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Evidence of 1991–2013 decrease of biogenic secondary organic aerosol in response to SO2 emission controls

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Abstract
Air quality policy to decrease fine particulate matter mass concentrations (PM2.5) in the US has mainly targeted sulfate aerosol through controls on sulfur dioxide (SO2) emissions. Organic aerosol (OA) instead of sulfate is now the dominant component of total PM2.5. Long-term surface observations (1991–2013) in the Southeast US in summer show parallel decreases in sulfate (2.8%–4.0% a\(^{-1}\)) and OA (1.6%–1.9% a\(^{-1}\)). Decline of anthropogenic OA emissions is uncertain but is unlikely to fully explain this trend because most OA in the Southeast US in summer is biogenic. We conducted a 1991–2013 simulation with the GEOS-Chem chemical transport model including inventory decreases in anthropogenic SO2, NO\(_x\) and volatile organic compounds (VOCs) emissions, constant anthropogenic primary OA emissions, and a new mechanism of aqueous-phase SOA formation from isoprene. This simulation reproduces the observed long-term decreases of sulfate and OA, and attributes the OA decrease to decline in the OA yield from biogenic isoprene as sulfate decreases (driving lower aqueous aerosol volume and acidity). Interannual OA variability in the model (mainly driven by isoprene) is also well correlated with observations. This result provides support for a large air quality co-benefit of SO2 emission controls in decreasing biogenic OA as well as sulfate.

1. Introduction
Air quality policy in the US to decrease mass concentrations of fine particulate matter (PM\(_{2.5}\)) in the US has focused primarily on sulfur dioxide (SO\(_2\)) emission controls. Anthropogenic SO\(_2\) emissions decreased by 3.3% a\(^{-1}\) over the 1991–2013 period according to the US Environmental Protection Agency (EPA 2015). This has successfully decreased the sulfate component of PM\(_{2.5}\) by 2.7% a\(^{-1}\) nationwide over 1992–2010 (Hand et al 2012). Organic aerosol (OA) is now the dominant component of PM\(_{2.5}\) in the eastern US in summer and particularly in the south (Attwood et al 2014, Kim et al 2015), but there is no clear emission control strategy to target that component. OA has a primary combustion source (POA) but appears to be predominantly secondary (SOA) in summer, formed when oxidation products of mostly biogenic volatile organic compounds (VOCs) condense to pre-existing aerosol (Weber et al 2007, Kleindienst et al 2010, Blanchard et al 2016). Recent field studies and models for the Southeast US in summer have pointed to isoprene, the dominant biogenic VOC emitted by vegetation, as a major contributor to OA (Kim et al 2015, Xu et al 2015).

Long-term observations of speciated PM\(_{2.5}\) at Southeast US sites show a decrease in summertime OA of 0.9% a\(^{-1}\) over 1992–2013 and 1.5% a\(^{-1}\) over 1998–2013 (Attwood et al 2014). The contribution to this decrease in anthropogenic OA sources is unclear but unlikely to fully explain the observed OA trend. Source apportionment studies and carbon isotope measurements indicate that anthropogenic sources
account for only 5%–10% of OA concentrations in the Southeast US in summer in Atlanta, Georgia (Zheng et al 2007) and at a regionally representative rural site (Blanchard et al 2008). A regional model analysis finds that anthropogenic sources contribute 28% of OA in the Southeast US in summer (Kim et al 2015). Anthropogenic VOC emissions decreased by 1.6% a$^{-1}$ over the 1991–2013 period (EPA 2015) but the link to SOA is uncertain (Attwood et al 2014). The EPA reports trends in annual primary PM$_{2.5}$ emissions but not the POA component (Blanchard et al 2013, EPA 2015). Blanchard et al (2016) estimate large decreases in annual mean combustion-derived OA (3.2%–4.2% a$^{-1}$) at urban sites in the Southeast US and attribute most of this trend to decline in vehicle emissions. On the other hand, in the rural Southeast US principal component analysis and multiple linear regression applied to long-term (1999–2013) observations show no significant trend in the anthropogenic OA component (Hidy et al 2014, Blanchard et al 2016).

Observations of OA in the Southeast US indicate a $\sim$30% contribution from isoprene epoxydiols (IEPOX SOA) that correlates strongly with sulfate (Budisulistiorini et al 2015, Hu et al 2015, Xu et al 2015). This correlation appears to reflect acid-catalyzed aqueous-phase IEPOX SOA formation (Marais et al 2016). Biogenic SOA produced from glyoxal by aqueous-phase aerosol pathways (Ervens and Volkamer 2010, McNeill et al 2012) would also depend on the availability of sulfate as a source of aerosol water (Nguyen et al 2015). One might therefore expect a decrease in biogenic SOA as SO$_2$ emissions decrease, and this has been suggested as a major co-benefit of SO$_2$ emission controls (Surratt et al 2010, Carlton and Turpin 2013, Pye et al 2013, Xu et al 2015, Marais et al 2016, Xu et al 2016).

Anthropogenic emissions of reactive nitrogen oxides (NO$_x$ ≡ NO + NO$_2$) have also decreased over the past decade to improve ozone air quality. Nitrate is a negligibly small component of PM$_{2.5}$ in the Southeast in summer because of high temperatures (Kim et al 2015). A potentially larger effect is that the SOA yield from VOC oxidation depends on whether this oxidation proceeds by high-NO$_x$ or low-NO$_x$ pathways (Pye et al 2010).

Here we conduct a 1991–2013 simulation of aerosol chemistry with the GEOS-Chem chemical transport model (CTM), including long-term trends in anthropogenic SO$_2$, NO$_x$, and VOC emissions as well as meteorological variability. We show that the observed OA trend in the Southeast US in summer can be explained at least in part by a decrease in isoprene SOA driven by decreasing SO$_2$ emissions. This result has major implications for air quality management as evidence of the co-benefit of SO$_2$ emission controls for decreasing PM$_{2.5}$.


Figure 1 shows time series of summertime average concentrations of sulfate and OA from the Southeastern Aerosol Research and Characterization (SEARCH) (1998–2013) (Edgerton et al 2005) and Interagency Monitoring of Protected Visual Environments (IMPROVE) (1991–2013) (Solomon et al 2014) networks in the Southeast US. There are also observations at Chemical Speciation Network (CSN) sites, but a shift in carbonaceous aerosol sampling and analysis protocols in 2007–2009 (Solomon et al 2014) obfuscates trend analysis. SEARCH sites are a mix of rural, urban, and suburban (Edgerton et al 2005); IMPROVE sites are mainly rural (Solomon et al 2014). Samples at both networks are collected every 3 days (Chow et al 2010). Measurements are reported as mass concentration of organic carbon (OC), and are converted here to OA using a mass conversion factor of 2.2 (OA/OC = 2.2) representative of summertime conditions in the Southeast US (Canagaratna et al 2015, Xu et al 2015). OA averages 30% lower at IMPROVE than SEARCH sites due to differences in measurement protocols (Chow et al 2010, Kim et al 2015) and greater urban influence at SEARCH sites (Blanchard et al 2016).

Mean decline in sulfate is 4.0% a$^{-1}$ at SEARCH and 2.8% a$^{-1}$ at IMPROVE sites, as compared to a national trend of 2.7% a$^{-1}$ (Hand et al 2012). Mean decline in OA is 1.9% a$^{-1}$ at SEARCH and 1.6% a$^{-1}$ at IMPROVE sites. Figure 1 further illustrates how OA instead of sulfate is now the dominant component of total PM$_{2.5}$ in the Southeast US in summer. The relationship between the trend in summertime sulfate and OA is 0.48 µg OA per µg sulfate at SEARCH and 0.37 µg OA per µg sulfate at IMPROVE, similar to interannual relationships previously reported by Blanchard et al (2016).

Figure 1 focuses on summertime when biogenic OA dominates. We find that wintertime (December–February) OA shows a decreasing trend similar to summer, 2.9% a$^{-1}$ at SEARCH and 1.6% a$^{-1}$ at IMPROVE. Wintertime OA mostly originates from biomass burning (residential heating and prescribed burns) and vehicles. Zheng et al (2007) use a chemical mass balance receptor model to estimate that the vehicle contribution to OA in Atlanta is 0.39 µg m$^{-3}$ (11% of OA) in summer but 1.46 µg m$^{-3}$ (30% of OA) in winter, in part because vehicles emit more OA in winter than summer (Zheng et al 2002, Zheng et al 2007, Chen et al 2012). Residential heating and prescribed burns are absent in summer (Tian et al 2009). Apart from extreme events such as the fall 2016 fires (Samuel 2016), wildfires and agricultural fires make little contribution to OA (< 20% of total OA) in the Southeast (Park et al 2007, Tian et al 2009, Kim et al 2015). We do not attempt to explain the wintertime OA trend here, but the causes would have to be different than in summer and we view the
similarity of trends as mostly coincidental. Combining the 3.2%–4.2% a\(^{-1}\) decrease in combustion-derived OC inferred by Blanchard et al (2016) with a 5%–10% contribution of this source to summertime OA in the Southeast (Zheng et al 2007, Blanchard et al 2008) would imply an overall OA trend of only 0.16%–0.42% a\(^{-1}\), much less than observed in figure 1.


We compare the observed 1991–2013 trends of figure 1 to a GEOS-Chem simulation for the same period including interannual meteorological variability and driven by EPA trends in anthropogenic emissions of SO\(_2\), NO\(_x\), and VOCs (EPA 2015). We assume no trend in anthropogenic POA emissions because of large uncertainty, as discussed in the Introduction, and to focus on the impact of the biogenic OA component. Anthropogenic SOA in the model is solely from aromatic VOCs and the associated long-term trends are very small as reported below. Model results are obtained for successive summers (June–August 1991–2013) following one month of spinup each year for chemical initialization. GEOS-Chem is driven with meteorology from the NASA MERRA consistent reanalysis product covering 1991–2013.
The MERRA data are produced at 0.5° x 0.667° horizontal resolution and are re-gridded here to 2° x 2.5° for input to GEOS-Chem.

Annual US anthropogenic emissions of SO2, NOx, and VOCs are from EPA (2015) and are distributed spatially and temporally using the EPA National Emission Inventory for 2005 (EPA/NEI2005, https://epa.gov/pub/EmisInventory/nei_criteria_summaries/2005summaryfiles/). Anthropogenic emissions decreased over 1991–2013 by 3.3% a⁻¹ for SO2, 2.1% a⁻¹ for NOx, and 1.6% a⁻¹ for VOCs. Anthropogenic emissions of ammonia are from NEI2005 and are constant over the period (Hidy et al 2014, Silvern et al. 2016). POA emissions are from Bond et al (2007) for fossil fuel and biofuel combustion and from the annual Global Fire Emissions Database (GFED3) (van der Werf et al 2010) for open fires. Fuel POA emissions are assumed constant over the 1991–2013 period, as explained above, while open fire emissions vary from year to year on the basis of satellite data.

Isoprene, monoterpene, and sesquiterpene emissions are from the Model of Emissions of Gases and Aerosols from Nature (MEGAN2.1) (Guenther et al 2012); they vary locally as a function of leaf area index (LAI), temperature, and (for isoprene) solar insolation. LAI values are monthly means from the MODIS satellite instruments for 2000–2008 (Yang et al 2006), and the 2000–2008 mean is applied for the remainder of the 1991–2013 period. There is no significant regional trend in LAI over 2000–2008 and IAV is less than 4%. We assume no trend in vegetation type over 1991–2013. Intannual variability (IAV) in isoprene emission in the Southeast US is driven predominantly by temperature (Abbot et al 2003, Palmer et al 2006). We find that isoprene emission IAV over 1991–2013 of 12% can be explained by temperature (R² = 0.81 using GEOS-Chem isoprene emissions and MERRA temperature).

The GEOS-Chem simulation includes detailed aerosol-oxidant chemistry as described by Marais et al (2016) for their summer 2013 simulation over the Southeast US. SOA formation from anthropogenic and biomass burning VOCs, monoterpenes, and sesquiterpenes is by reversible partitioning of VOC oxidation products to pre-existing OA (Pye et al 2010). Isoprene SOA formation is by reactive uptake of isoprene oxidation products to aqueous aerosol and is coupled to a detailed gas-phase chemical mechanism for isoprene oxidation. The rate of reactive uptake depends on aqueous aerosol volume, and also for the IEPOX pathway on aerosol acidity (Eddingsaas et al 2010). GEOS-Chem isoprene SOA mass yields (3.3%) and composition, dominated by IEPOX (58% of isoprene SOA mass) and glyoxal (28%) as immediate precursors, are consistent with surface and aircraft observations for the summer 2013 (Marais et al. 2016).

Isoprene SOA formation depends strongly on sulfate but is relatively insensitive to NOx. Partitioning of isoprene oxidation between high-NOx and low-NOx pathways is only moderately dependent on anthropogenic NOx emissions (Pye et al 2013, Zheng et al 2015). NOx contributes to particle-phase organonitrone formation from oxidation of isoprene and monoterpenes by the nitrate radical (Boyd et al 2015, Xu et al 2015), but in the Southeast US organonitrites account for only 3%–8% of observed OA (Lee et al 2016), while IEPOX SOA accounts for 28%–32% of OA (Budisulistiorini et al 2013, Budisulistiorini et al 2015, Hu et al 2015).

We find in our model that isoprene SOA contributes on average 59% of total OA over the Southeast US in summer 1991–1995. Biogenic SOA from terpenes contributes an additional 13%, so that 72% of total OA is biogenic. The remaining 28% are contributed by anthropogenic and biomass burning (open fires and biofuel use) sources as POA (together 21%) and SOA (together 7%). By 2009–2013 biogenic SOA has declined to 62% of total OA (40% isoprene SOA; 22% terpene SOA) and the remainder is anthropogenic and biomass burning sources as POA (together 25%) and SOA (together 13%). This is consistent with the previous GEOS-Chem study by Kim et al (2015), which attributed OA over the Southeast US in summer 2013 as 42% from isoprene, 20% from terpenes, 28% anthropogenic, and 10% from open fires. Our results suggest that the biogenic contribution was greater in the past.

Aqueous volume used to compute the reactive uptake of isoprene SOA precursors (mostly IEPOX and glyoxal) is determined in GEOS-Chem from the mass concentrations of different aerosol components with relative humidity (RH) dependent hygroscopic growth factors from the Global Aerosol Data Set (GADS) (Koepke et al 1997). Sulfate growth factors are applied to sulfate-nitrate-ammonium (SNA) aerosol and OC growth factors are applied to OC. Most aerosol growth is associated with SNA aerosol because of its greater hygroscopicity. Aerosol acidity for IEPOX SOA formation is computed with the ISORROPIA thermodynamic equilibrium model (Fountoukis and Nenes 2007). Hygroscopic growth factors for sulfate from GADS and ISORROPIA agree within 10%.

1991–2013 model trends for the Southeast US in summer are shown in figure 1. The long-term declines over 1991–2013 are 2.4% a⁻¹ for sulfate and 1.4% a⁻¹ for OA, roughly consistent with observed trends from SEARCH and IMPROVE. The majority of the model trend in OA is driven by isoprene SOA, which declines by 2.2% a⁻¹ as also shown in figure 1. The IEPOX SOA component similarly declines by 2.2% a⁻¹. In GEOS-Chem 1 μg decline in sulfate leads to a 0.35 μg decline in IEPOX SOA. This can be compared to the observed relationships between IEPOX SOA and sulfate of 0.42 μg μg⁻¹ at the Centreville, AL site (Xu et al 2015) and 0.23 μg μg⁻¹ from aircraft observations downwind of a power plant (Xu et al 2016). There is no significant
model trend in OA from open fires, and decline in anthropogenic SOA due to decline in VOC precursor emissions is only 0.7%/C0. SOA from terpenes increases by 1.7%/C0 due to increase in isoprene SOA yields with decline in NOx (Pye et al 2010), partly offsetting the isoprene SOA trend. As also shown in figure 1, the model trend in isoprene SOA is not seen if the aqueous-phase chemistry mechanism is replaced by the commonly used mechanism involving reversible partitioning of semivolatile oxidation products to pre-existing OA (Pye et al 2010).

We find in the model that isoprene SOA mass yields per unit isoprene oxidized decrease from 13% in 1991 to 3.5% in 2013. Decrease in NOx emissions increases the isoprene SOA yield in the model, due to an increase in the formation of IEPOX under low-NOx conditions, but the effect is small compared to that of SO2. The branching ratio of the IEPOX-forming hydroperoxyl radical (HO2) oxidation channel for isoprene peroxy radicals increases from 24% in 1991 to 32% in 2013. An isoprene SOA yield of 13% in 1991 is higher than the range (0.1%–10%) obtained for chamber studies reviewed by Marais et al (2016), but the chamber conditions are generally not representative of the atmosphere. Surratt et al (2010) reported a yield of 28% in an experiment under low-NOx conditions using highly acidic inorganic seed aerosol.

Figure 2 compares the spatial distributions of observed and simulated OA over the Southeast US in summer for 1991–1995 and 2009–2013. The spatial pattern in the observations is consistent with a dominant biogenic source. The model normalized mean bias (NMB) is −9.7% in 1991–1995 and −7.9% in 2009–2013. Mean OA concentrations in the Southeast US decrease from 1991–1995 to 2009–2013 by 25% in the observations and 23% in the model. There is no significant change in spatial pattern, either in the observations or the model, offering supporting evidence that biogenic SOA is driving the trend.

4. Discussion

The decline in isoprene SOA is driven in the model by decreases in aqueous aerosol volume and acidity (figure 3) that are both driven in turn by decreasing SO2 emissions. Aqueous aerosol volume mass concentration decreases by 54% over 1991–2013. Nguyen et al (2015) estimated a 79% decrease in aerosol water over 2001–2012 by applying ISORROPIA to the SEARCH observations. Decline in aerosol mass concentrations in GEOS-Chem for the same time period is 40%. SEARCH sites show steeper decline in sulfate than the domain sampled by the
model and the IMPROVE network (figure 1). Aerosol acidity decreases by 83%. We conducted a separate GEOS-Chem simulation for summer 2011 using summer 2013 aerosol acidity and find that acidity alone is responsible for half of the long-term trend in isoprene SOA, with the rest due to decline in aerosol water. We further find in additional sensitivity simulations with aerosol [H$^+$] fixed at 0.1, 0.2, 0.5, 0.8, and 1.1 mol l$^{-1}$ that the relationship between isoprene SOA and aerosol acidity is logarithmic, due to limitation of the overall rate by mass accommodation of IPPOX at low pH. Within the above range, a decrease in aerosol pH of 0.1 increases isoprene SOA by $\sim$0.2 $\mu$g m$^{-3}$.

Decline in aerosol acidity over 1991–2013 as shown in figure 3 would be expected from standard thermodynamics as sulfate decreases with constant ammonia. However, observations in the Southeast US in summer show that the ammonium–sulfate aerosol ratio is actually decreasing (Weber et al. 2016). This decrease is inconsistent with simple SNA thermodynamics and might reflect an OA effect on the thermodynamics (Kim et al. 2015, Silvern et al. 2016).

We examined the implications of possible model error in the 1991–2013 trend of aerosol acidity. Assuming constant acidity in the model would decrease the isoprene SOA trend by half, as pointed out above, and would underestimate the observed trend in OA. This deficit could be compensated by a decrease in anthropogenic POA or by a dependence of monoterpene and sesquiterpene SOA formation on aqueous aerosol volume, not included in our simulation. The laboratory study of Aljawhary et al. (2016) suggests that aqueous-phase processing may be an important SOA formation pathway for monoterpenes. Glyoxal is an oxidation product of monoterpenes (Fu et al. 2008, Chan Miller et al. 2016) and would also contribute to dependence of monoterpene SOA on aqueous aerosol volume. Assuming that the terpene SOA yield increases linearly with aqueous aerosol volume (as for isoprene SOA) and the trend in isoprene SOA is due to aqueous aerosol volume only, we find that the deficit between the observed OA trend and the model could be compensated by an effective terpene SOA yield (mass SOA formed per unit mass of monoterpene/sesquiterpene oxidized) of 13% in 1991 dropping to 5% in 2013. This is within the range of terpene SOA yields measured in chamber studies (Ng et al. 2007, Shilling et al. 2008, Saathoff et al. 2009, Fry et al. 2014), although chamber conditions may differ from the actual atmosphere (Hallquist et al. 2009).

We also examined the interannual variability (IAV) superimposed on the long-term trends (figure 1) to confirm the importance of biogenic SOA to the long-term trend. IAV should be driven mainly by weather, including effects on biogenic VOC emissions. Isoprene SOA IAV in the model accounts for 95% of the IAV in total OA and is correlated with the IAV in isoprene emission ($R = 0.68$). The model OA IAV, obtained as the relative departure from the regression line of long-term trends in figure 1, is correlated with the observed OA IAV at SEARCH ($R = 0.49$) and IMPROVE ($R = 0.55$), but is 60%–80% higher than the observations. The overestimate is due to very high model OA in 1998–2000 and 2005–2007 that is not seen in the observations. These years correspond to drought in the Southeast US (Seager et al. 2009) that may suppress isoprene emission (Pegoraro et al. 2004). This effect is not included in MEGAN as implemented in GEOS-Chem and thus model isoprene emission may be too high. OA IAV is correlated with mean surface air temperature both in the model ($R = 0.71$, using MERRA temperature) and in the observations ($R = 0.44$ at SEARCH sites using collocated temperature data; $R = 0.47$ at IMPROVE sites using temperature from nearby EPA monitoring sites).

In summary, observations of organic aerosol (OA) over the Southeast US in summer show a large 1991–2013 decrease. We find with the GEOS-Chem model that this trend can be largely explained by a decrease in the yield of secondary OA (SOA) from biogenic isoprene as SO$_2$ emissions have decreased. This decline in isoprene SOA yield in GEOS-Chem is based on an aqueous-phase mechanism for isoprene SOA formation that is dependent on aqueous aerosol volume and acidity, both of which decrease as SO$_2$ emissions decrease. Better understanding is needed of the factors controlling aerosol acidity and its trends in the Southeast US, and of the role of trends in anthropogenic emissions of OA and VOC precursors. Nevertheless, this study provides support that SO$_2$ emission controls to decrease sulfate aerosol have had a large co-benefit by concurrently decreasing OA.

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