at PNNL were used in the proposed project.

Notable Outcomes: It is expected that this research will be included in a peer-reviewed journal article. However, at this time there are no archival peer-reviewed journal articles, patent disclosures, laboratory technical reports, etc. from research performed under this appointment.

Research Vibrancy: The work done at PNNL during the summer of 2013 was the impetus for the successful proposal submitted for the VFP during the summer of 2014. In a similar fashion, it is our intention to use the 2014 experience to generate a VFP proposal for the summer of 2015. Ten weeks is a very small window in the timeframe of this type of research. Therefore, the work on this project is far from complete. Since Ryan and Felisha are not graduating from Concordia University this year, they have the ability to come back ready to work at PNNL in the summer of 2015.

Connection to Programs at Home Academic Institution: Concordia University is a small liberal arts institution with very little experience with cutting edge research. This summer we will be purchasing an instrument called a differential scanning calorimeter (DSC). Essentially, the DSC can be used to study phase transition (i.e., liquid to solid) in small particles. We have already discussed the possibility of studying phase transitions of SOA particles generated in Dr. Shilling's aerosol chamber. Concordia University does not collaborate very often with high level research institutions. Therefore the possibility of this collaboration is very exciting!