

Estimates of non-traditional secondary organic aerosols from aircraft SVOC and IVOC emissions using CMAQ

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Abstract

Utilizing an aircraft-specific parameterization based on smog chamber data in the Community Multiscale Air Quality (CMAQ) model with the Volatility Basis Set (VBS), we estimated contributions of non-traditional secondary organic aerosols (NTSOA) for aircraft emissions during landing and takeoff (LTO) activities at the Hartsfield-Jackson Atlanta International Airport. NTSOA, formed from the oxidation of semi-volatile and intermediate volatility organic compounds (S/IVOCs), is a heretofore unaccounted component of fine particulate matter ($PM_{2.5}$) in most air quality models. We expanded a prerelease version of CMAQ with VBS implemented for the Carbon Bond 2005 (CB05) chemical mechanism to use the Statewide Air Pollution Research Center 2007 (SAPRC-07) chemical mechanism, and added species representing aircraft S/IVOCs and corresponding NTSOA oxidation products. Results indicated the maximum monthly average NTSOA contributions occurred at the airport, and ranged from 2.4 ng m^{-3} (34% from idle and 66% from non-idle aircraft activities) in January to 9.1 ng m^{-3} (33 and 67%) in July. This represents 1.7% (of 140 ng m^{-3}) in January and 7.4% in July (of 122 ng m^{-3}) of aircraft-attributable $PM_{2.5}$, compared to 41.0–42.0% from elemental carbon and 42.8–58.0% from inorganic aerosols. As a percentage of $PM_{2.5}$, impacts were higher downwind of the airport, where NTSOA averaged 4.6–17.9% of aircraft-attributable $PM_{2.5}$ and, considering alternative aging schemes, was high as 24.0% – thus indicating the increased contribution of aircraft-attributable SOA, as a component of $PM_{2.5}$. However, NTSOA contributions were generally low compared to smog chamber results, particularly at idle, due to the considerably lower ambient organic aerosol concentrations in CMAQ, vs. those in the smog chamber experiments.

1 Introduction

Aircraft engines emit multiple pollutants during their various modes of activity from landing and takeoff (LTO) as well as from cruise which negatively impact air quality (Moussiopoulos et al., 1997; Brasseur et al., 1998; Tarrasón et al., 2004; Unal et al., 2005; Schürmann

et al., 2007; Yim et al., 2013). For example, emissions from commercial aircraft in the US during the LTO phase have shown to contribute approximately 3.2 ng m^{-3} to annual average US fine particulate matter ($\text{PM}_{2.5}$), or 0.05 % of total $\text{PM}_{2.5}$ (Woody et al., 2011). Aircraft also represent the third largest producer of greenhouse gas emissions (11.6% of the total) within the US transportation sector behind light duty vehicles (58.7%) and freight trucks (19.2%) (U.S. Department of Transportation, 2010) and account for 3.5% of global anthropogenic radiative forcing (Lee et al., 2009). However, uncertainty associated with the treatment of aircraft emissions in air quality models has led to a wide range of estimated aviation-attributable impacts. For example, air quality model estimates of aviation-attributable premature mortalities range from 620 per year (Jacobson et al., 2013) to as high as 12 600 (Barrett et al., 2010) for full-flight global aircraft emissions and from 75 (Levy et al., 2012) to 210 (Brunelle-Yeung et al., 2014) for LTO emissions in the US. Additionally, air quality model estimates of aircraft-attributable $\text{PM}_{2.5}$ range from less than 1 % in winter and statistically insignificant impacts in summer from full flight emissions globally (Lee et al., 2013) to approximately 1.3% of annual average $\text{PM}_{2.5}$ from aircraft LTO activities at the Hartsfield-Jackson Atlanta International Airport (ATL) (Arunachalam et al., 2011) and as high as 9.4% of daily average $\text{PM}_{2.5}$ from LTO activities at ATL (Woody and Arunachalam, 2013). Similar uncertainty exists in organic aerosols from aircraft as well as other emission sources, due to the large number of organic compounds and multiple pathways involved, many of which are not fully understood and some are possibly yet to be discovered (Kroll and Seinfeld, 2008; Miracolo et al., 2011).

Organic aerosols (OA) as a whole represent a significant fraction of the total fine particulate matter ($\text{PM}_{2.5}$) mass in the atmosphere, comprising approximately 20–70% of $\text{PM}_{2.5}$ in the US, Europe, and East Asia (Zhang et al., 2007) and as high as 90% in the tropics (Kanakidou et al., 2005). However, air quality model predictions have shown that aircraft emissions produce little to no secondary organic aerosols (SOA) near airports (and in some instances decrease SOA concentrations) despite the presence of SOA precursors (e.g. xylene, toluene, benzene) (Woody et al., 2011; Arunachalam et al., 2011). Woody and Arunachalam (2013) indicated that these cases of reductions in modeled SOA in the

presence of aircraft emissions are attributable to aircraft NO_x emissions reacting with and thereby lowering radical concentrations near the airport, slowing the oxidation of SOA precursors from other emission sources, and that this effect is a function of grid resolution. This reduction in SOA due to aircraft emissions in air quality models contrasts recent sampling and experimental results from Miracolo et al. (2011). Aircraft emissions from a CFM56-2B engine formed significant amounts of secondary particulate matter (PM) after three hours of photo-oxidation in a smog chamber at typical summertime OH concentrations. SOA production was approximately 1200 mg kg^{-1} fuel at 4 % power and 15 mg kg^{-1} fuel at 85 % power compared to 150 mg kg^{-1} fuel and 70 mg kg^{-1} fuel for secondary sulfate and 35 mg kg^{-1} fuel and 40 mg kg^{-1} fuel for primary PM emissions (Miracolo et al., 2011). These values are based on conventional JP-8 jet fuel, which contain significantly more aromatics (17% by volume) compared to Fischer-Tropsch (FT) synthetic jet fuel (0.7%) and hydrotreated esters and fatty acids biojet fuel (0.3%) (Moore et al., 2015) and produce 20 times more SOA than FT jet fuel or 2 times more than a 50:50 blend of FT and JP-8 jet fuels (Miracolo et al., 2012).

Box model predictions of SOA were unable to reproduce the total SOA formed in the chamber, suggesting that there are possible missing precursors from aircraft emission estimates being used in air quality models. Miracolo et al. (2011) proposed that semi-volatile and intermediate volatile organic compounds (S/IVOC) may be these missing precursors. S/IVOCs are species with volatilities between primary organic aerosols and VOC gas-phase species or C^* values ranging from 10^0 to $10^7 \mu\text{g m}^{-3}$. These species are generally considered to be missing from traditional emission inventories, and measurements have confirmed their existence in aircraft emissions (Miracolo et al., 2011; Cross et al., 2013).

Jathar et al. (2012), building on the work of Miracolo et al. (2011), published yields mapped to the volatility basis set (VBS) (Donahue et al., 2006) for unidentified non-traditional SOA (NTSOA) precursors (S/IVOCs) from a CFM56-2B aircraft engine and a T63 helicopter engine. NTSOA was assumed to be the difference in measured SOA and box model estimates of traditional SOA (TSOA, i.e., SOA formed from traditional SOA precursors such as xylene, toluene, benzene, etc.). Incorporating NTSOA yields into the box

model significantly enhanced SOA predictions and provided better agreement with measurements. Jathar et al. (2012) also provide the inputs necessary to predict NTSOA formed from aircraft emissions in an air quality model using the VBS, which has previously been shown capable of representing particle formation from S/IVOC (Robinson et al., 2007; Presto et al., 2009).

In this work, we use the Community Multiscale Air Quality (CMAQ) model (Byun and Schere, 2006; Foley et al., 2010) with VBS to estimate NTSOA formed from S/IVOCs, representing unidentified SOA precursors previously considered missing in air quality models, from aircraft LTO emissions at ATL. VBS is the preferred model framework for OA here as the binning of species based on volatility (typically representing 4–9 orders of magnitude of volatilities) is better suited to represent the range of volatilities of S/IVOC emissions. Contrast this to the Odum 2-product model (Odum et al., 1996), traditionally used in CMAQ to represent semi-volatile oxidization products of SOA precursors, where SOA precursors (and emissions) are typically represented using more explicit species (e.g. toluene, xylene, benzene). NTSOA predictions were made by incorporating the aircraft-specific NTSOA parameterization developed by Jathar et al. (2012) into CMAQ with VBS and modeling two months, January and July 2002, to capture seasonal variability. The end goal is to provide a more accurate representation of OA and PM formation from aircraft emissions in CMAQ.

2 Methodology

Organic aerosol concentrations were estimated in January and July 2002 over a 12 km eastern US domain (which was selected to simultaneously test VBS in CMAQ (see the Supplement) and predict NTSOA formed from aircraft emissions) using CMAQ v5.0.1 with the VBS framework. VBS in CMAQ, implemented for the Carbon Bond 2005 (CB05) chemical mechanism (Yarwood et al., 2005) by Koo et al. (2014), provides for the treatment of four distinct organic aerosol groups: primary anthropogenic (representing hydrocarbon-like OA), secondary anthropogenic and biogenic (representing oxygenated OA), and primary biogenic (biomass burning). Each organic aerosol group is treated as semi-volatile, includ-

ing primary organics (Robinson et al., 2007), using five volatility bins. The lowest bin is treated as non-volatile particles with the other four bins representing particles with C^* values ranging from 10^0 to $10^3 \mu\text{g m}^{-3}$. Primary organic aerosol (POA) emissions are replaced by SVOCs, which partition between the particle and gas phase. Additionally, gas-phase IVOC emissions are included which, when oxidized, form SVOCs and SOA.

In this study, we expanded the Koo et al. (2014) CMAQ VBS implementation for CB05 for use with the more explicit Statewide Air Pollution Research Center 2007 (SAPRC-07) chemical mechanism (Carter, 2010). In CMAQ, our VBS implementation for SAPRC-07 includes 150 gas phase species (13 representing SOA precursors – 9 anthropogenic (8 contained in aircraft emissions) and 4 biogenic) and 413 reactions compared to 80 gas phase species (6 representing SOA precursors – 3 anthropogenic and 3 biogenic) and 205 reactions in CB05. The SAPRC-07 chemical mechanism was selected due to the more explicit treatment of VOCs and specifically SOA precursors, as we theorized this would provide a better representation of TSOA formed from aircraft emissions. It also maintains consistency with the Jathar et al. (2012) study, which used SAPRC VBS yields for TSOA formed from aircraft emissions.

In our SAPRC-07 implementation of VBS in CMAQ, TSOA precursors with VBS are the same as with the CMAQ aerosol 6 module (AE6) (Carlton et al., 2010). However, we updated their semi-volatile oxidation products to map to VBS products with yields taken from Murphy and Pandis (2009) and Hildebrandt et al. (2009), similar to Koo et al. (2014). The aerosol module remained unchanged from Koo et al. (2014) except for the addition of NTSOA formed from aircraft S/IVOC emissions as described below. Additional details regarding our SAPRC-07 VBS implementation in CMAQ, including comparisons of VBS results against the traditional AE6, can be found in the Supplement.

Specific for aircraft, we introduced aircraft S/IVOC species into CMAQ with a parameterization based on work by Jathar et al. (2012). The new species, in addition to using an aircraft-specific parameterization, allow for aircraft contributions to be tracked separately from other sources. Similar to the VBS representation of anthropogenic TSOA, five volatility bins were used to represent aircraft-specific NTSOA, with the lowest bin representing

non-volatile organics and the other four bins spanning C^* values from 10^0 to $10^3 \mu\text{g m}^{-3}$. Emissions and chemistry of gas-phase IVOCs were included using 4 volatility bins with C^* values ranging from 10^4 to $10^7 \mu\text{g m}^{-3}$. At engine idle, aircraft emit considerably more organic PM and unburned hydrocarbons per unit fuel burned compared to other engine modes due to incomplete combustion (Herndon et al., 2008; Timko et al., 2010; Miracolo et al., 2011; Beyersdorf et al., 2014). For this reason, the production of NTSOA from idle and non-idle activities is tracked separately, with unique model species, precursors, and yields for both sets of activities. The parameterization also includes multi-generational aging reactions of NTSOA, using a rate constant of $1 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ with each oxidation step lowering the volatility of the product by one order of magnitude (Murphy and Pandis, 2009; Farina et al., 2010; Jathar et al., 2011, 2012).

After implementation of the Jathar et al. (2012) aircraft parameterization in CMAQ, CMAQ predictions of NTSOA were evaluated using results from Jathar et al. (2012). Note, that while a number of studies have measured PM from aircraft, those studies either report total PM (Herndon et al., 2005, 2008; Mazaheri et al., 2008), total primary vs. secondary PM (Lobo et al., 2012), or organic carbon in the near field (1-50 m) of the aircraft engine (Agrawal et al., 2008; Kinsey et al., 2010; Timko et al., 2014). Only the Miracolo et al. (2011) study, which the Jathar et al. (2012) NTSOA yields are based on, provide measurements of SOA formed from aircraft emissions (a CFM56-2B aircraft engine and T63 helicopter engine at various power settings) that the authors are aware of. Our evaluation compared NTSOA production (normalized for OH concentrations using OH exposure) for the CFM56-2B aircraft engine in a box model version of CMAQ (transport processes turned off) and the Jathar et al. (2012) box model using an identical NTSOA mechanism and similar inputs. CMAQ predictions of NTSOA from the CFM56-2B engine were lower at all power settings while TSOA results were generally in good agreement, with the exception of the 85 % power setting (Fig. 1). The NTSOA results suggest that the Jathar et al. (2012) yields in CMAQ would underpredict NTSOA from aircraft.

We conducted a series of sensitivity analyses in our CMAQ box model and found that increasing the Jathar et al. (2012) yields by $1.5\times$ provided better agreement of the CFM56-2B

experiments at 4 and 7 % power (Fig. 1), the two power settings with the highest emissions of S/IVOCs. At 30 % power, the Miracolo et al. (2011) OA measurements exceeded the measured S/IVOCs emissions, and to reproduce the Jathar et al. (2012) results, S/IVOC emissions would have to be increased by $15\times$ in addition to the $1.5\times$ increase in yields. However, this increase in emissions is unrealistic, producing more S/IVOC emissions at 30 % power than 7 % power, which measurements do not support (Miracolo et al., 2011; Cross et al., 2013). Note, only one experiment was conducted at 30 % power by Miracolo et al. (2011); therefore there is a higher level of uncertainty associated with results at this power setting compared to others. Given the better agreement at 4 and 7 % power settings, our CMAQ simulations were conducted using the higher ($1.5\times$) yields applied to all four power settings (Table 1).

The SAPRC-07 mechanism in CMAQ includes the formation of anthropogenic TSOA from eight model species contained in aircraft emissions: benzene (BENZ), toluene (TOL), xylene (MXYL, OXYL, PXYL), aromatics (ARO1 and ARO2), and alkanes (ALK5). Note, CMAQ also includes 1,2,4-trimethylbenzene (TRIMETH_BENZ124) as a TSOA precursor but it is not contained in aircraft emissions. In addition to the eight CMAQ model species contained in aircraft emissions, the box model used by Jathar et al. (2012) to develop the NTSOA parameterization included the formation of TSOA from aircraft emissions of model species representing alkenes (OLE1 and OLE2) and alkanes (ALK4). To be consistent with that study and because the Jathar et al. (2012) NTSOA yields were based on the difference in measured SOA and predicted TSOA, we added the formation of TSOA from aircraft emissions of OLE1, OLE2, and ALK4 into CMAQ using yields based on Murphy and Pandis (2009) to provide for a more accurate prediction of total SOA formed from aircraft.

Meteorological inputs were generated using the Pennsylvania State University/NCAR mesoscale (MM5) model (Grell et al., 1994). Non-aviation emissions were generated using the Sparse Matrix Operator Kernel Emissions (SMOKE) model (Houyoux et al., 2000) and estimated using the US EPA's 2002 National Emissions Inventory (NEI) (U.S. Environmental Protection Agency, 2004). Non-aviation S/IVOC emissions were estimated using the high internal estimate option in CMAQ with VBS, where SVOC emissions are 3 times

the traditional POA emissions and IVOC emissions are 4.5 times POA emissions. This option was selected based on our comparisons of our SAPRC-07 implementation of CMAQ with VBS against OC ambient measurements, which indicated better agreement compared to CMAQ with VBS's conservative estimate of S/IVOC emissions (SVOC = traditional POA emissions and IVOC emissions = twice POA emissions). Additional details on CMAQ with VBS's internal S/IVOC emission estimates from non-aviation sources and comparisons of ambient measurements of OC and PM_{2.5} against our SAPRC-07 CMAQ with VBS implementation can be found in the Supplement.

Our investigation focused on aircraft-attributable PM_{2.5} contributions (calculated as difference between CMAQ predictions with and without aircraft emissions) from LTO activities below 1 km at ATL, which is the busiest airport in the world with approximately 2400 flights daily (Federal Aviation Administration, 2013). Aircraft emissions estimates for NO_x, SO₂, CO, total organic gases (TOG), and primary PM (sulfate, organic aerosols, and elemental carbon) at ATL were based on the Aircraft Environmental Design Tool (AEDT) global aircraft emission inventory for 2006 (Wilkerson et al., 2010). The inventory provides high resolution emissions data both in space and time for individual flights globally. Gas-phase emissions in AEDT were based on International Civil Aviation Organization (ICAO) reported mode-specific emission factors (EFs) while primary PM emissions were based on the First Order Approximation v3 (FOA3) (Wayson et al., 2009). Primary organic emissions were treated as non-volatile, consistent with the assumption used by FOA3. Also, this prevents any possible double counting of NTSOA, as VBS in CMAQ converts a portion of volatile POA (SVOCs) to SOA. However, measurements collected by Presto et al. (2011) indicate the majority of aircraft POA emissions are semi-volatile. Furthermore, comparisons against measurements have shown FOA3 estimates of POA and elemental carbon (EC) vary by an order of magnitude for 40% of aircraft engines (Stettler et al., 2011), suggesting alternative estimates of aircraft PM emissions, which include a semi-volatile treatment of aircraft POA emissions, should be considered in future studies.

CMAQ-ready emission files for aircraft sources were generated using the AEDTproc tool (Baek et al., 2012), which allocates aircraft emissions in four dimensions (column, row,

layer, and time) using aircraft trajectories taken from the AEDT database, and performs appropriate conversions of inventory pollutants into model species. These aircraft emissions were then merged with the non-aviation emissions files from the NEI to create the final files used in the CMAQ simulations. TOG was speciated into SAPRC-07 model species using the most recent EPA speciation profile (SPECIATE profile 5565B, Table 2) which is based on results of a joint Federal Aviation Administration (FAA) and EPA effort (U.S. Environmental Protection Agency, 2009a, b). Aircraft S/IVOC emissions were estimated using the mode-specific EFs for a CFM56-2B engine reported by Jathar et al. (2012) and normalized by ICAO hydrocarbon (HC) EFs calculated as

$$EF_{S/IVOC,engine\ i} = \frac{EF_{S/IVOC,CFM56-2B} \times EF_{HC,engine\ i}}{EF_{HC,CFM56-2B}} \quad (1)$$

Table 3 provides monthly total aircraft emissions estimates of S/IVOCs during the modeling period. These emissions, when oxidized, form NTSOA, and modeled NTSOA is discussed in Sect. 3.1. IVOC emissions are similar in magnitude to aircraft emissions of long-chain alkanes (ALK5) (Table 4). Also note, the majority of idle S/IVOC emissions are primarily at higher volatilities (C^* values of 10^6 – 10^7 $\mu\text{g m}^{-3}$) while non-idle emissions are at slightly lower volatilities (10^3 – 10^4 $\mu\text{g m}^{-3}$). Therefore, while the total S/IVOC mass from idle emissions is higher than for non-idle emissions, additional oxidation steps are required to lower the volatility enough for significant partitioning to the particle phase.

Table 4 provides similar aircraft emissions estimates for TOG and TSOA precursors in CMAQ (ALK4, ALK5, ARO1, ARO2, BENZ, OLE1, OLE2, TOL, and XYL). The non-idle SOA precursor emissions in Table 4 represent those traditionally considered when assessing aircraft contributions to TSOA. The TSOA idle emissions are those estimated using the Fuel Flow Method2 as described below and are not included in AEDT by default. They represent approximately a 50 % increase in TOG and TSOA precursor emissions from aircraft. Results of TSOA formed from the precursors in Table 4 are presented in Sect. 3.2. Finally, Table 5 provides aircraft emissions estimates of primary PM species (sulfate, organic aerosols, and elemental carbon) and inorganic PM precursors (NO_x and SO_2) for the modeling period.

One limitation to our approach for estimating S/IVOC aircraft emissions is that the ICAO database assumes a 7% power setting for idle activities while most modern aircraft engines generally idle below this setting (Herndon et al., 2009). Here a value of 4% was assumed for aircraft idle. To estimate S/IVOC idle emissions at 4% power, the Boeing Fuel Flow Method2 (FF2) (DuBois and Paynter, 2007) was used to extrapolate idle hydrocarbon EFs for each flight at Atlanta during the modeling episode. The FF2 method assumes a bilinear fit of ICAO-reported hydrocarbon EFs (one linear fit for 85 to 30% power settings and a separate linear fit for 4 to 30% power settings) and a linear fit of ICAO-reported fuel flows. For each flight, time-in-mode for idle activities was calculated as the difference between total time spent in taxi/idle modes (reported as one value in AEDT) and the average unimpeded taxi time at the Atlanta airport reported by the FAA's Aviation Performance Metrics (Federal Aviation Administration, 2013). Hydrocarbon (and S/IVOC) emissions from idle activities were then estimated by flight as the product of idle time, fuel flow, and S/IVOC EF. Using this methodology, we estimated that, due to long idle times and despite low fuel flows at idle, approximately 23–33% of LTO fuel burn occurs during aircraft idling. For comparison, taxi accounted for 31–36% of fuel burn, approach 22–26%, and takeoff 12–15%. It should be noted that applying a normalized EF for SVOC and IVOC emissions from all aircraft based on a single engine type introduces some uncertainty as the CFM56-2B engine is primarily used for military aircraft and represents older technology with higher emissions than newer, more efficient engines. That said, the CFM56 engine family (which includes ~80 different types) was used on approximately 20% of commercial U.S. flights in 2006 and normalizing SVOC and IVOC emission factors based on ICAO reported hydrocarbon emission factors is meant to, at least partially, account for differences in engine type and technology. Without the normalization, we would expect the SVOC and IVOC emission estimates to be biased high and future work is needed to test if a bias, either high or low, remains after normalization. At this time, limited data currently exist on SVOC and IVOC emissions from other engines and therefore we consider this an acceptable means to approximate emissions for this work.

3 Results and discussion

3.1 CMAQ predictions of NTSOA from aircraft

Monthly average $\text{PM}_{2.5}$ contributions from aircraft operations in the grid cell containing the airport (the grid cell with the highest absolute aircraft contribution in the domain) ranged from 140 ng m^{-3} in January (daily averages ranging from 32 to 311 ng m^{-3}) to 122 ng m^{-3} in July (daily averages of 58 – 312 ng m^{-3}) (Figs. 2 and 3). This is lower than aircraft impacts at ATL reported by Arunachalam et al. (2011) (annual average impacts of approximately 200 ng m^{-3}), which used a different (higher) emission inventory that was based upon the Emissions Dispersion Modeling System (EDMS) (Federal Register, 1998). Similar to previous 12 km CMAQ modeling studies at ATL (Arunachalam et al., 2011; Woody and Arunachalam, 2013), aircraft emissions reduced biogenic TSOA concentrations in July, which is further discussed in Sect. 3.2. Newly added NTSOA formed from aircraft S/IVOC emissions accounted for 2.4 ng m^{-3} in January (1.7% of total $\text{PM}_{2.5}$ from aircraft; daily averages of 0.2 – 9 ng m^{-3}) and 9.1 ng m^{-3} in July (7.4%, daily averages of 1 – 38 ng m^{-3}), which is approximately 4–6 times higher than TSOA formed from idle and non-idle aircraft TSOA precursor emissions (Sect. 3.2). Idle activities accounted for 34% in January and 33% in July of the total NTSOA formed. Additional photochemistry in July compared to January produced higher average OH concentrations at ATL ($2.4 \times 10^6 \text{ molecules cm}^{-3}$ compared to $2.4 \times 10^5 \text{ molecules cm}^{-3}$). This allowed for more aircraft S/IVOCs to be oxidized in July and, despite similar non-idle emissions in January and July (Table 3), produce approximately four times more NTSOA from non-idle activities. Furthermore, while idle emissions were approximately 50% higher in July due to longer idle times, the ratio of idle to non-idle NTSOA was similar in July and January.

Impacts on $\text{PM}_{2.5}$ in January and July were highest near the airport, although impacts as high as 10 ng m^{-3} extended up to 100 km away from the airport in July (Fig. 4a and b). NTSOA contributions were generally confined to grid cells surrounding the airport, similar to primary PM species, though impacts of 1 ng m^{-3} or higher were located 50 km away from the airport (Fig. 4c and d). Given uncertainty in model inputs and outputs, values

at these low concentrations are not meant to represent absolute concentrations, but are, however, indicative of the general magnitude of incremental contributions of aviation at the modeled scales and provide context adequate to make informed inferences about aviation-attributable PM_{2.5}.

The percentage of aircraft-attributable PM_{2.5} comprised of NTSOA increased moving away from the airport as aircraft S/IVOC were oxidized (Figs. 4e, f and 5). At distances 6–30 km away from the airport, NTSOA averaged 4.6 % in January and 11.8 % in July of aircraft-attributable PM_{2.5}; 14.0 % in January and 7.7 % in July at distances 31–54 km away from the airport; and 17.9 % in January and 4.0 % in July at distances 55–102 km away from the airport. Note that while percentages were higher in January, PM_{2.5} (and NTSOA) concentrations dropped off more rapidly moving away from the airport in January as absolute aircraft-attributable PM_{2.5} concentrations were approximately 15 (6–30 km), 94 (31–54 km), and 196 (55–102 km) times lower than the grid cell containing ATL in January and 8, 13, and 16 times lower in July. NTSOA was important away from the airport, but aircraft-attributable PM_{2.5} was dominated by inorganic species (secondary ammonium, nitrate, and sulfate) formed from aircraft emissions of NO_x and SO₂ (Fig. 5), similar to previous modeling studies in CMAQ (Arunachalam et al., 2011; Woody et al., 2011; Rissman et al., 2013).

Absolute NTSOA contributions were generally low compared to elemental carbon and inorganic aerosols, which contributed 59 ng m⁻³ (38.9 % of PM_{2.5}) and 63 ng m⁻³ (41.6 %) in January and 50 ng m⁻³ (41.1 %) and 70 ng m⁻³ (57.9 %) in July in the grid cell containing ATL, respectively. This is somewhat contradictory to the smog chamber results of Miracolo et al. (2011, 2012), where reported aircraft SOA production were comparable to secondary sulfate and higher than primary PM except at the highest power setting. OA concentrations and the volume into which aircraft emissions mix can significantly influence aircraft-attributable SOA (Woody and Arunachalam, 2013). OA concentrations serve a key role in gas-particle partitioning, with higher values promoting partitioning to the particle phase. In the smaller volume of the smog chamber, where aircraft emissions were concentrated, total OA concentrations (POA + SOA + NTSOA) ranged between 6 μg m⁻³ at 85 % power to 250 μg m⁻³ at 4 % power (Jathar et al., 2012). Contrast this with the larger volume of the

grid cell (12 km × 12 km × 38 m) containing ATL, where average OA concentrations ranged from 3–4 $\mu\text{g m}^{-3}$ and were largely determined by emissions from sources other than aircraft. The differences in partitioning due to OA were highest at idle, where smog chamber OA concentrations were highest, emissions of IVOCs were highest (highest potential for NTSOA formation), and NTSOA products were of relatively higher volatilities (C^* values of 10^2 to 10^4).

To test the impact of OA concentrations on NTSOA concentrations, we conducted a sensitivity analysis again using our CMAQ box model. Two test cases were simulated, one using typical ambient OA concentrations (5 $\mu\text{g m}^{-3}$) and the other using mode-specific OA concentrations measured in the smog chamber (6–250 $\mu\text{g m}^{-3}$) during the Miracolo et al. (2011) experiments. Results indicated that when ambient OA concentrations were used, NTSOA and SOA production at the 4% power setting were approximately a factor of six lower compared to the same simulation using smog chamber OA concentrations. This also provides one indication of why the majority of NTSOA contributions were from non-idle aircraft activities, despite the higher potential from idle emissions. NTSOA model results at a finer scale, such as plume scales where aircraft emissions would be more concentrated (Rissman et al., 2013), would likely be higher, particularly for idle emissions.

3.2 CMAQ predictions of TSOA from aircraft

Aircraft contributions to TSOA in the grid containing the airport were generally lower than NTSOA contributions. Aircraft increased anthropogenic TSOA in January by 1.3 ng m^{-3} (0.9% of $\text{PM}_{2.5}$; daily average ranging from -9 to 3 ng m^{-3}) and lowered it by 1.7 ng m^{-3} (-1.4% ; daily averages ranging from -136 to 1 ng m^{-3}) in July (Fig. 3). TSOA formed directly from aircraft emissions of SOA precursors contributed 0.1 ng m^{-3} (0.1%) in January and 0.7 ng m^{-3} (0.6%) in July with the remainder (1.2 ng m^{-3} and -2.4 ng m^{-3}) attributable to the interaction of aircraft emissions and TSOA precursors emitted from other anthropogenic sources. With the inclusion of idle emissions listed in Table 4, TSOA formed directly from aircraft TSOA precursors increased to 0.4 ng m^{-3} (0.4%) in January and 2.4 ng m^{-3} (2.0%) in July. Finally, the interaction of aircraft emissions with biogenic TSOA precursors

lowered biogenic TSOA by 0.1 ng m^{-3} (-0.1%) in January and 23.6 ng m^{-3} (-19.4%) in July (Fig. 2).

The reduction in TSOA near the airport is similar to previous studies (Arunachalam et al., 2011; Woody et al., 2011; Woody and Arunachalam, 2013) and attributable to the NO_x -dependent TSOA pathways in CMAQ with VBS. Aircraft NO_x has been shown to lower free radicals in the grid cell containing the airport, slowing oxidation of precursors (particularly the low NO_x pathway), and thereby reduce TSOA formation from all sources (Woody and Arunachalam, 2013). With the traditional treatment of aircraft in grid-based models, aircraft emissions are instantaneously diluted into a grid cell and interact with non-aviation emissions which may or may not occur near the airport (e.g. biogenic TSOA precursors). Plume-in-grid modeling techniques would provide an alternative modeling approach to possibly prevent this result, where aircraft emissions would evolve in plumes prior to interacting with non-aviation emissions when the plumes are merged back into the underlying grid (Rissman et al., 2013).

To evaluate TSOA CMAQ results, we compared CMAQ box model results to the Jathar et al. (2012) box model predictions. The two models use similar mechanisms, utilizing SAPRC VBS SOA yields taken from Murphy and Pandis (2009). However, CMAQ used 11 lumped SOA precursors compared to 91 explicit SOA precursors used by the Jathar et al. (2012) box model. The comparison, normalized for OH concentrations by using OH exposure, indicated that the two models generally agreed (Fig. 1). The underprediction of the CMAQ box model at taxi and takeoff is likely due to the lumping of SOA precursors. However, grid-based SOA contributions from aircraft again appear low compared to the chamber experiments, providing further evidence to support the influence that model grid resolution and OA concentrations have on SOA contributions from aircraft emissions as detailed in Woody and Arunachalam (2013).

3.3 CMAQ predictions of POA from aircraft

At ATL, POA contributed 26 ng m^{-3} (16.9% of $\text{PM}_{2.5}$) in January and 20 ng m^{-3} (16.6% of $\text{PM}_{2.5}$) in July. However, these values may be biased high due to our non-volatile treatment

of aircraft POA. Also, while FOA3 is widely used for aircraft PM emission estimates in air quality models (including this work), it has known limitations. For example, two versions of FOA3 are currently in use, FOA3 (Wayson et al., 2009) and FOA3a (Ratliff et al., 2009), where FOA3a accounts for uncertainties in PM emissions science and characterization at the time it was developed and estimates five times more PM emissions than FOA3. Also, comparisons against measurements have shown FOA3 estimates vary by an order of magnitude for 40 % of aircraft engines (Stettler et al., 2011). FOA3 assumes POA emissions are non-volatile and does not account for variations in primary organic emissions due to changes in ambient temperature. However, measurements have shown that organic aerosol formation 30 m downwind of the engine is highly dependent on ambient temperature due to their volatility (Beyersdorf et al., 2014). These limitations highlight the uncertainties associated with aircraft POA emissions estimates, and the need to improve methods of estimating POA emissions from aircraft and their representation in air quality models.

3.4 Alternative modeling techniques to predict NTSOA

We conducted three sensitivity simulations to determine if alternative modeling techniques could capture NTSOA formation from aircraft without an aircraft-specific parameterization. In the first sensitivity simulation (sensitivity A), aircraft IVOC emissions were remapped to traditional CMAQ SOA precursors using AE6 yields (Carlton et al., 2010) to determine if altering emission estimates could provide similar results to the updated NTSOA parameterization. While contributions from aircraft to anthropogenic TSOA contributions increased in the sensitivity case using AE6 (e.g. from approximately 0.1 to 0.3 ng m^{-3} in January, leading to a 200 % increase), total aircraft contributions to anthropogenic TSOA were below 0.3 % of the total $\text{PM}_{2.5}$ formed from aircraft emissions in January and below 0.8 % in July. In the second sensitivity simulation (sensitivity B), TOG emissions (and thus traditional SOA precursors) were updated to include estimates of idle emissions at 4 % engine thrust levels. This sensitivity case increased TOG emissions by approximately 50 % (Table 4). However, the overall impact of anthropogenic TSOA was small, comprising less than 0.3 % of $\text{PM}_{2.5}$ in January and 0.4 % in July. The third sensitivity simulation used the default configuration

of CMAQ with VBS to estimate SOA formed from S/IVOC emissions, where S/IVOCs estimates for aircraft were keyed to POA emissions (sensitivity C where SVOC = $3 \times$ POA and IVOC = $4.5 \times$ POA). While this case predicted the highest SOA from aircraft in January of the three sensitivity cases (0.5% of total PM_{2.5}), July predictions of SOA lowered total PM_{2.5} from aircraft by 2%.

None of these three sensitivity cases were able to reproduce the NTSOA estimates in CMAQ as represented in Sect. 3.1. Ratios of SOA to POA in the sensitivity cases ranged from -0.14 (sensitivity C in July) to 0.04 (sensitivity A in July) compared to values ranging from 0.16 to 0.48 in the explicit NTSOA case, which was still below the SOA to primary PM ratios (ranging from 0.4 at 85% engine load to 30 at 4% engine load) reported by Miracolo et al. (2011). While aircraft impacts to PM_{2.5} are, in general, low compared to other anthropogenic emission sources (Arunachalam et al., 2011; Woody et al., 2011), without this parameterization, predictions of aircraft impacts to PM near airports would likely be underpredicted by up to 10% in air quality models, particularly in summer months.

3.5 NTSOA sensitivity to aging

One limitation to the Jathar et al. (2012) parameterization is the uncertainty associated with aging of NTSOA. The Miracolo et al. (2011) chamber experiments were conducted over a relatively short time period (hours) and did not capture aged SOA formed over longer time scales (days). Therefore, to test how sensitive aged NTSOA formation from aircraft was to the aging scheme used, two sensitivity simulations were conducted. The first doubled the aging rate constant from $1 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ to $2 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. This rate constant is consistent with CMAQ VBS TSOA aging reactions. The second sensitivity test used the aging scheme used by Pye and Seinfeld (2010), and is based on wood smoke experiments. The Pye and Seinfeld (2010) aging scheme uses a rate constant of $2 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, lowers the volatility of products by two orders of magnitude, only allows for one oxidation step per parent hydrocarbon (vs. multi-generational aging), and assumes that oxidation produces a product 50% heavier than the parent hydrocarbon.

By doubling the aging rate constant, total NTSOA concentrations in the grid cell containing ATL increased by 1 % (from 2.38 ng m^{-3} to 2.40 ng m^{-3}) in January (0.2 % increase in non-idle NTSOA and 2.2 % increase in idle NTSOA) and 10.5 % in July (2.8 % increase in non-idle NTSOA and 28.6 % increase in idle NTSOA). Alternatively, using the Pye and Seinfeld (2010) aging scheme, NTSOA concentrations increased by 13.3 % in January (18.4 % increase in non-idle NTSOA and 2.9 % increase in idle NTSOA) and 38.6 % in July (16.7 % increase in non-idle NTSOA and 76.2 % increase in idle NTSOA). These aging schemes, could produce NTSOA concentrations as high as 10.1 ng m^{-3} ($2\times$ aging) or 12.6 ng m^{-3} (Pye and Seinfeld (2010) aging) in July, which corresponds to 7.2 and 10.3 % of aircraft-attributable $\text{PM}_{2.5}$, respectively.

Further away from the airport, the percent increase of NTSOA was higher as the increased distance provided additional time for aging reactions to occur. At distances of 6–30 km, 31–54 km, and 55–102 km away from ATL, the $2\times$ aging scheme increased NTSOA by 2.9, 3.9, and 6.4 % in January and 24.0, 37.8, and 48.5 % in July, respectively. The Pye and Seinfeld (2010) aging scheme increased NTSOA by 22.1, 26.0, and 33.9 % in January and 65.5, 84.9, and 91.0 % in July at the same set of distances. As a percentage of aircraft-attributable $\text{PM}_{2.5}$, the Pye and Seinfeld (2010) NTSOA aging results correspond to contributions of 5.6 % in January and 19.5 % in July 6–30 km away from ATL, 17.7 and 14.3 % 31–54 km away, and 24.0 and 7.5 % 55–102 km away, suggesting aircraft-attributable $\text{PM}_{2.5}$ could be underpredicted by as much as 20–24 % downwind of the airport.

4 Conclusions

An aircraft-specific parameterization of NTSOA formed from S/IVOC emissions from aircraft engines and based on smog chamber data was successfully incorporated into CMAQ with VBS using SAPRC-07 chemical mechanism. The newly represented NTSOA, a heretofore unaccounted for $\text{PM}_{2.5}$ component in most air quality models, was generally confined to near the airport and increased monthly average $\text{PM}_{2.5}$ contributions by 2.4 ng m^{-3} (34 % from idle and 66 % from non-idle) in January and 9.1 ng m^{-3} (33 and 67 %) in July. This

represents an increase of 1.7% (of 140 ng m^{-3}) and 7.4% (of 122 ng m^{-3}) of aircraft-attributable $\text{PM}_{2.5}$ and is approximately 6 times higher than TSOA contributions from aircraft emissions. Downwind of the airport, NTSOA as a percentage of aircraft-attributable $\text{PM}_{2.5}$ was higher, where NTSOA averaged 4.6% in January and 11.8% in July 6–30 km downwind, 14.0 and 7.7% 31–54 km downwind, and 17.9 and 4.0% 55–102 km downwind. These results suggest that grid-based air quality models may underestimate the impacts of aircraft emissions on $\text{PM}_{2.5}$ by 2–7% near airports and 4–18% downwind due to missing contributions from NTSOA, and could be as high as 10% near the airport and 20–24% downwind when considering uncertainty associated with NTSOA aging.

However, as a percentage of aircraft-attributable $\text{PM}_{2.5}$, SOA results were generally low compared to other PM components, such as inorganic aerosols and elemental carbon, particularly near the airport. We, at least partially, attribute this to the spatial scales (modeled grid resolution) at which SOA was considered. SOA gas-particle partitioning is dependent on the total OA concentration. At smaller volumes, such as inside aircraft plumes or smog chambers, OA concentrations can potentially reach much higher levels due to concentrated POA emissions, partitioning a large fraction of semi-volatile organics to the particle phase.

Additional research to assess aircraft impacts on PM could include the treatment of POA emissions as semi-volatile as well as use a sub-grid scale treatment, or other alternate approaches to include sub-grid variability, to track the formation of aerosols due to aircraft emissions near the aircraft engine and downstream. Specifically, this would include obtaining additional information from previous and ongoing field campaigns that include measurements of volatile components of PM from aircraft engines (Kinsey et al., 2010) and newly developed techniques to estimate aircraft PM emissions in place of FOA3, such as the 1-D plume-scale Aerosol Dynamics Simulation Code (ADSC) model (Wong et al., 2008) which has recently been expanded to provide aircraft emission estimates of S/IVOCs. With the sub-grid scale treatment, the impacts of aircraft NO_x emissions on reductions in biogenic TSOA concentrations seen in previous studies (Arunachalam et al., 2011; Woody et al., 2011; Woody and Arunachalam, 2013) would likely be mitigated and the ratio of SOA to POA may increase.

This study is a part of a larger effort to create an integrated modeling system to model aircraft emissions at airports – using an enhanced VBS framework in CMAQ (to improve OC contributions), to incorporate plume-scale models such as CMAQ-APT (Karamchandani et al., 2014) (to improve sub-grid scale characterization), and ADSC (to improve near-field estimates) with an end goal of improved characterization of PM_{2.5} contributions from aircraft emissions at multiple spatial scales.

**The Supplement related to this article is available online at
doi:10.5194/acpd-0-1-2015-supplement.**

Acknowledgements. This work was funded by PARTNER under grants to UNC. PARTNER is funded by FAA, NASA, Transport Canada, US DOD, and EPA. We would like to thank William Hutzell of the US EPA for providing the base CMAQ model inputs, ENVIRON for providing a prerelease version of CMAQv5.0.1 with VBS, Alexis Zubrow of the US EPA for providing the SPECIATE 5565B speciation profile, Sergey Napelenok of the US EPA for providing a version of CMAQ v4.7 with VBS used in preliminary testing, B. H. Baek of the UNC Institute for the Environment for providing the AEDTproc tool, and Christopher Sequeira and Mohan Gupta of the FAA for managing this research and for many helpful discussions. The aviation emissions inventories used for this work were provided by US DOT Volpe Center and are based on data provided by the US Federal Aviation Administration and EUROCONTROL in support of the objectives of the International Civil Aviation Organization Committee on Aviation Environmental Projection CO₂ Task Group. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the US DOT, Volpe Center, the US FAA, EUROCONTROL or ICAO.

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Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *Geophys. Res. Lett.*, **34**, L13801, doi:10.1029/2007GL029979, 2007.

Table 1. Aircraft-specific mass yields for reactions of S/IVOC gas-phase species (NTSOA precursors) with OH. Values represent the mass transferred and the corresponding reduction in volatility ($\log_{10} C^*$) for each oxidation step and are $1.5\times$ higher than the values reported by Jathar et al. (2012). For example, when reacted with OH, 1 g of NTSOA precursor from idle activities with a C^* value of 10^7 would produce 0.15 g of SVOC with a C^* of 10^2 (7 minus 5), 0.15 g of SVOC with a C^* of 10^3 , and 0.3 g of SVOC with a C^* of 10^4 .

Change in Volatility Bin ($\log_{10} C^*$)	-6	-5	-4	-3
Idle	0	0.15	0.15	0.3
Non-Idle	0.075	0.15	0	0

Table 2. SPECIATE v4.3 speciation profile 5565B used to speciate aircraft TOG emissions to SAPRC-07 model species.

Common Name	Model Species	Mass Fraction	Molecular Weight (g mol ⁻¹)
1,3-Butadiene	BDE13	0.0169	54.0904
Acetone	ACET	0.0036898	58.0791
Acrolein	ACRO	0.0245	56.0633
Acetylene	ACYE	0.0394	26.0373
Alkanes*	ALK1	0.0052098	30.069
Alkanes*	ALK2	7.8005E-4	44.0956
Alkanes*	ALK4	0.0066996	82.5378
Alkanes*	ALK5	0.1765	147.1058
Aromatics*	ARO1	0.0027295	111.0468
Aromatics*	ARO2	0.0246	133.8579
1,2,4-Trimethylbenzene	B124	0.0035	120.1916
Aromatic aldehydes	BALD	0.0103	113.2886
Benzene	BENZ	0.0168	78.1118
Acetaldehyde	CCHO	0.0427	44.0526
Phenols and Cresols	CRES	0.0072597	94.1112
Ethene	ETHE	0.1546	28.0532
Glyoxal	GLY	0.0182	58.0361
Formaldehyde	HCHO	0.1231	30.026
Isoprene products	IPRD	0.0103	70.0898
Methacrolein	MACR	0.0042902	70.0898
Methanol	MEOH	0.018	32.0419
Methylglyoxal	MGLY	0.015	72.0627
m-Xylene	MXYL	0.0014099	106.165
Alkenes*	OLE1	0.091	95.61
Alkenes*	OLE2	0.058	110.2306
o-Xylene	OXYL	0.0016604	106.165
Propene	PRPE	0.0453	42.0797
p-Xylene	PXYL	0.0014099	106.165
C3+ Aldehydes	RCHO	0.0697	127.1741
Toluene	TOLU	0.0064202	92.1384

* Lumping based on reaction rate with OH.

Table 3. Monthly total aircraft emissions (short tons) in January (Jan) and July (Jul) from LTO activities at ATL of SVOCs and IVOCs (non-traditional SOA precursors).

	C^*	SVOCs				IVOCs			
		10^0	10^1	10^2	10^3	10^4	10^5	10^6	10^7
Non-Idle	Jan	0.52	0.88	1.03	4.14	5.6	1.0	2.4	2.4
	Jul	0.54	0.92	1.09	4.43	6.0	1.1	2.5	2.5
Idle	Jan	0.05	0.03	0.03	0.08	0.2	0.6	10.6	10.6
	Jul	0.07	0.06	0.06	0.13	0.3	0.9	16.9	16.9

Table 4. Monthly total aircraft emissions (short tons) in January (Jan) and July (Jul) of total organic gases (TOG, the speciation of which is listed in Table 2) and CMAQ SOA precursors (alkanes (ALK4 and ALK5), aromatics (ARO1 and ARO2), benzene (BENZ), alkenes (OLE1 and OLE2), toluene (TOL), and xylene (XYL, which includes MXYL, OXYL, and PXYL)). Note that SOA production from ALK4, ARO1, and ARO2 was only considered from aircraft and that idle emissions, which are not included in AEDT emissions by default, were only considered in sensitivity simulations described in Sects. 3.2 and 3.4.

		TOG	ALK4	ALK5	ARO1	ARO2	BENZ	OLE1	OLE2	TOL	XYL
Non-Idle	Jan	64.3	0.41	9.2	0.15	1.4	1.1	4.4	2.6	0.41	0.29
	Jul	78.1	0.49	11.1	0.18	1.7	1.3	5.4	3.1	0.50	0.35
Idle	Jan	39.8	0.25	5.7	0.09	0.9	0.7	2.7	1.6	0.30	0.18
	Jul	64.9	0.41	9.3	0.15	1.4	1.1	4.5	2.6	0.42	0.29

Table 5. Monthly total aircraft emissions (short tons) in January (Jan) and July (Jul) of NO_x and SO₂ (inorganic PM precursors) and primary elemental carbon (PEC), organic carbon (POA), and sulfate (PSO₄).

	NO _x	SO ₂	PEC	POA	PSO ₄
Jan	466.6	37.2	1.6	1.3	1.1
Jul	511.9	42.7	1.7	1.4	1.3

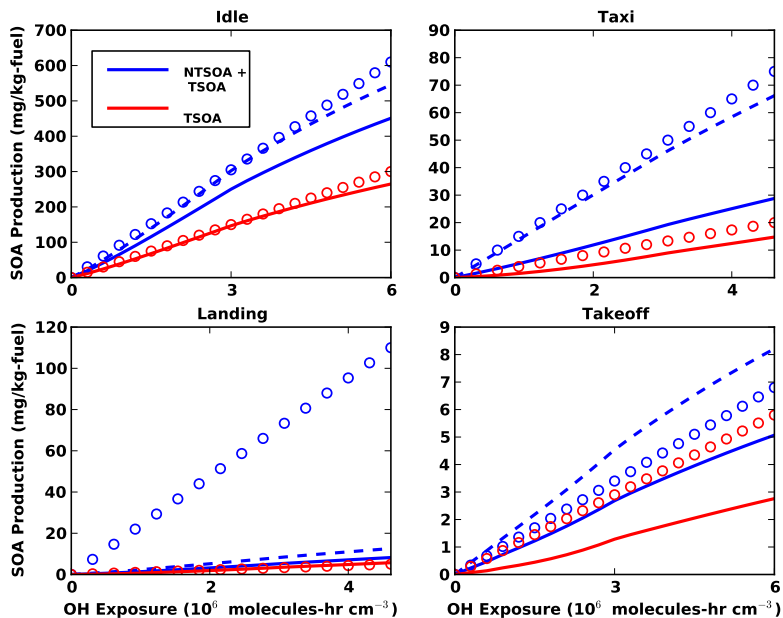


Figure 1. Comparison of traditional (TSOA) and non-traditional SOA (NTSOA) predictions in CMAQ (solid lines), box model results reported by Jathar et al. (2012) (circles) based on measurements from Miracolo et al. (2011), and NTSOA predictions in CMAQ with $1.5\times$ increased yields (dashed lines) for a CFM56-2B engine at idle (4% power), taxi (7%), landing (30%), and takeoff (85%). OH exposure is the integration of OH concentrations over time to account for differences in OH concentrations between the two models.

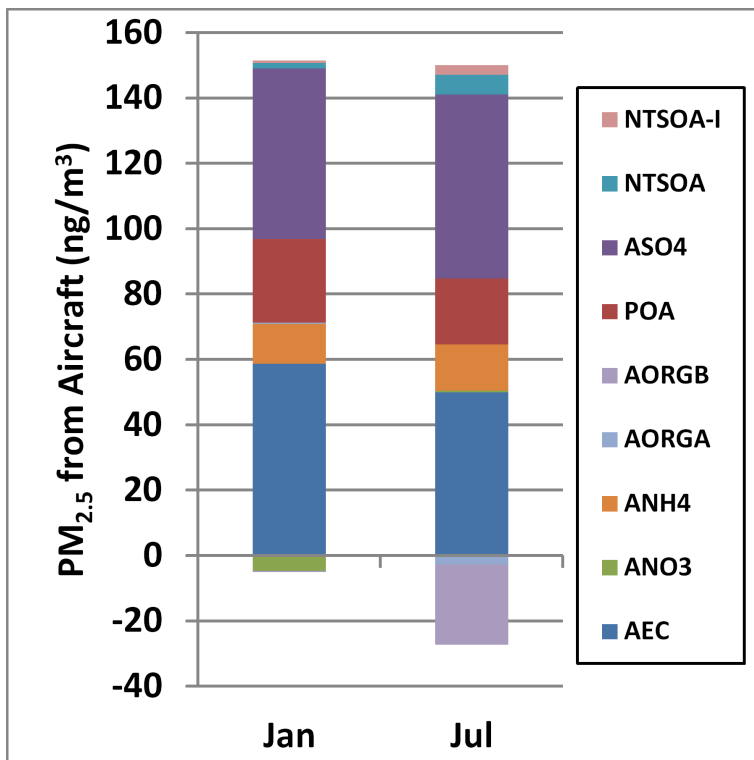


Figure 2. Speciated monthly average PM_{2.5} contributions from aircraft in the grid cell containing the Atlanta airport in January and July. Species include non-traditional SOA from engine idle activities (NTSOA-I), non-traditional SOA from all other engine modes (NTSOA), sulfate (ASO₄), primary organics (POA), biogenic TSOA (AORGB), anthropogenic TSOA (AORGA), ammonium (ANH₄), nitrate (ANO₃), and elemental carbon (AEC) aerosols.

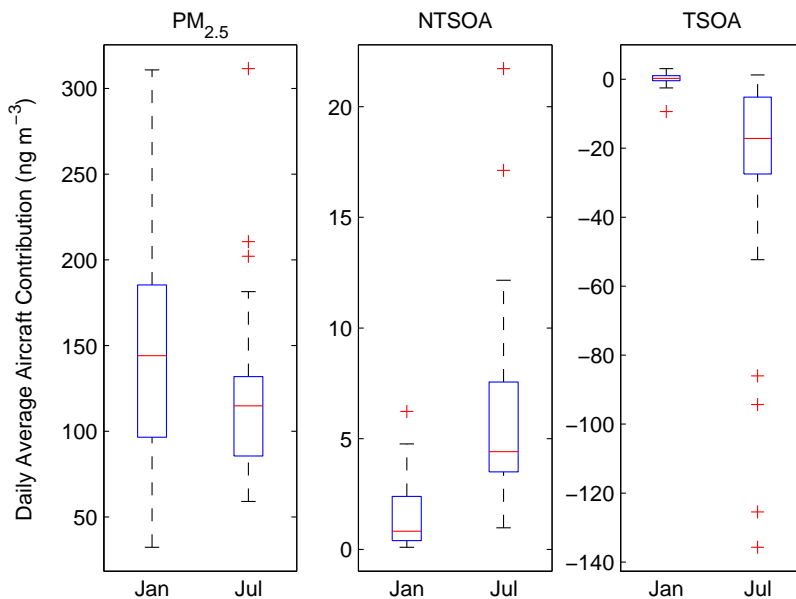


Figure 3. Box-and-whisker plots showing the 25th, 50th (red line), and 75th percentiles, and minimum and maximum values of daily average aircraft-attributable PM_{2.5}, non-typical SOA (NTSOA), and traditional SOA (TSOA) in the grid cell containing ATL. Outliers are defined as values more than 1.5 times the inter-quartile range above the 75th percentile and below the 25th percentile.

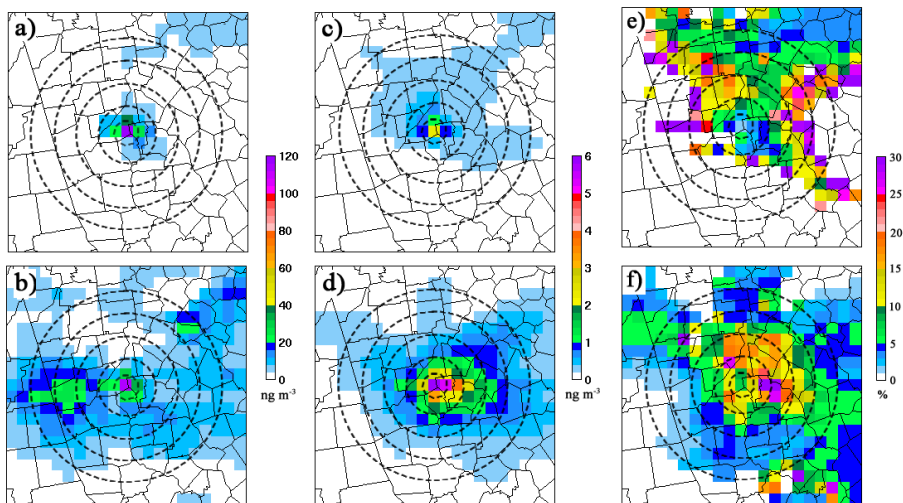


Figure 4. Monthly average contributions from aircraft to $\text{PM}_{2.5}$ in (a) January and (b) July, to non-traditional SOA (NTSOA) in (c) January and (d) July, and NTSOA ($> 0.1 \text{ ng m}^{-3}$) as a percentage of aircraft-attributable $\text{PM}_{2.5}$ in (e) January and (f) July. Note the differences in scales, that the absolute maximum impacts occur in the grid cell containing ATL but the percentage of aircraft-attributable $\text{PM}_{2.5}$ comprised of NTSOA is higher away from the airport, and that the map covers an area of $720 \text{ km} \times 720 \text{ km}$. Circles indicate the location of ATL and 30, 54, 78, and 102 km away from ATL.

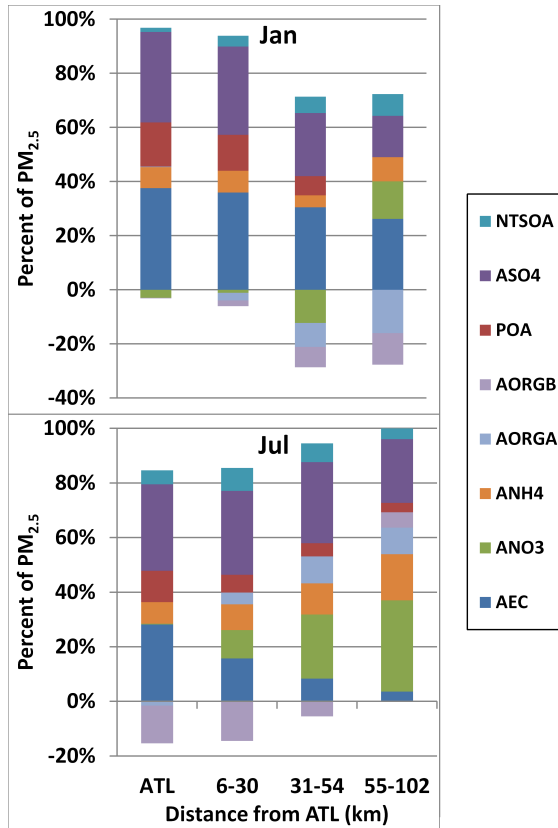


Figure 5. Monthly average composition of aircraft-attributable $PM_{2.5}$ at the grid cell containing ATL and at various distances away from ATL. Note that absolute aircraft-attributable $PM_{2.5}$ concentrations are approximately 15 (6–30 km), 94 (31–54 km), and 196 (55–102 km) times lower moving away from ATL in January and 8, 13, and 16 times lower in July.