



# Aircraft Emissions' Contributions to Organic Aerosols in a Regional Air Quality Model using the Volatility Basis Set

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## Abstract

A framework that employs the Volatility Basis Set (VBS) within the Community Multiscale Air Quality Model (CMAQ) was applied to predict organic aerosol concentrations from aircraft emissions. This framework was further expanded to include the formation of secondary organic aerosols from semi and intermediate volatile organic compounds which are traditionally missing from emission inventories used in air quality models. Results indicated that CMAQ with VBS predicted similar total contributions to fine particulate matter compared to CMAQ without VBS but with variations in the composition of organic species.

## Introduction

The Federal Aviation Administration (FAA) projects that passenger traffic will increase 2.1% per year over the next 20 years (FAA, 2010). This growth, along with projected reductions of emissions from other source sectors due to planned control strategies, indicates the environmental concerns associated with aircraft emissions are likely to increase in significance in the coming years. Therefore, there is a strong need to better understand and quantify aircraft emissions and their impacts on air quality. This work focuses on updating the current representation of the organic aerosol component of fine particulate matter ( $PM_{2.5}$ ) produced from aircraft emissions in a regional air quality model by incorporating emerging scientific developments in the field of organic aerosols.

## $PM_{2.5}$ and Organic Aerosols

Fine particulate matter, or  $PM_{2.5}$ , is the term used for a mixture of solid particles and liquid droplets suspended in ambient air smaller than 2.5 micrometers in diameter.  $PM_{2.5}$  is considered harmful to human health, as there is evidence for cardiovascular health effects and cardiopulmonary morbidity and mortality (Pope and Dockery, 2006). It is also one of six criteria air pollutants regulated by the U.S. Environmental Protection Agency (EPA) under the National Ambient Air Quality Standards (NAAQS) established by the Clean Air Act (Federal Register, 1997).

Approximately 20%-50% of  $PM_{2.5}$  mass at mid latitudes of the lower troposphere is comprised of organic aerosols (Kanakidou et al., 2005). Organic aerosols can either be primary (directly emitted) or secondary (formed from organic gases that have undergone chemical transformations). Secondary organic aerosols (SOA) are

commonly understood to be formed by oxidation of volatile organic compounds (VOCs) by free radicals—mainly the hydroxyl (OH) radical, ozone (O<sub>3</sub>), and nitrate (NO<sub>3</sub>) radicals (Kroll and Seinfeld, 2008). SOA particle formation from these oxidation products is driven by thermodynamic equilibrium based on volatility (or vapor pressure) between the particle and gas phase.

The most commonly accepted methods to estimate atmospheric organic carbon (OC), both primary and secondary, are (1) use of elemental carbon (EC) as a tracer for primary OC concentrations (Turpin and Huntzicker, 1995) which estimates primary OC based on EC, finding secondary OC as the difference between total and primary OC (Lim and Turpin, 2002), (2) use of source-oriented mathematical modeling approaches which combine emissions estimates with meteorological transport, chemistry, and other atmospheric processes (Heald et al., 2005; Lane et al., 2008; Tsimpidi et al., 2010, 2011), and (3) use of receptor models to identify primary organic aerosol (POA) and estimate SOA (Brook et al., 2004; Zhang et al., 2009), which is initialized with ambient measurements and modeled in a back trajectory to determine the source contributions to the ambient measurement. Comparisons of these three methods typically produce roughly comparable estimates for SOA predictions (Lim and Turpin, 2002; Lee et al., 2010). In the next section, theories incorporated into mathematical modeling approaches to predict OC formation are presented and explored as possible methods to quantify OC formation from aircraft emissions.

## **Modeling Approaches for Primary Organic Aerosols**

Traditionally, primary organic aerosols are treated as inert and non-volatile in regional air quality models. That is, POA is directly emitted from wood burning, combustion, and other industrial sources and undergoes transport but does not react or interact with the gas phase. Recent work by Robinson et al. (2007) has indicated that modeling, field, and laboratory data contradict this theory. Instead, POA should be modeled as semi-volatile compounds that partition between the gas and particle phase much like oxidized SOA precursors. Additionally, Robinson et al. (2007) suggested that POA reacts with OH radicals, producing semi-volatile oxygenated organic aerosols (OOA) with lower vapor pressures than the parent POA species.

## **Modeling Approaches for Secondary Organic Aerosols**

The traditional approach to modeling SOA formation in regional air quality models employs the Odum et al. (1996) two-product model. The two-product model incorporates the absorptive partitioning theory for semi-

volatile gas-phase species developed by Pankow (1994a, 1994b) to predict the partitioning of species between gas and particle phases based on the mass of the absorbing particle phase and saturation vapor pressure ( $c^*$ ). The two-product model uses 2 surrogate products to represent SOA oxidation products from the parent precursors rather than attempting to represent explicit products, many of which are unknown or poorly characterized. Because it is computationally manageable and supported by laboratory data, it has commonly been used in atmospheric transport and general circulation models (Hallquist et al., 2009).

However, estimates using the two-product model to predict SOA yields have consistently been shown to underpredict SOA formation when compared against the limited number of ambient measurements currently available (de Gouw et al., 2005; Johnson et al., 2006; Volkamer et al., 2006). For example, Volkamer et al. (2006) indicated that a two-product model that included 51 SOA precursors underpredicted SOA concentrations by a factor of 8 in Mexico City when compared against measurements. The Community Multiscale Air Quality (CMAQ) model, developed by the EPA and used for regulatory and research purposes, has similarly underpredicted SOA concentrations in both rural and urban areas using the two-product model, particularly during summer months (Tesche et al., 2006; McKeen et al., 2007; Yu et al., 2008). Recent updates to CMAQ have aimed to address this issue by incorporating the emerging science of SOA formation. Updates include newly discovered SOA pathways such as aqueous cloud chemistry (Carlton et al., 2008) and additional SOA precursors such as benzene and sesquiterpene (Carlton et al., 2010). The inclusion of these updates has improved predictions of SOA, as CMAQ has been shown to now better represent seasonal variations but overall still tends to underpredict SOA (Carlton et al., 2010), highlighting the need for continued modeling improvements and updates.

## **Volatility Basis Set**

Given the tendency of the 2-product model to underpredict SOA formation, Donahue et al. (2006) developed the “volatility basis set” (VBS) as a new method to predict SOA concentrations. It also employs the Pankow partitioning theory and lumps oxidation products of volatile organic compounds into volatility bins (typically between 4 to 9 bins) based on the volatility of compounds modeled. The saturation vapor pressure ( $c^*$ ) values assigned to each volatility bin differ by an order of magnitude between bins. The VBS provides an intermediate step between the two product and more explicit models. Instead of only 2 possible volatilities of products, products can instead be represented by a much wider range of volatilities spanning up to 9 orders of

magnitude. At the same time, lumping VOCs allows for a wide range of compounds to be represented without the need to track individual species separately, thus simplifying the model and allowing it to be used in chemical transport models.

Results of predictions of SOA formation using VBS have indicated good performance of organic aerosol predictions when compared against observations (Lane et al., 2008; Tsimpidi et al., 2010, 2011). Using VBS in the PMCAMx regional air quality model, Lane et al. (2008) compared modeled OA (primary and secondary) concentrations against daily average observations from the eastern U.S. They indicated that while their results typically underpredicted OA concentrations in urban areas, it was a significant improvement over using the two-product parameterization. Tsimpidi et al. (2010, 2011) used VBS as part of the PMCAMx regional air quality model to predict OA in Mexico City. Model results indicated good agreement with both the magnitude and diurnal pattern of OA when compared against observations made during the MILAGRO field measurement campaign.

## **PM<sub>2.5</sub> Contributions from Aircraft Emissions**

PM emissions from aircraft are generally perceived of as containing a non-volatile portion, comprised of elemental carbon or soot, and a semi-volatile and/or a volatile portion, comprised of sulfate and organics. However, there is considerable uncertainty associated with the semi-volatile and volatile portions of aircraft emissions. Stettler et al. (2011) indicated that the organic PM emission index predicted by the First Order Approximation v3 (FOA3) (Wayson et al., 2009), typically used to estimate PM emission from aircraft, was off by an order of magnitude 40% of the time when compared against measured organic PM emission index values. Additionally, Woody et al. (2011) excluded aircraft emissions of sulfate and organic aerosols due to the high level uncertainty associated with estimating their emissions. This suggests that future considerations are needed to better quantify semi-volatile and volatile components of aircraft emissions.

For SOA, a limited number of studies have focused on their production from aircraft emissions, and suggest different results. Estimated speciated contributions from aircraft emissions to PM<sub>2.5</sub> using CMAQ with the Odum 2-product model have indicated that OC was only a minor constituent, while inorganic species and EC comprised the majority of health and air quality impacts near the airport (Arunachalam et al., 2011; Woody et al., 2011). In fact, Woody et al. reported at the Hartsfield-Jackson Atlanta International Airport (ATL) emissions from aircraft lowered SOA concentrations. Conversely, recent smog chamber results from Miracolo et al. (2010) suggest

otherwise. Aircraft emissions from a CFM56-2B engine were allowed to undergo 3 hours of photooxidation and the subsequent  $PM_{2.5}$  mass formed was dominated by secondary components, SOA at low engine power settings and sulfate aerosol at high engine power setting.

Miracolo et al. (2010) also modeled SOA production from aircraft emissions using VBS incorporated into a box model and compared the results with measurements. The modeling results underpredicted SOA measurements by 40-60%, depending on the power setting. They attributed this underprediction to missing SOA precursors in the emission inputs to the model, specifically what they term as recently discovered semi and intermediate volatile organic carbon (SVOC and IVOC) emissions which have traditionally been excluded from emission inventories. Two observations support this theory 1) SOA formation could not be explained by single ring aromatics alone; all of the aromatics emitted would have had to be oxidized to produce the SOA levels measured and 2) measurements were made of an unresolved carbon material (SVOCs and IVOCs) which followed actual SOA formation, suggesting they are possible precursors. Given the amount of time aircraft spend with low engine power settings at airports during the LTO cycle, this has relevance for accurate assessment of air quality impacts in the vicinity of the airports.

As discussed, VBS provides an effective method for estimating organic aerosols produced from gas phase chemistry in chemical transport models and would likely be the best approach currently available for modeling OC formed from aircraft emissions. It also provides a platform to introduce new and emerging science of OC, such as SOA formed from SVOCs and IVOCs (Miracolo et al., 2010) and the semi-volatile nature of POA and OOA (Robinson et al., 2007). Furthermore, given the variation of aircraft emission in space and time and the generally large grid cell sizes associated with chemical transport models, it may be necessary to model each aircraft individually using a plume-in-grid technique, or other alternate approaches to including sub-grid variability. For example, plume scale modeling efforts using the one-dimensional Aerosol Dynamics Simulation Code (ADSC) model have shown the ability to accurately predict sulfate aerosol formation in aircraft exhaust plumes when compared against direct measurements (Wong et al., 2008). Coupled with VBS, a model such as ADSC could be used to capture plume scale formation of OC and then passed off to a chemical transport model allowing the overall modeling system to encompass all the necessary spatial and temporal scales. This represents the end goal of the

work presented here, with the first step being to use VBS to represent contributions from aircraft emissions to organic carbon, including non-traditional SOA formed from emissions of SVOCs and IVOCs.

## Methodology

The focus of this work was to estimate contributions of aircraft emissions from ATL to  $PM_{2.5}$ , focusing on organic aerosols, using a research version of CMAQ v4.7 (Byun and Ching, 1999; Byun and Schere, 2006; Foley et al., 2010) with the VBS framework provided by the EPA. SOA precursors were unchanged between the standard version of CMAQ and the VBS implementation; however, VBS served as a replacement to the traditional 2-product model used to predict partitioning of SOA between the gas and particle phases. The implementation also includes updates to the treatment of POA as a semi-volatile compound and allowed to partition between the gas and particle phase. Additionally, reactions of POA with OH radicals to form OOA were included.

In addition to the VBS treatment of OC from all sources (including aircraft), the ability to predict the formation of SOA from aircraft emissions of SVOC and IVOC emissions was added. SVOC and IVOC emissions are generally considered to have been missing from previous emission inventories and therefore are new SOA precursors in addition to the previously known SOA precursors from aircraft (e.g. alkanes, aromatics). New gas phase and corresponding particle phase species were introduced into CMAQ with parameterizations based on recent work by Jathar et al. (2012). Similar to the CMAQ VBS representation of POA, the aircraft specific SVOC and IVOC species were considered semi-volatile and underwent reactions with OH radicals to form products with saturation vapor pressures one order of magnitude lower than the parent SVOC/IVOC. Note that while SVOC and IVOC emissions likely occur from other sources, estimations of their emissions and their subsequent formation of SOA were outside the scope of this work.

A total of 4 model simulations were performed for the period July 3-4, 2002 plus a two day spin-up period at a 12-km horizontal grid resolution with 14 vertical layers over the Eastern United States (Table 1). Meteorological inputs were generated using the Pennsylvania State University/NCAR mesoscale v3.6.1 model (MM5) (Grell et al., 1994) and based on 2002 conditions. Base case (base05) emissions were estimated using the EPA's 2002 National Emissions Inventory (NEI) (EPA, 2004) and speciated for the SAPRC99 chemical mechanism (Carter, 2003) using



**Table 1. List and description of model scenarios.**

Simulation	Description
base	2002 base case emissions with the publicly available version of CMAQ v4.7
base_VBS	2002 base case emissions with CMAQ v4.7 plus the VBS framework to represent organic aerosols
airc	2002 base case emissions plus landing and take off emissions from ATL with the publicly available version of CMAQ v4.7
airc_VBS	2002 base case emissions plus landing and take off emissions from ATL with CMAQ v4.7 plus the VBS framework to represent organic aerosols from all sources and additional particle formation from aircraft SVOC and IVOC emissions

SMOKE 2.0. Additional details regarding the meteorological and base case emission inputs can be found in Hutzell et al. (2012).

Aircraft emissions at ATL were generated using 2002 engine specific landing and takeoff (LTO) cycle data at ATL (CSSI, 2007). For each engine, mode specific (taxiing, takeoff, approach and landing) emission factors for total organic gases (TOG), NO<sub>x</sub>, CO, and SO<sub>2</sub> were taken from the ICAO database (ICAO, 2010). TOG was speciated first into explicit species using the most recent speciation profile developed by the FAA and EPA (EPA, 2009a; EPA, 2009b) and then into model specific SAPRC99 species using speciation profiles obtained from Carter (2003). PM emission factors of EC, POA, and sulfate aerosol (ASO4) were estimated using the FOA3a (Ratliff et al., 2009) methodology which is an expansion of FOA3 (Wayson et al., 2009). Computed emission factors were then applied to activity data from Atlanta for an entire year to produce an annual inventory. The annual inventory was allocated in time and space (including the vertical profile of a typical LTO cycle) into gridded emission files for ATL over the modeled time period.

IVOC and SVOC emissions for aircraft, which were previously considered missing from emission inventories, were estimated using emission factors for a CFM56-2B engine taken from Jathar et al. (2012) normalized by the mode specific ICAO HC emission factor for the same engine. This normalized emission factor was then applied across all engines, scaled up to an annual inventory, and similarly allocated in time and space. It should be noted that while applying a normalized emission factor for SVOC and IVOC emissions from aircraft based on a single engine introduces some uncertainty, limited data currently exists on these emissions from other engine types.

Note that SOA concentrations in CMAQ are separated out into those formed from anthropogenic (ASOA) and biogenic (BSOA) precursors. Aircraft emissions can impact anthropogenic SOA by way of direct emissions of anthropogenic precursors (e.g. alkanes, aromatics) as well as gas phase interactions with radicals that oxidize anthropogenic SOA precursors. Similarly, those same gas phase interactions of aircraft emissions with radicals can also impact the formation of SOA from biogenic precursors (e.g. monoterpenes, sesquiterpenes).

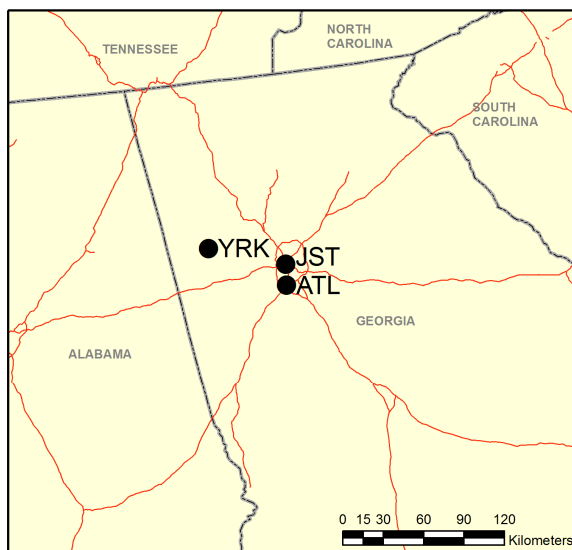
## Results and Discussion

### Base Case Model Performance

Base case model results for July 3 and 4 were compared with hourly measurements of PM<sub>2.5</sub> and total carbon (TC, organic carbon + elemental carbon) from the Jefferson Street (JST, located in downtown Atlanta approximately 18 km north of ATL) and the Yorkville, GA (YRK, rural GA located approximately 70 km northwest of ATL) Southeastern Aerosol Research and Characterization (SEARCH) Network (Hansen et al., 2003) ambient air quality monitors (Table 2 and Figure 1). At both monitors, the base\_VBS case resulted in improved Normalized Mean Bias (NMB) and Normalized Mean Error (NME) for PM<sub>2.5</sub> and TC with the exception of NME for PM<sub>2.5</sub> at the Yorkville site. Much of this improvement is attributable to higher predictions of SOA in the base\_VBS simulations. The improved base\_VBS model performance could potentially improve the reliability of the modeling framework used to assess air quality impacts from aircraft.

**Table 2. Comparison of PM<sub>2.5</sub> and TC observations from the SEARCH monitoring network against model results.**

		PM <sub>2.5</sub>		Total Carbon	
		NMB	NME	NMB	NME
JST	base	-12.8	45.3%	-51.5%	52.0%
	base_VBS	-6.7%	43.2%	-35.8%	35.9%
YRK	base	-4.4%	26.4%	-54.9%	54.9%
	base_VBS	2.3%	27.0%	-19.6%	25.2%



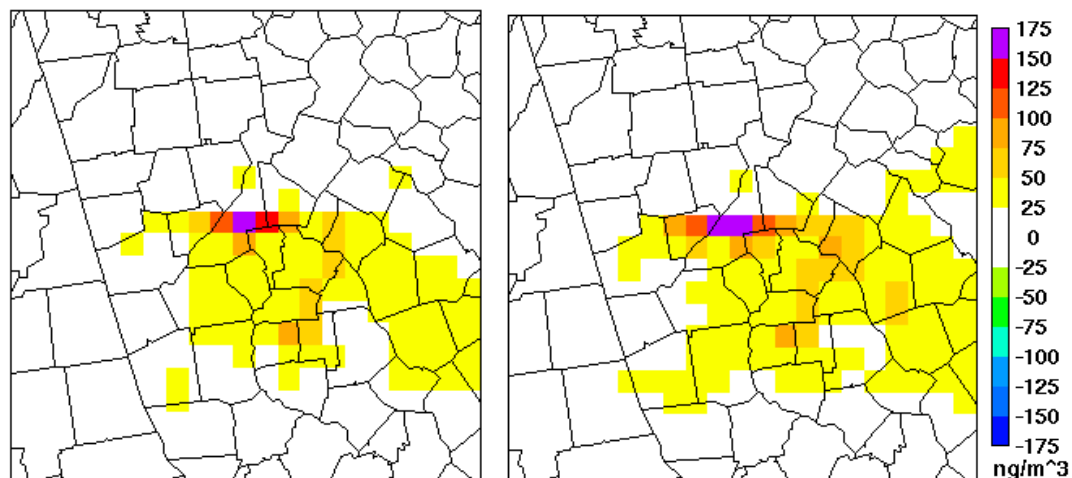
**Figure 1. Location of the Hartsfield-Jackson Atlanta International Airport (ATL) and Jefferson Street (JST) and Yorkville (YRK) SEARCH ambient monitoring sites.**

## Contributions of Aircraft Emissions to $PM_{2.5}$

Predicted contributions from aircraft emissions were calculated by taking the difference in base case model simulations (base and base\_VBS) and model simulations with ATL aircraft emissions added (airc and airc\_VBS). In both the CMAQ (airc-base) and CMAQ\_VBS (airc\_VBS-base\_VBS) simulations, impacts from aircraft emissions were highest at the grid cell containing the airport, with aircraft contributing  $361 \text{ ng m}^{-3}$  in the CMAQ simulations and  $325 \text{ ng m}^{-3}$  in the CMAQ\_VBS simulations to the two day average  $PM_{2.5}$  concentrations for July 3 and 4, 2002. Figure 2 indicates the spatial extents of impacts to  $PM_{2.5}$  from aircraft emissions. Overall, contributions from aircraft greater than  $25 \text{ ng m}^{-3}$  occurred more often in CMAQ\_VBS simulations.

## Comparison of CMAQ and CMAQ\_VBS Results

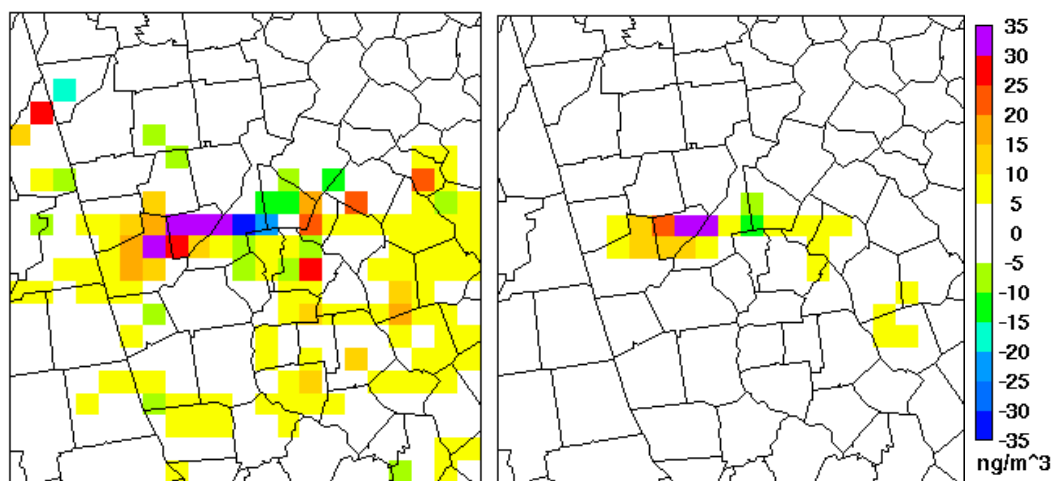
Figure 3 provides the difference in contributions from aircraft emissions in the CMAQ simulations vs. CMAQ\_VBS simulations [(airc\_VBS-base\_VBS)-(airc-base)] to  $PM_{2.5}$  and anthropogenic SOA. While the CMAQ\_VBS simulation predicted lower  $PM_{2.5}$  contributions at ATL and in the grid cells immediate east and northeast of ATL, it predicted higher contributions at most grid cells downwind of ATL, particularly those occurring



**Figure 2.** Two day average contribution from aircraft emissions to  $PM_{2.5}$  in CMAQ (left) and CMAQ with VBS (right). Note: ATL is located in the grid cell in the center of the plot indicated by the single purple grid cell in the CMAQ plot (left).

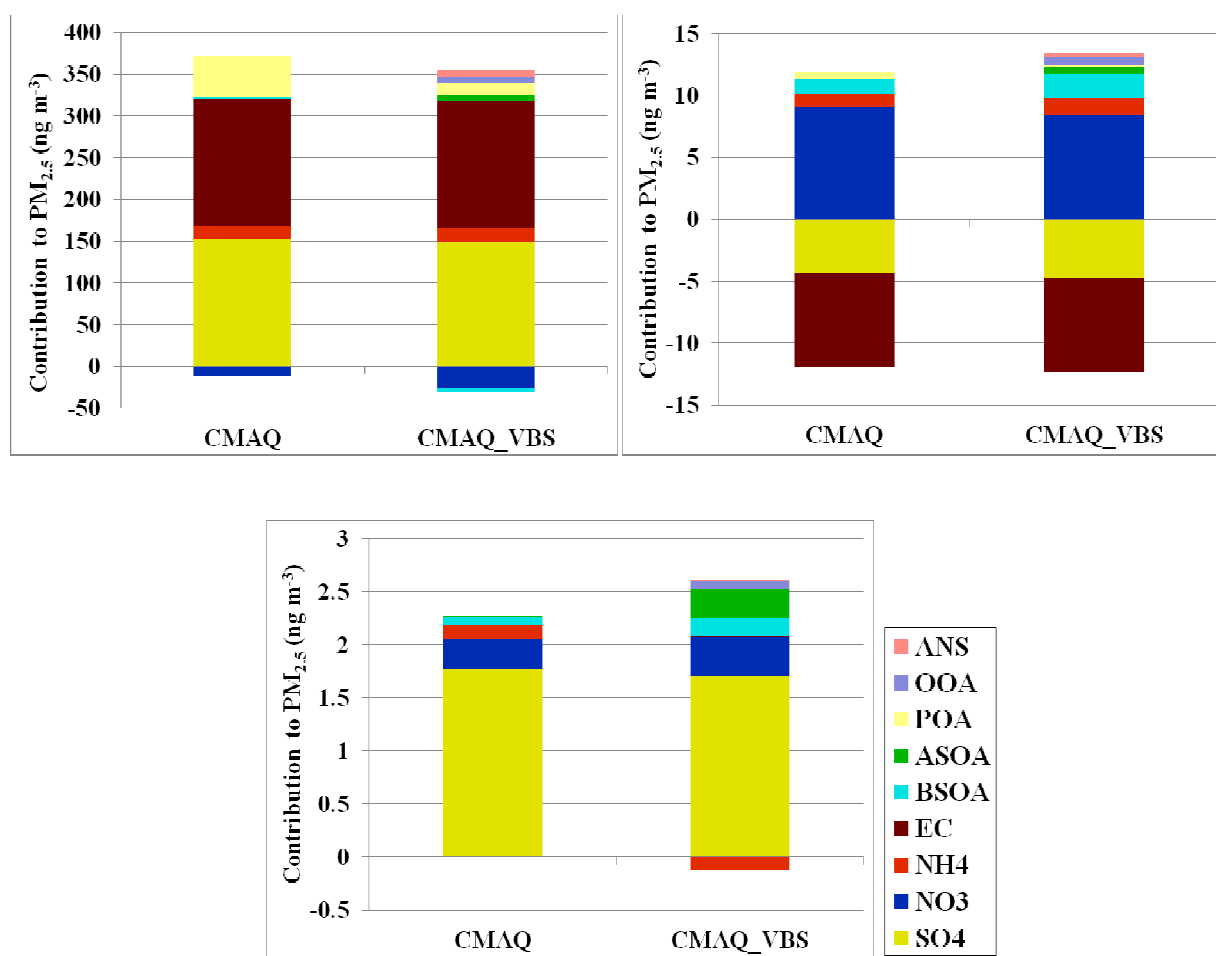
along the east-west flight path from ATL. These higher contributions were largely attributable to contributions from anthropogenic SOA (Figure 3).

Two day average total contributions to  $PM_{2.5}$  from aircraft emissions in the grid cells containing ATL, JST, and YRK, were comparable between the CMAQ and CMAQ\_VBS simulations (Figure 4). However, speciated contributions of organic aerosols varied between the two. At ATL, organic aerosols in the CMAQ case were

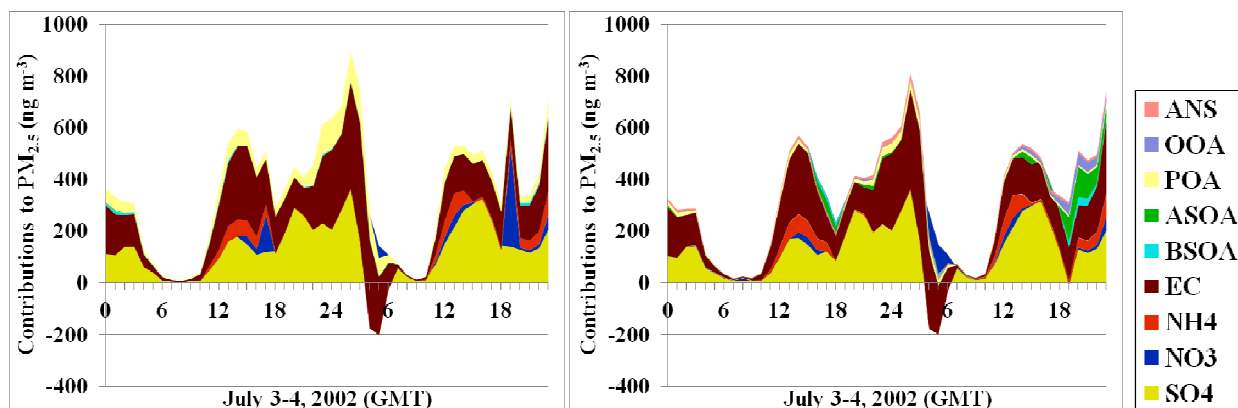


**Figure 3.** Difference in two day average contributions to  $PM_{2.5}$  (left) and anthropogenic SOA (right) between CMAQ and CMAQ\_VBS simulations (CMAQ\_VBS minus CMAQ).

composed primarily of POA compared to the CMAQ\_VBS case which was comprised of approximately equal parts of anthropogenic SOA (ASOA), POA, oxygenated organic aerosols (OOA), and non-traditional SOA formed from SVOC and IVOC emissions (ANS). At JST (just north of ATL), CMAQ and CMAQ\_VBS predicted approximately equal contributions of biogenic SOA (BSOA) and POA, whereas CMAQ\_VBS predicted additional contributions from ASOA, OOA, and ANS. At YRK, the CMAQ\_VBS simulation predicted higher contributions from aircraft emissions to biogenic and anthropogenic SOA which led to overall higher contributions of  $PM_{2.5}$ .



**Figure 4.** Two day average speciated contributions from aircraft emissions to  $PM_{2.5}$  at the grid cells containing ATL (top left), JST (top right), and YRK (bottom) for sulfate (ASO4), nitrate (ANO3), ammonium (ANH4), elemental carbon (EC), biogenic SOA (BSOA), anthropogenic SOA (ASOA), primary organic (POA), oxygenated organic (OOA) and non-traditional SOA (ANS) aerosols.



**Figure 5. Time series of speciated contributions from aircraft emissions to  $PM_{2.5}$  at the grid cell containing ATL for CMAQ (left) and CMAQ\_VBS (right) for sulfate (ASO4), nitrate (ANO3), ammonium (ANH4), elemental carbon (EC), biogenic SOA (BSOA), anthropogenic SOA (ASOA), primary organic (POA), oxygenated organic (OOA) and non-traditional SOA (ANS) aerosols.**

Speciated time series over the two days at the grid cell containing the airport indicated similar diurnal profiles between CMAQ and CMAQ\_VBS (Figure 5). The notable differences occurred in the afternoon of July 4, 2002 when CMAQ\_VBS predicted that a considerable fraction of the  $PM_{2.5}$  formed from aircraft emissions was comprised of organic aerosols (40-50%). On the other hand, CMAQ predicted only 5-10% of  $PM_{2.5}$  was comprised of organic carbon during this same time period.

Predicted contributions from aircraft emissions to non-traditional SOA from SVOC and IVOC precursors were small overall, comprising only 2.7% on average of the  $PM_{2.5}$  contributions for aircraft at the airport. However, smog chamber data obtained by Miracolo et al. (2011) suggests that SVOCs and IVOCs account for a significant portion of SOA from aircraft. One possible difference in results is the scales each were considered at. The 12 km model grid volume is significantly larger than the 7 m<sup>3</sup> smog chamber used to represent plume scale chemistry by Miracolo et al. Concentrations inside the smog chamber were likely much higher and therefore would lead to higher SOA yields. One possible approach to rectify scale differences would be to use plume-in-grid modeling techniques, or other alternate approaches to including sub-grid variability at a fine scale using a model such as ADSC. Coupled with VBS, ADSC could be used to capture plume scale formation of SOA. These results could then be passed off to a chemical transport model, such as CMAQ, which would model larger atmospheric scale processes allowing the modeling system to encompass all the necessary spatial and temporal scales.

## Conclusions

A framework has been applied to model the contributions of aircraft emissions to  $PM_{2.5}$  and organic aerosols using VBS within CMAQ. Added to this framework was the inclusion non-traditional SOA particle formation from aircraft emissions of SVOCs and IVOCs. Results compared against urban and rural monitoring sites in Georgia indicate that this new framework provides better predictions of  $PM_{2.5}$  and total carbon.

Overall contributions from aircraft to  $PM_{2.5}$  in CMAQ and CMAQ\_VBS were comparable in the grid cells containing ATL, JST, and YRK. The CMAQ results indicated slightly higher contributions from  $PM_{2.5}$  at the airport while the CMAQ\_VBS results indicated higher  $PM_{2.5}$  contributions downwind of the airport at YRK. The increased downwind contributions are largely attributable to higher contributions from anthropogenic SOA and the oxidized organic aerosols.

This work is a portion of a larger body of work that involves collaborating with multiple research groups to enhance the VBS framework in CMAQ and incorporate plume scale models, such as CMAQ-AMSTERDAM (Karamchandani, 2000) and ADSC with an end goal of developing an enhanced modeling system to predict OC contributions from aircraft. Additionally, future work is needed to accurately quantify and characterize emissions from aircraft, particularly SOA precursors (including SVOCs and IVOCs), possibly through measurement campaigns.

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