CRC Report No. E-120

Assessment of Anthropogenic and Biogenic Secondary Organic Aerosol (SOA) Source Apportionment

May 2017

COORDINATING RESEARCH COUNCIL, INC.
5755 NORTH POINT PARKWAY SUITE 265 · ALPHARETTA, GA 30022

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Final Report
CRC Project No. E-120
Assessment of Anthropogenic and Biogenic Secondary Organic Aerosol (SOA) Source Apportionment

Performing Organization

Consulting for Health, Air, Nature, & a Greener Environment, LLC
Corporate Headquarters
14 Stonehurst Drive
Queensbury, NY 12804

Principal Investigator

Philip K. Hopke

CHANGE

(315) 212-0798

hopkep@airqualitychange.com

November 30, 2016

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Acronyms

2-D GC	Two-dimensional gas chromatography
AMS	Aerosol Mass Spectrometer
BEIS	Biogenic Emissions Inventory System
C-14	Carbon with mass number 14 (radioactive)
CALNEXT	California Nexus of Air Quality and Climate Change
CAMx	Comprehensive Air quality Model with extensions
CMAQ	Community Model of Air Quality
CMB	Chemical Mass Balance
CRC	Coordinating Research Council
CTM	Chemical transport model
HR-AMS	High Resolution aerosol mass spectrometer
HULIS	HUmic-LIke Substances
IEPOX	Isoprene epoxydiols
IMPROVE	Interagency Monitoring of PrOtected Visual Environments
IVOC	Intermediate Volatility Organic Compound
L-TOF AMS	Long Time-of-Flight Aerosol Mass Spectrometer
MEGAN	Model of Emissions of Gases and Aerosols from Nature
NAAQS	National Ambient Air Quality Standard
OA	Organic aerosol
OH	Hydroxyl radical
OC	Organic carbon
OPOA	Oxidized Primary Organic Matter
PCA	Principal Components Analysis
PM	Particulate Matter
$PM_{2.5}$	Particulate Matter less than 2.5 µm aerodynamic diameter
PM_{10}	Particulate Matter less than 10 µm aerodynamic diameter
PMF	Positive Matrix Factorization
POA	Primary Organic Aerosol
ROS	Reactive Oxygen Species
SEARCH	SouthEastern Aerosol Research and Characterization Network

SOA	Secondary Organic Aerosol
SOAS	Southern Oxidant and Aerosol Study
SOC	Secondary Organic Carbon
Tg	Teragram (10^{12} (one trillion) grams)
SVOC	Semivolatile Organic Compound
VOC	Volatile Organic Compound

Executive Summary

Secondary organic aerosol (SOA) is now recognized as a major component of ambient fine particular matter ($PM_{2.5}$). SOA is formed through the atmospheric oxidation of precursor compounds emitted by anthropogenic and biogenic sources. To appropriately manage air quality and protect public health from the adverse effects of exposure to ambient PM including SOA, it is necessary to be able to estimate the relative importance of these two classes of precursors. This area of active research has only begun to develop the understanding and necessary tools to estimate the relative importance of these two classes of precursors.

The impetus for this report were the results from a recent modeling study of air quality in California. The Community Model of Air Quality (CMAQ) was used in its standard form and in a modified version in which the volatility basis set approach was used to provide semi-volatile and reactive treatment of primary organic aerosol and secondary organic aerosol contributions from intermediate volatility organic compounds (IVOCs, effective saturation concentrations between 10^3 and 10^6 $\mu g/m^3$, roughly the same range as C12 ~ C22 n-alkanes) and volatile organic compounds and their multiple generation products. Because of the large number of isomers and similarities in their vapor pressures, they are difficult to fully separate and quantify in standard gas chromatography/mass spectrometry analyses. The second model provided results that were substantially different than the conventional approach with respect to the relative importance of emissions from spark-emission vehicles relative to compression -ignition vehicles. They predicted that there was 7 times more SOA formed from gasoline vehicle emissions relative to diesel vehicle emissions. However, vehicular emissions only accounted for approximately 25% of the SOA formation. Emissions from other anthropogenic sources such as meat cooking and solvent use led to 50% of the SOA and biogenic emissions and wildfires accounted for the remaining 25%. However, these estimates are subject to considerable uncertainty particularly with respect to the role of intermediate volatility organic compounds given their difficulty in measurement and the limited kinetic data currently available to model their multiple generation reactions. Thus, this report was commissioned to review the available tools for such apportionments and suggest critical research needs that if addressed would reduce the uncertainties in the resulting apportionments.

The available approaches to estimate the relative roles of biogenic and anthropogenic precursors include measurements of the components of SOA and data analytical methods, use of ^{14}C measurements to distinguish contemporary from fossil carbon, and chemical transport modeling. All of these methods have been applied to the apportionment of SOA sources, but the literature is relatively limited and it is an area of growing interest. The advantages and disadvantages of these methods are outlined in Table ES1.

Table ES-1. Summary of advantages and disadvantages of the methods to apportion biogenic and anthropogenic SOA.

Approach	Advantages	Disadvantages
Receptor Modeling	Uses measured molecular tracer species to identify SOA from specific precursor compounds	Requires complex chemical separation and analysis CMB analysis requires tracer fraction data is not available for all precursor compounds Tracer fraction used in CMB is dependent on other species (e.g., NO; acid particles) concentrations Atmospheric secondary aerosol formation processes preclude the separation of anthropogenic and biogenic SOA
Chemical Transport Modeling	Can estimate SOA formation from any precursor species for which the chemical pathways are known quantitatively	Multigenerational chemistry is not well described and incorporated. Issues of using smog chamber data for rate constants due to wall losses and other artifacts Limited availability of accurate emissions inventories particularly for biogenic species.
Aerosol Mass Spectrometry (AMS)	Can use m/z ions 82 and 53 to identify isoprene derived SOA	Good marker m/z ions are not available for terpene or anthropogenic precursor derived SOA
C-14	Distinguishes contemporary from fossil carbon	Does not distinguish between primary and secondary carbonaceous species

Introduction

The Global Burden of Disease consortium (http://www.healthdata.org/gbd) reports that exposure to ambient air pollution is now recognized as one of the most important environmental or behavioral drivers of adverse human health outcomes with most of the risk attributed to airborne particulate matter (PM)(GBD, 2016). Thus, effective and efficient control of ambient PM concentrations is an important public health objective. To produce that control, it is necessary to understand the origins of the ambient aerosol and thus, be able to focus attention where it will be most advantageous. The two major size classes of the ambient aerosol really need to be considered separately. Generally, airborne particles with aerodynamic diameters greater than 1 µm are aerosolized by mechanical processes while submicron particles are formed through chemical processes including combustion and atmospheric chemistry. The primary regulatory focus since the mid-1990 has been on $PM_{2.5}$ with the National Ambient Air Quality Standard (NAAQS) levels being reduced each time it has been reviewed.

Over the past two decades, carbonaceous particles and particularly secondary organic aerosol (SOA) have been recognized as major constituents of $PM_{2.5}$. SOA is formed by the reaction of oxidants such as ozone (O_3) and hydroxyl radicals (OH) with organic compounds leading to a series of free radical reactions (Kroll and Seinfeld, 2008). As oxygen is added to the carbon backbone, the resulting compounds become less volatile and can then either condense onto existing particles or nucleate to form new particles. The resulting particles also contain high concentrations of reactive oxygen species (ROS) (Docherty et al., 2005; Chen et al., 2011; Pavlovic and Hopke, 2012; Hopke, 2015). Secondary particulate matter has been more strongly associated with particular health effects such as myocardial infarctions (Rich et al., 2014; Hopke et al., 2015) likely due to the presence of ROS or its ability to generate ROS (Hopke, 2015). Thus, understanding the sources of the SOA precursors is important.

In this report, the major types of SOA-forming precursors will be reviewed including both biogenic and anthropogenic emitted species. Since biogenic emissions depend on the nature of the biota in a given area, a regional analysis will be performed to divide the United States into a series of domains in which similar mixtures of biogenic VOCs and SVOCs might be present because of the similarity of biota within the given domain. There are two approaches that can be taken to ascertain the sources of the SOA: measurements coupled with appropriate data analysis methods and chemical transport modeling. These approaches will be described, the relevant literature reviewed and the current state-of-the-art presented. Those results will provide the basis for conclusions on what can currently be achieved in terms of assigning SOA to source types and outlining what additional research is needed to help improve the accuracy of identifying and apportioning SOA source types.

SOA Precursors

SOA precursors include volatile (VOCs) and semivolatile (SVOCs) compounds emitted by both natural and anthropogenic sources. In terms of total global biogenic emissions, isoprene dominates with an estimated 594 ± 34 Tg yr^{-1} while the sum of the monoterpenes is 95 ± 3 Tg yr^{-1} (Sindelarova et al., 2014). The specific mixture of compounds in a given location depends on the nature of the biota in that area.

Table 2. Major anthropogenic and biogenic VOCs that are SOA precursors

Anthropogenic	**Biogenic**
Benzene	Isoprene
Toluene	α-pinene
Xylenes	β-pinene
1,3,5-trimethylbenzene	d-limonene
p-cymene	Camphene
Mesitylene	Δ-3-carene
Hexamethyl benzene	B-myrcene

In addition to the VOCs listed in Table 1, another important source of precursors is biomass burning. These compounds include: henol, naphthalene, benzene, *o*-benzenediol, isomers of *m*-/*o*-cresol, 2-methoxyphenol, isomers of 2,4-/2,6-/3,5-dimethylphenol, toluene, 2,6-dimethoxyphenol, isomers of 2-/3-methylfuran, isomers of 1-/2-methylnaphthalene, furan, prop-2-enal, isomers of 2-methylprop-2-enal/(2*E*)-2-butenal, *m*-xylene, acenaphthylene, 1,2-dimethylnaphthalene and 1,2-dihydroacenaphthylene (Bruns et al., 2016).

Anthropogenic emission patterns may potentially be more similar from location to location given that they are largely related to motor vehicles and related facilities such as gas stations. However, specific local sources such as refineries, petrochemical plants, and similar industrial facilities can produce high concentrations of VOCs, some of which may result in SOA formation.

Regional Analysis

Because the amount and chemical composition of the biogenic emissions from natural biota will vary by region of the United States and the majority of the biogenic VOCs are emitted by trees, the country will be delineated using the U.S Forest Service's forest cover maps for four major species that define major spatial domains across the United States: Douglas fir, loblolly pine, white oak, and sugar maple. These domains are shown in Figures 1, 2, 4, and 5, respectively (http://forestry.about.com/od/forestresources/tp/Forest_Cover_Type.htm). Douglas fir (Figure 1) grows in an area from the Pacific Northwest through the Sierra Nevada Mountains and along the Rocky Mountains.

Figure 1. Spatial Domain of Douglas Fir (U.S. Forest Service)

The second forest domain is loblolly pine as shown in Figure 2. It covers the southeastern United States and includes areas that are known to be substantial sources of isoprene.

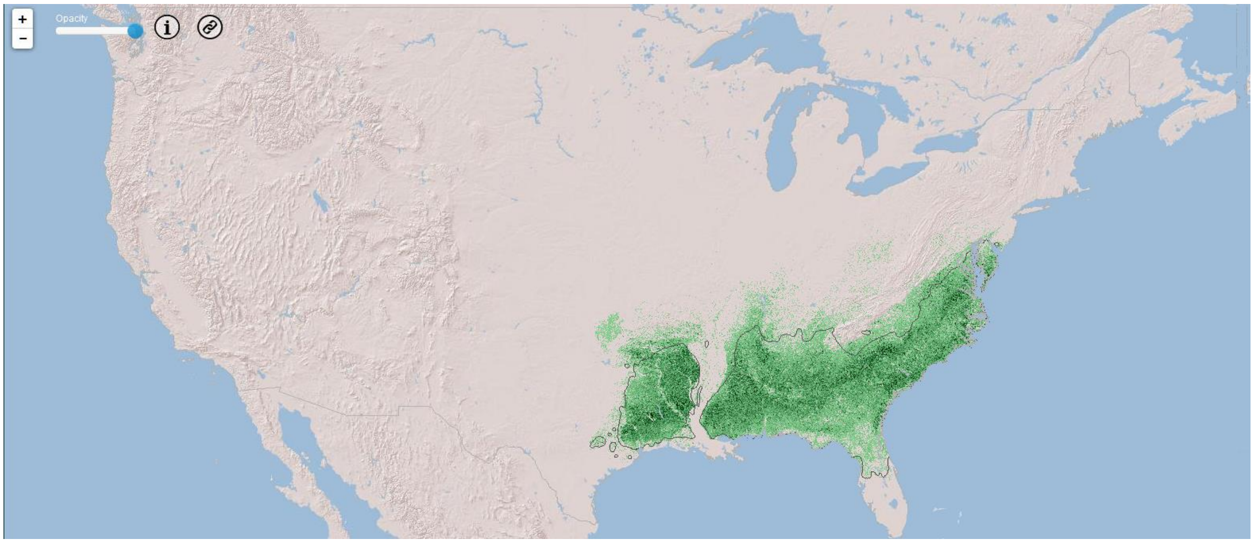

Figure 2. Spatial Domain of Loblolly Pine (U.S. Forest Service)

Given the importance now assigned to isoprene in producing SOA, it is possible to examine the area with the highest isoprene emissions (Figure 3). Wang et al. (2017) have provided new modeling results using one of the two biogenic emissions model, the Model of Emissions of Gases and Aerosols from Nature (MEGAN). Wang et al. report that the predicted monthly average vertical column density of formaldehyde (HCHO), a reactive volatile organic compound with significant contributions from isoprene oxidation, generally agree with the spatial distribution of HCHO column density derived using satellite data. However, summer month vertical column densities in the southeast US were overestimated, which suggests that isoprene emission might still be overestimated in that region. This isoprene rich area of the Southeastern U.S. is also part of the spatial domain for white oak as shown in Figure 4 as modeled for July 2011 (Wang et al., 2017).

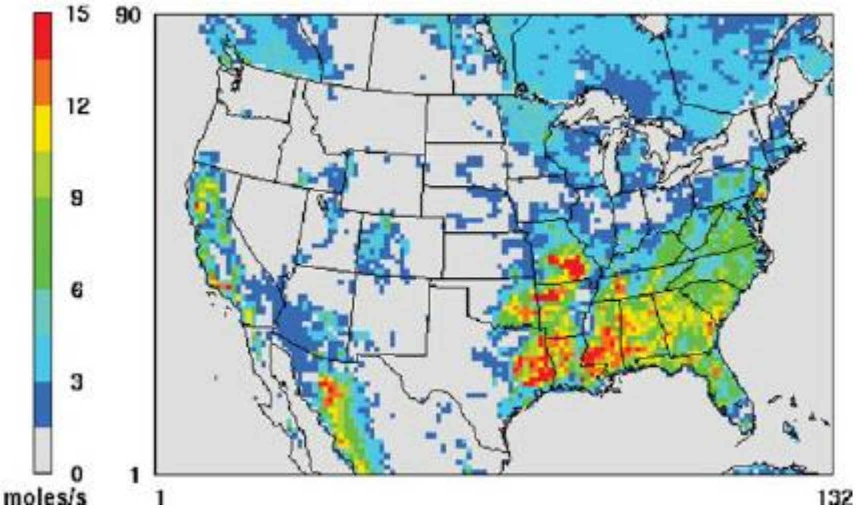

Figure 3. Estimated emissions of isoprene during July 2011 (taken from Wang et al., 2017)

The white oak domain includes the Appalachian Mountains from Pennsylvania and south as well as the Ozark Mountains in Missouri and Arkansas. White oak is likely to be one of the primary sources of isoprene. Isoprene emissions from white oak leaves respond strongly to temperature, increasing rapidly between 15 and 35°C (Fehsenfeld *et al*., 1992; Feuntes *et al*., 2000; Guenther *et al*., 2000, 1999, 1993, 1991; Lerdau *et al*., 1997; Monson *et al*., 1994; Monson and Fall, 1989; Sharkey *et al*., 1991; Tingey *et al*., 1979). Above 35°C, the rate of increase slows, and an optimum is reached, typically between 40 and 44°C.

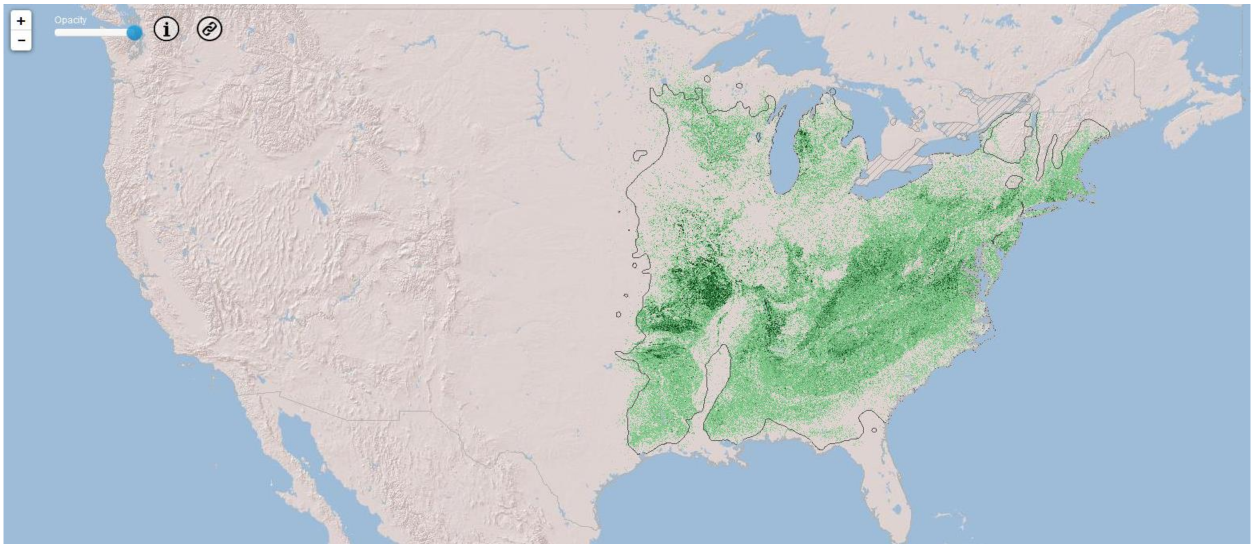

Figure 4. Spatial Domain of White Oak (U.S. Forest Service)

The final forest domain is that for Sugar Maple shown in Figure 5. It covers the northern portion of the Appalachian Mountains and extends westward to the Great Lakes region.

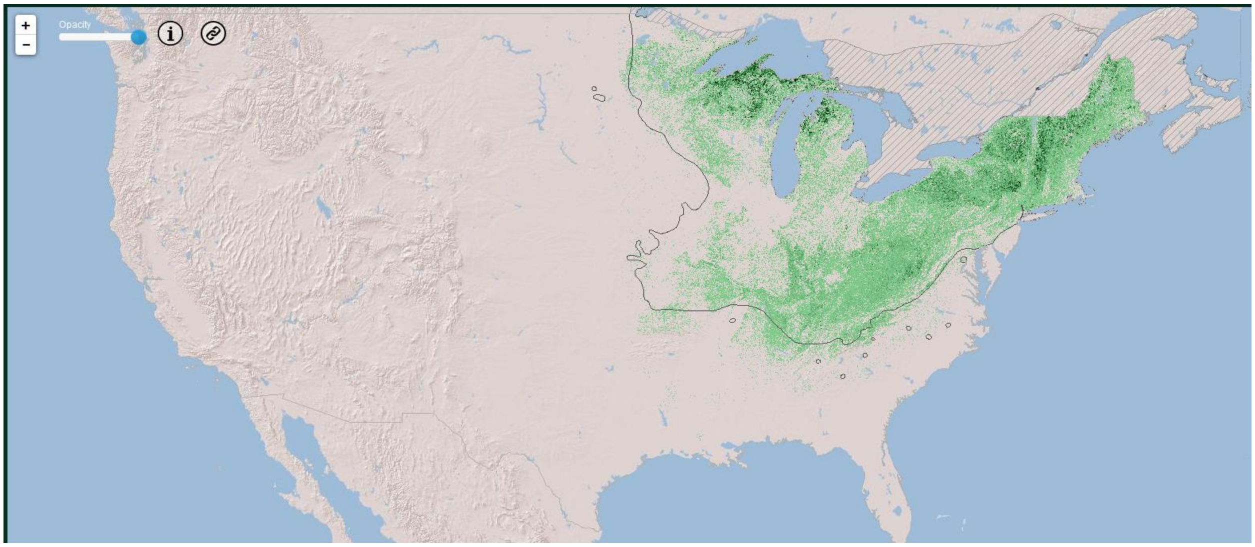

Figure 5. Spatial Domain of Sugar Maple (U.S. Forest Service).

These domains do not cover all of the area of the contiguous 48 states. The plains is the large region between the eastern forests and the front range of the Rocky Mountains where there is extensive field crop agriculture including corn, wheat, soybeans, and sorghum. There are areas of southwestern desert and the dry intermountain west and finally the agricultural areas of California including the Central Valley and the Imperial Valley. Alaska and Hawaii are each their own domains. Across these various domains, there are a wide variety of mixtures of flora and thus, emissions of VOCs varying in composition and emission rates. These regions were defined to provide a basis for separating work on determining the origins of SOA as presented in the following sections of this report.

Apportionment Based on Measurements

Organic Species Monitoring and Receptor Modeling

The use of organic compounds (molecular markers) to identify and quantify the sources of organic carbon associated with the ambient aerosol was initiated by Glen Cass and his group at CalTech in the early 1990s. There were a series of source sampling studies resulting in a library of source profiles for various primary organic carbon emissions. However, in the interim period, it has become clear that SOA represents a significant portion of the observed OC. Subsequently, work by Kleindienst and coworkers at the US EPA identified the markers for SOA precursors (Kleindienst et al., 2004; 2007) and opened the use of receptor models for the identification and quantification of biogenic and anthropogenic contributions to the observed OC. In order to estimate the mass of SOA, the mass fraction of the molecular markers in the organic carbon formed from specific precursor species are needed. Table 2 provides these fractions for α-pinene, toluene, isoprene, and β- caryophyllene (Kleindienst et al., 2007). These values have been developed using a flow chamber and the quantification is based on using cis-ketopinic acid. Since no standards exist for the majority of these compounds, the concentrations of all of the tracers were measured as KPA, which was selected as the surrogate for SOA tracer compounds because it is not found in atmospheric samples. A number of studies have now utilized the results presented in Table 2 to perform apportionment studies. Only 3 biogenic and 1 anthropogenic species have quantitative results and thus, there is not yet a basis for quantifying the reaction products from the other biogenic and anthropogenic species noted in Table 1. However, Kleindienst et al. (2007) provide a warning that "the tracer-based method is subject to considerable uncertainty due to the simplification of replacing the complex set of chemical reactions responsible for SOA with a laboratory-derived single-valued mass fraction."

Table 3. Laboratory determined of tracer mass fractions for laboratory-generated SOA and SOC (adapted from Kleindienst et al., 2007).

Precursor hydrocarbon	hc_o (ppm C)	$NO_{X,o}$ (ppm)	[SOA] (μg/m^3)	Σ [tr_i] (μg/m^3)	f_{soa}
α-Pinene	2.18	0.186	111.6	10.3	0.0923
α-Pinene	4.18	0.45	74.2	11.9	0.16
α-Pinene	4.18	0.45	86.7	12.9	0.148
α-Pinene	2.19	0.272	72	5.8	0.0806
α-Pinene	2.19	0.25	101.3	31	0.306
α-Pinene	3.13	0.317	128	16.7	0.13
α-Pinene	4.95	0.494	333.8	79.3	0.237
α-Pinene	5.27	0.49	298.3	39.4	0.132
α-Pinene	5.27	0.49	271	49.1	0.181
α-Pinene	2.43	0.307	80.9	29.8	0.368
α-Pinene	2.28	0.307	269	30.6	0.114
α-Pinene	2.32	0.279	65.4	10.3	0.157
α-Pinene	3.97	0.279	165	18.9	0.115
α-Pinene	1.04	0.409	9.7	0.99	0.102
α-Pinene	2.20	0.420	102	19.7	0.193
				Average $f_{soa,\ \alpha\text{-}p}$	0.168 ± 0.081
				Average $f_{soc,\ \alpha\text{-}p}$	0.231 ± 0.111
Toluene	6.55	0.201	28.9	0.13	0.0045
Toluene	7.04	0.459	77.8	0.4	0.00514

Toluene	10.2	0.332	73.5	0.18	0.00245
Toluene	10.8	0.332	97.6	0.3	0.00307
Toluene	10.9	0.334	103.4	0.25	0.00242
Toluene	10.2	0.334	94.7	0.28	0.00296
Toluene	12.6	0.42	125.6	0.58	0.00462
Toluene	12.6	0.42	116.9	0.49	0.00419
Toluene	9.6	0.37	88.1	0.56	0.00636
				Average $f_{soa, tol}$	0.0040 ± 0.0013
				Average $f_{soc, tol}$	0.0079 ± 0.0026
Isoprene[a]	8.05	0.627	99.94	4.39	0.0439
Isoprene[a]	7.99	0.475	45.47	3.7	0.0814
Isoprene[a]	7.99	0.475	77.36	5.22	0.0675
Isoprene	12.2	0.291	15.58	0.91	0.0584
				Average $f_{soa, iso}$	0.063 ± 0.016
				Average $f_{soc, iso}$	0.155 ± 0.039
β-Caryophyllene	3.98	0.329	194.03	2.58	0.0133
β -Caryophyllene	0.92	0.109	106.8	0.97	0.0091
β -Caryophyllene	4.6	0.146	236.15	2.44	0.0103
				Average $f_{soa, bcp}$	0.0109 ± 0.0022
				Average $f_{soc, bcp}$	0.0230 ± 0.0046

Tracer concentrations ($\mu g\ m^{-3}$) are given as ketopinic acid

[a] With SO_2 to promote particle formation

Kleindienst et al. (2010) applied this methodology to samples collected in the SEARCH network. The specific marker compounds are as follows:

α-pyrene: 3-isopryl pentanedioic acid, 3-acetyl pentanedioic acid, 3-acetyl hexanedioic acid, 2-hydroxy-4-isopropyladipic acid, 3-hydroxyglutaric acid, 2-hydroxy-4,4-dimethylglutaric acid, 3-(2-hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid, pinic acid, and pinonic acid

isoprene: 2-methylglyceric acid, 2-methylthreitol, 2-methylerythritol (Pye et al., 2013)

β-caryophyllene: β-caryophyllinic acid

toluene: 2,3-dihydroxy-4-oxopentanoic acid; aliphatic diacids and aromatic di-, tri-, and tetraacids (Sheesley et al., 2004); 1,2-benzenedicarboxylic acid (Fine et al., 2004).

naphthalene: 1,2-dicarboxybenzene (Kleindienst et al., 2012)

There are two primary approaches in receptor modeling depending on whether it is assumed that the sources and their profiles are known or unknown (Hopke, 2016). If the sources are known, then the chemical mass balance (CMB) model can be employed. If they are not or cannot be employed, then factor analysis must be applied. The most commonly used method is positive matrix factorization (PMF) (Hopke, 2016). The other quantitative approach is Unmix that has been used in some applications.

To apportion SOA arising from the precursor gases using the CMB approach, the amounts of SOC are estimated based on the measured fractions presented in Table 2. There are many caveats on this approach. For these precursor species, there are different reaction pathways depending on the concentration of NOx. However, it often will not be possible to know the upwind NOx concentrations at the time the SOA was being formed. Thus, there is significant but difficult to quantify uncertainty in the resulting apportionments.

In PMF or Unmix analyses, the relationships between the tracer species and the amount of SOA mass are derived from the analysis. The critical aspect is assigning the pattern of compounds in a given factor to source type. The work of Kleindienst et al. (2007) and others who have identified the marker species permits the identification of factors that have high concentrations of compounds derived from biogenic or anthropogenic precursors. These methods depend on the covariation of the measured species. Since both biogenic and anthropogenic precursors will react with the ambient oxidants to form the SOA, there can be considerable induced covariance because of their mutual dependence on the oxidant concentrations.

There are a limited number of applications of receptor models to the separation of biogenic and anthropogenic SOA sources in the United States based on chemical characterization of the PM samples to quantify the marker species. They are listed in Table 3. The profiles for CMB and the use of the f-values in Table 2 have been most commonly employed. There has been some use of PMF to provide a estimates without the direct use of the Kleindienst et al. (2007) yields and one classical factor analysis that only provides a qualitative assessment of the SOA sources.

Another major issue that has not been discussed in the reviewed literature is that there are significant amounts of isoprene-derived SOA that is formed through heterogeneous processes (George et al., 2015). The Kleindienst et al (2007) values are all based on homogeneous formation of SOA, but it is known that there is substantial formation of additional SOA including oligomeric species in cloud droplets (e.g., Szmigielski, 2016; Renard et al., 2016; Rudziński et al., 2016). Thus, the laboratory generated yield values that are in use are mostly based on the first generation of products. However, one of the important recent findings is that multiple generation processes are important in the formation of SOA. It is only in long smog chamber experiments that oligomeric species are formed via homogeneous processes (Tolocka et al., 2004; Kalberer et al., 2004). Although there can be some formation of second and later generation products if there are sufficient oxidant present in the chamber, the results are likely to underestimate the overall yield of SOA in chamber studies.

For example, Kleindienst et al. (2007) use a flow system for their measurements so their results will not include later generation products. There are thus very limited studies that measure the quantitative relationships between gaseous precursors and the total mass of SOA that can subsequently be formed. These oligomeric materials commonly termed HULIS (HUmic-LIke Substances) have been observed (e.g., Stone et al., 2009a; Pavlovic and Hopke, 2012). Major classes of these oligomeric species include organosulfate and organonitrate fulvic-like compounds (Reemstma et al., 2006). There has been one study (Meade et al., 2016) that has identified organosulfate oligomers that were attributed to both anthropogenic and biogenic precursors. Nguyen et al. (2015) have identified that decreasing liquid water content in the atmosphere of the southeastern US between 2001 and 2012 appears consistent with the increase in visibility over that period. They suggest that this result supports the hypothesis that liquid phase processes contribute significantly to the SOA concentrations in this region. However, their relationship to the total mass of SOA was not quantified. Thus, it is likely that at this time, a significant portion of the SOA cannot be identified or apportioned.

Table 3 provides a listing of all of the published results of receptor modeling studies that have utilize SOA molecular markers to identify biogenic and/or anthropogenic SOA sources. In some cases, CMB was used following the procedure of Kleindienst et al. (2007; 2010). In others, PMF was used to derive profiles that were identified as biogenic or anthropogenic depending on the specific marker compounds that appear in the given factor. In some cases, such as Wang et al. (2012), there was a clear terpene factor and another factor that included markers of isoprene and aromatic compound oxidation. There were not a sufficient number of papers to be able to assess the impacts of biogenic and anthropogenic SOA on the total $PM_{2.5}$ mass concentrations. The available studies covered limited time periods and varied in the completeness of the identification and quantification of marker species. More such studies would be needed with more uniform methodologies to be able to draw quantitative assessment of the relative roles of SOA precursor types. However, in general, more biogenic markers have been reported.

Table 3. Summary of prior receptor modeling studies that separate biogenic and anthropogenic SOA

Location	Region	Methods	Isoprene	Other Biogenic	Anthropogenic	Reference
SEARCH Sites	loblolly pine/white oak	CMB	X	X	X	Kleindienst et al., 2010
SEARCH Sites	loblolly pine/white oak	CMB	X	X	X	Ding et al , 2008
Pasadena/Bakersfield	urban west coast			X	X	Baker et al. 2015
Rochester, NY	sugar maple	PMF	X	X		Wang et al 2012
Los Angeles, CA	urban west coast	CMB, PMF		X	X	Heo et al, 2013
Los Angeles, CA	urban west coast	CMB, PMF	X	X	X	Heo et al., 2015
Various IMPROVE sites	Douglas fir	CMB, isoprene only	X			Holden et al., 2011
Iowa City, Iowa	Agricultural Midwest	CMB	X		X	Jayarathne et al., 2016
National	Many	CMB	X	X	X	Lewandowski et al., 2013
Alaska	Alaska	tracer measurements	X	X		Haque et al., 2016
Research Triangle Park, NC	white oak	CMB	X	X	X	Offenberg et al., 2011
Sierra Nevada Mountains, CA	Douglas fir	PCA		X	X	Worton et al., 2011
Northern Ohio	Sugar maple	PMF	X	X	X	Piletic et al., 2013
Northern Ohio	sugar maple	CMB	X	X	X	Rutter et al., 2014
Northern Midwest	sugar maple	CMB	X	X	X	Stone et al., 2009b
Midwestern US	sugar maple/Agricultural Midwest	PMF	X	X	X	Zhang et al., 2009

Aerosol Mass Spectrometry and Data Analysis

The Aerosol Mass Spectrometer (AMS) was developed to provide near real-time measurements of non-refractory components of the atmospheric aerosol in the aerodynamic size range of 0.040 to 1.30 µm (Jayne et al., 2000). Initially a quadrupole mass spectrometer (MS) was employed that gave a mass resolution of 500, but later a higher resolution time-of-flight (TOF) mass spectrometer was used to provide a mass resolution of 5000 (DeCarlo et al., 2006). This improved resolution permits further resolution of ions of similar, but not identical mass and better tracer ions that can be used to identify likely sources of the observed organic matter. Subsequently, a lower cost, more robust monitoring system was developed, the Aerosol Chemical Speciation Monitor (ACSM), that again started with a quadrupole MS and now with a TOF MS.

Ng et al. (2008) used the HR-AMS to provide the first indication of the use of AMS data to identify SOA formed from the homogeneous oxidation of isoprene using the intensities of the ,m/z 53 and 82 ions. The primary isoprene oxidation pathway producing SOA involves isoprene epoxydiols (IEPOX) that occur under low NOx conditions (Surratt et al., 2010; Pye et al., 2013). Robinson et al. (2011) first reported an SOA factor from AMS spectra collected in a high isoprene emission area of Borneo that had high values at ,m/z equal to 82. They suggested that methylfuran
(C_5H_6O), consistent with $C_5H_6O^+$ being the major ion at ,m/z 82 in isoprene-influenced areas. The peak at 54 was identified as $C_4H_5^+$, the most abundant electron ionization product of methylfuran. Lin et al (2012) subsequently showed that this assignment was reasonable. This approach has been applied in a number of studies as summarized in Table 1 of Hu et al. (2015). Figure 6 shows a PMF-derived mass spectrum attributed to IEPOX-SOA (Hu et al., 2015). Similar intensity patterns are observed in the PMF analyses of AMS data and are assigned to be an IEPOX-SOA factor (Robinson et al., 2011; Lin et al., 2012; Budisulistiorini et al., 2013; Nguyen et al., 2014).

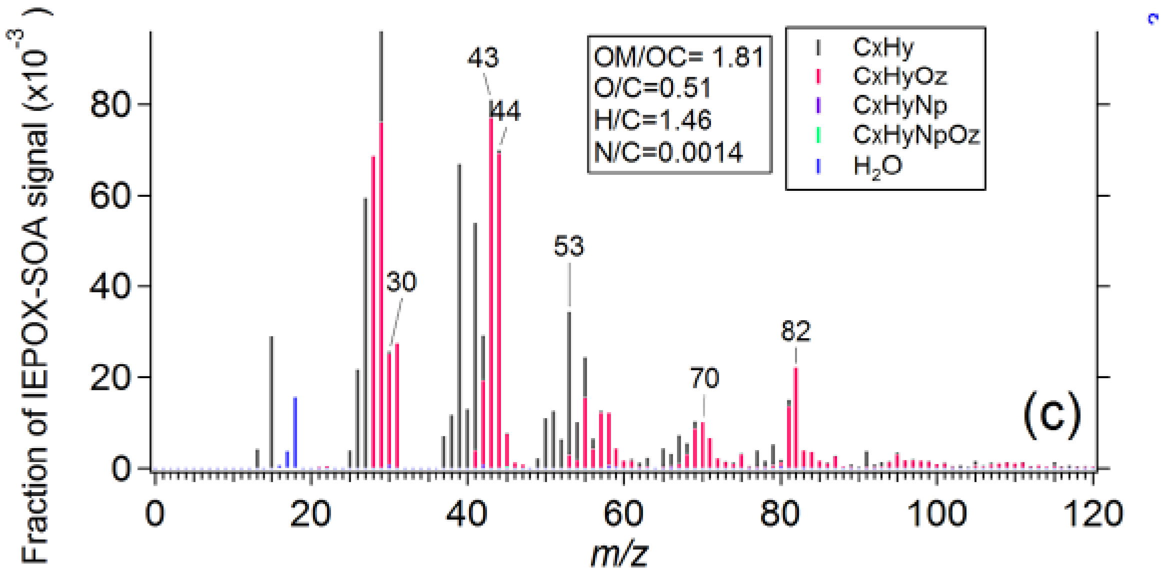

Figure 6. Mass spectrum of IEPOX-SOA taken from Figure 2 of Hu et al. (2015)

Although m/z 82 was identified as the primary marker ion, there is evidence that it can be strongly influenced by monoterpene emissions (Hu et al., 2015). Thus, Hu et al. (2015) present an approach for real-time estimation of IEPOX-SOA by subtracting estimates of background concentrations from urban, biomass burning, and monoterpene emissions.

The state of the art in AMS was reviewed in an interview with Dr. Nga Lee (Sally) Ng of the Georgia Institute of Technology who did the critical initial work on identifying isoprene SOA tracer, m/z peaks in AMS spectra. At this time, the only SOA tracer is a PMF factor that highlights m/z values at 53 and 82 that are assigned as IEPOX-SOA. It can be seen if Figure 6 that there are several other ions including 53 and 80 (not marked) that appear in the spectrum. There is some indication from chamber studies that m/z 67 and 91could indicate α-pinene-derived SOA. However, such a factor has not been clearly separated in ambient samples and these mass values have other possible sources. Thus, currently, there does not seem to be any reliable AMS markers for terpene-derived SOA. Similarly, there are not yet identified reliable AMS tracers of anthropogenic SOA.

A new Long Time-of-Flight Aerosol Mass Spectrometer (L-TOF-MS) system has recently been developed by Aerodyne. They are not yet advertising it, but it is being made available to some of their research partners like PSI if funding becomes available. The L-ToF-

AMS improves mass resolution by approximately a factor of 4 relative to the HR-ToF-AMS without sacrificing sensitivity. This increased resolution enables measurement of organonitrate ions and separation of the CO+ ion from gaseous N2+, neither of which were routinely possible with the HR-ToF-AMS. It also extends the m/z range accessible to quantitative ion-resolved analysis and improves the certainty of ion identification at high m/z. These improvements should produce the opportunity to better characterize oligomeric species in the ambient aerosol and potentially provide real-time separation of the SOA types.

Carbon-14 Measurements

The presence of C-14 in a molecule is an indication that the compound was formed from “contemporary” carbon. Fossil-derived carbon has been separated from the atmosphere where C-14 is formed for a sufficiently long time that all of the C-14 has decayed away. Thus, it is possible to separate fossil fuel derived carbon from biogenic carbon. However, it does not allow the separation of primary and secondary carbonaceous particles. For example, biomass burning will produce primary contemporary carbon particles as well as precursors that can form SOA. Thus, C-14 needs to be used in combination with other methods to help separate the origins of the observed particulate carbon concentrations.

Ding et al. (2008) examined the carbonaceous particles observed in the SEARCH network in the southeastern US by combining C-14 and CMB analysis using the molecular markers. The fossil secondary organic carbon (SOCF) was higher at urban sites and exhibited only small seasonal variations. The contemporary secondary organic carbon (SOCC) was higher at the rural site and exhibited obvious seasonal variation at all sites.

Piletic et al. (2013) used C-14 to constrain the PMF analysis of molecular marker data collected in downtown Cleveland, OH and Chippewa Lake, OH. C-14 concentrations were included in the PMF analysis to obtain the modern carbon fraction (f_{mod}) individually for each source. These fractions aided the interpretation of the factors. SOA represented the largest carbon source during summer. A separate tracer based mass fraction analysis (Kleindienst et al., 2007) found that biomass burning and other combustion sources were dominant in winter. Elevated EC and fossil carbon concentrations in downtown Cleveland were attributed to traffic and coal combustion emissions.

Baker et al. (2013) also used C-14 to help interpret and constrain the modeling results for CalNext (see next section). There are several other applications of C-14 in China, but it remains a limited tool to apply to the problem of biogenic/anthropogenic SOA source identification and apportionment.

An interesting development that may permit more routine use of C-14 in apportionment studies is described by Agrios et al. (2015). They have coupled pure O_2 thermo-optical methods with 14C accelerator mass spectrometer system. Their initial system couples a Sunset OC/EC analyzer and a MICADAS (MIniradioCArbon DAting System) accelerator mass spectrometer equipped with a gas ion source. The initial implementation facilitates the direct measurement in the low sample size range (<10 lg C) with high throughput on a routine basis. They are working on a continuous monitoring system (Salazar et al., 2016). The initial applications of this system have been to the sources of carbonaceous aerosol in China (Liu et al., 2016; Zhang et al., 2016) and in Preila, Lithuania (Ulevicius et al., 2016). This approach appears promising, but requires more testing and verification.

Apportionments Based on Models

Chemical transport models such as the Community Model for Air Quality (CMAQ) (https://www.epa.gov/air-research/community-multi-scale-air-quality-cmaq-modeling-system-air-quality-management) or the Comprehensive Air quality Model with extensions (CAMx) (http://www.camx.com/download/default.aspx) are Eulerian grid models that permit regional modeling of air quality over a wide variety of spatial scales. They require meteorological data, information of source emissions from both anthropogenic and biogenic sources, and chemical mechanisms. They have been evolving for more than 20 years and now provide reasonable accuracy for particulate sulfate, but continue to have difficulties accurately predicting particulate nitrate and organic carbon (Appel et al., 2011; 2016, Koo et al., 2012, Solazzo and Galmarin, 2016).

Although many studies have used these models to provide speciated PM across various domains in the United States, few applications have attempted to separate SOA from anthropogenic and biogenic precursors.

Napelenok et al. (2014) compare CMAQ model results with measurements made at four midwestern United States locations over the period of March 2004 to February 2005. Four precursor-specific classes of secondary organic aerosol (SOA),
isoprene, terpenes, aromatics, and sesquiterpenes, were included in the model. The largest absolute bias of −0.55 μgC/m^3 was attributed to insufficient summertime isoprene SOA. The agreement at the various site varied by season. They suggest there may be compensating errors. It is not clear if the problems are with the emissions inventory, the chemical model, or both.

Data collected in CalNext has also been used to explore CMAQ predictions for the measurement period. Ryerson et al. (2013) described the sampling and analysis program conducted in 2010 at two sites in California, Pasadena and Bakersfield. Baker et al. (2015) report a comparison of the molecular marker receptor modeling and C-14 analysis with the CMAQ results. The CMAQ results for the anthropogenic precursors such as benzene and toluene were within a factor of 2 of the measured concentrations. However, the estimates of the SOC tracer 2,3-dihydroxy-4-oxo-pentanoic acid were consistently underestimated by more than a factor of 2. The biogenic terpenes and their SOC products were also underestimated at both site. However, isoprene was underestimated at Pasadena and overestimated at Bakersfield while the resulting SOC was underestimated at both sites. Baker et al. (2015) suggest that the problem is the parameterization of the yields of SOC that are formed from the oxidation of the precursor species.

Woody et al. (2016) summarizes the application of CMAQ using the volatility basis set to the CalNext data. Even with this state-of-the-art approach, their results were a factor of 1.6 to 2 too low. They suggest the need for more study of "aging" or better treatment of multiple generation chemistry as well as intermediate volatility organic carbon (IVOC) species (Zhao et al. 2016). IVOCs are species with effective saturation concentrations between 10^3 and 10^6 μg/m^3, roughly the same range as C12 ~ C22 n-alkanes (Zhao et al., 2014).

Additional currently unpublished work on the CalNext data was performed by Allen Robinson and colleagues. They used CMAQ to include SOA formation from unspeciated IVOCs (Zhao et al., 2016). They find that mobile sources contributed about 30-40% of the OA in southern California, half of which is SOA. Thus, they see IVOCs as the explanation for a substantial amount of the organic carbon and helps to reduce the underestimation of OC in the CMAQ model results. The remainder of the OA can be attributed to non-mobile anthropogenic sources (e.g., cooking, biomass burning) with biogenic sources contributing less than 5% to the total OA. Gasoline sources are predicted to contribute about thirteen times more OA than diesel sources because of the amount of SOA generated from the IVOCs.

Kim et al. (2015) have modeled the southeastern US using the GEOS-Chem chemical transport model. They find that biogenic isoprene and monoterpenes account for 60% of OA, anthropogenic sources for 30%, and open fires for 10%. However, they do not provide a detail comparison of their results with the SOAS results in this area so evaluation of their results relative to actual values determined in the region is not possible.

Ying et al. (2015) used CMAQ modified SAPRC-11 (S11) photochemical Mechanism and found that photochemical oxidation products of isoprene, such as glyoxal and isoprene epoxydiols, can lead to the formation of a significant amount of SOA. They report good agreement with the total OC concentrations, but could not compare their specific biogenic SOA concentrations with resolved amounts to test the details of their apportionment. However, as a result of this study, the same group has suggested improvements to the MEGAN prediction of biogenic isoprene across the United States (Wang et al., 2017).

Because of the limited publications of modeling applications to apportioning biogenic and anthropogenic SOA, several prominent modelers were interviewed to help provide their perspectives on the current ability of these models to perform such apportionments. Dr. Robinson expressed concerns regarding the state of the CTM models, particularly about the emissions inventories. They have been focusing on the IVOC-based mechanisms that he believes are quite important in SOA formation and that their role has not yet been recognized by the atmospheric chemistry (Zhao et al., 2014; 2015, 2016). However, at this time, the IVOCs have not yet been fully separated, identified, and quantified and there are not identified tracers for their byproducts in the anthropogenic SOA. He expressed concern that the results that they presented in the report of their CRC project report have considerable uncertainties because of issues with multigenerational chemistry and the application of chamber-derived kinetics to open atmospheric systems. There is really a need to extend smog chamber experiments to longer durations so that the results will better reflect the multiple generations of reactions that are occurring. There also remain considerable uncertainties regarding heterogeneous reactions both in cloud water and in water layers on existing particles. The model results still do not fully reflect the amounts of modern carbon that are seen in places like Los Angeles and the sources of this extra current carbon are very uncertain. Cooking emissions are often cited as a major source, but they really have not been well quantified and totals properly bounded in the inventories. Although there is a lot of literature on both sides of the issue, he does not think particle acidity plays a large role in SOA formation.

Dr. Armistead (Ted) Russell of the Georgia Institute of Technology commented that off-the-shelf CMAQ does not work well at all for SOA predictions. His group has had to do a lot of work to modify the chemistry module to get reasonable results. They have developed a simplified multiple generation model that seems to improve their total OC estimates, but there is much work yet to be done. There remain serious issues with taking the smog chamber chemistry into the open atmosphere. He noted that there are significant differences between the two biogenic precursor emission estimation models, BEIS and MEGA, and neither appears to accurately predict the precursor VOC concentrations very well. Thus, they do a lot of work integrating field measurements to tweak the emissions to obtain better fits to the carbonaceous particulate matter concentrations. They are currently not doing a lot to keep track of the origins of SOA precursors and is not aware of others who are taking on this challenge. He feels that the high resolution AMS data does help to provide useful inputs to the modeling effort for total SOA and allows then to do nudging in the right direction. However, he is not overly confident that the AMS fragments provide a lot of information on the origins of the SOA since there is so much fragmentation typically occurring with the 70 eV electron impact ionization used to produce the molecular ions.

To obtain further insights into the modeling of isoprene SOA formation, Dr. Havala Pye of US EPA was interviewed on August 31. She has been focusing on isoprene and improving liquid phase chemistry modeling (Karambelas et al., 2014). Her feeling was that they are getting better with modeling SOA in rural areas but urban areas are still “challenging.” She thinks that particle associated acidity is important in SOA formation. Even in rural areas, the emissions inventories are not well defined and she needed to double the isoprene emission rate to be able to adequately model the SOAS experiments. MEGAN generally provides higher estimates than BEIS, but both are currently inaccurate given the ambient concentrations that have been observed. There is a lack of IVOCs in the inventories, particularly there are likely a number of currently unidentified IVOCs that are of importance in SOA formation. Field data are essential to constrain the model inputs (such as doubling the isoprene emission rate). Source apportionment of the VOCs might help provide a basis for improving the emissions inventory. She also mentioned issues with the lab measurements such as the wall losses of the SVOCs resulting in lower actual precursor concentrations that previously assumed.

Conclusions

It is clear that SOA is a major portion of the ambient $PM_{2.5}$ aerosol mass. To effectively assess its importance in health effects and develop efficient control strategies, it is necessary to fully understand its formation from biogenic and anthropogenic precursors. A body of work has been done to develop methods and models to provide such apportionments. However, at this time, significant issues remain with both the measurement/data analysis approaches and the models. The most serious problem is the lack of a deep understanding of the multiple generations of reactions and products. Typical chamber experiments do not provide a sufficient length of time to fully “age” the aerosol to produce the larger oligomeric systems. There is also limited understanding of liquid phase chemistry that represents some of the later reaction generations particularly for isoprene. Thus, it is difficult to identify marker species and develop the quantitative relationships between precursor concentrations, reaction conditions, and time that will permit accurate identification and apportionment of SOA to its precursors.

The chemical transport models similarly suffer from the limited understanding of the multigenerational chemistry as well as problems with the accuracy of the biogenic emissions inventories. It is often necessary to substantially inflate the emissions estimates to get concurrence with field measurements.

Research Needs

Measurements

There will be groups obtaining the new L-TOF AMS and it will be important to fully characterize its capabilities to support both laboratory and field studies of SOA formation. Its substantially improved resolution offers separation of species and better opportunities to identify the chemical formulae of species evolved from the collected particles. However, at this point, the capabilities of this instrument are not well known and careful characterization is important to provide the community with a clear idea of its capabilities.

The integrated carbon – C14 system seems very promising and it would be useful to so a series of rigorous tests to compare its results with the other methods described above. It has not really been fully evaluated by other than its inventors so it needs appropriate field testing in the United States. It has generally been used in conjunction with aerosol mass spectrometers and a suite of other methods, but it could and should be included in an integrated assessment program as discussed below.

There needs to be chamber studies of homogeneous and laboratory studies of heterogeneous oxidation of various VOC and IVOC precursors with sufficiently long running time that it is possible to obtain a better gauge of the effect of multiple generation chemistry. To perform such experiments effectively will require the use of large chambers like CLOUD to reduce the effect of wall loses and maximize the residence time of the reactants. These studies would permit the identification of marker species for the lower volatility products that are only formed over extended time periods as well as providing the necessary inputs to the CTMs to help achieve model results that are more in accordance with measured OC values.

It appears that IVOCs are an important, but weakly studied class of SOA precursors. With our improved chemical characterization methods such as 2-D GC coupled with very high resolution mass spectroscopy, it may be possible to better characterize the currently unresolved compounds that appear to be present in urban atmospheres.

There is also a need to continue to assess the biogenic VOC emission inventories (MEGAN and BEIS) to determine if the problems in the model underprediction of SOA is the result of incorrect emissions estimates, missing multigenerational chemistry, or both.

Modeling

The models appear to continue to underestimate the formation of SOA. In some cases, the agreement is improved by adjusting the emissions, but it is not known if it is the emissions that are underestimated or if the reaction mechanisms incorporated into the models account sufficiently for multiple generation chemistry. The measurement needs outlined above will provide assistance in identifying where the problems exist and how the models and the inputs might be adjusted to provide more accurate predictions.

There is clearly a need to include the IVOCs into these models, particularly in urban areas where gasoline vehicle traffic represents significant emission sources. These compounds have not been given much consideration in SOA formation until very recently and their full influence has not yet really been assessed in multiple locations.

Integrated Assessment

There is a need for several large integrated research projects of the order of SOAS or CalNext. There needs to be such programs conducted in several locations that represent regions that are dominated by either anthropogenic or biogenic VOC, IVOC, and SVOC sources. Such programs are expensive and thus, collaboration among agencies that are interested in both the basic atmospheric processes and in the role of SOA in creating air quality non-attainment or driving human health or environmental impacts. The ability to have better data on ambient concentrations of the precursors will help constrain the emissions models and allow the model developers to assess the quality of their chemistry modules. There has been sufficient development of monitoring tools, improved understanding of the chemical processes, and the opportunity to put these inputs into improved models that the investment in several of these studies will pay off with significant improvements in our ability to assess the roles of biogenic and anthropogenic sources of SOA precursors.

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