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CMAQ Model Performance Enhanced When In-Cloud Secondary Organic Aerosol is Included: Comparisons of Organic Carbon Predictions with Measurements

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Mounting evidence suggests that low-volatility (particle-phase) organic compounds form in the atmosphere through aqueous phase reactions in clouds and aerosols. Although some models have begun including secondary organic aerosol (SOA) formation through cloud processing, validation studies that compare predictions and measurements are needed. In this work, agreement between modeled organic carbon (OC) and aircraft measurements of water soluble OC improved for all 5 of the compared ICARTT NOAA-P3 flights during August when an in-cloud SOA (SOA_{cld}) formation mechanism was added to CMAQ (a regional-scale atmospheric model). The improvement was most dramatic for the August 14th flight, a flight designed specifically to investigate clouds. During this flight, the normalized mean bias for layer-averaged OC was reduced from −64 to −15% and correlation (r) improved from 0.5 to 0.6. Underpredictions of OC aloft by atmospheric models may be explained, in part, by this formation mechanism (SOA_{cld}). OC formation aloft contributes to long-range pollution transport and has implications to radiative forcing, regional air quality and climate.

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Introduction

Despite the importance of atmospheric organic particulate matter (PM) to climate, air quality, and health, its sources and formation remain poorly understood (*1, 2*). Most global and regional models fail to accurately predict particulate organic carbon (OC) concentrations. Organic PM is underpredicted in summer (*3*), especially in the free troposphere (*4*); variations in OC concentrations are not captured well by atmospheric models (*5*). Errors in emission estimates, meteorology, and uncertainties in secondary organic aerosol (SOA) partitioning are considered unlikely causes for the disagreement between predicted and observed particulate OC aloft (*4*). Discrepancies are believed to result largely from poorly understood SOA formation processes; 20−50% of continental organic PM at the mid latitudes is of secondary origin (*1*).

The cloud processing hypothesis for SOA formation (*6*) is that water-soluble oxidation products of reactive organic compounds partition into cloud droplets, oxidize further, and create low-volatility compounds that remain, in part, in the particle phase upon droplet evaporation (>90% of cloud droplets evaporate (*7*)). Cloud-production of SOA (SOA_{cld}) is a secondary PM formation process supported by laboratory and field evidence but currently missing from most atmospheric models. This missing pathway provides a plausible explanation for the recently noted failure of models to predict accurate vertical, spatial, and temporal OC profiles. Including (SOA_{cld}) in atmospheric models will add OC at multiple elevations with temporal and spatial variability. Results from a recent modeling study that included SOA_{cld} suggest that this process is atmospherically important (*8*). However, validating measurement comparisons are still needed. In this work, model OC predictions were evaluated using aircraft water soluble OC concentrations from five flights (summarized in Table 1) and a month of OC concentrations from two ground-level air monitoring networks.

In-Cloud SOA: Plausibility and Current Understanding

Cloud production of secondary inorganic aerosol (i.e., sulfate) is well documented and growing evidence supports cloud production of SOA. Temporal and diurnal concentration dynamics support in-cloud production of low volatility carboxylic acids in the atmosphere (e.g., oxalic acid) from precursor water-soluble aldehydes (e.g., glyoxal and methylglyoxal) (*9*) and zero-dimensional modeling demonstrates kinetic feasibility for a variety of additional precursors (e.g., glyocolaldehyde, glycolic acid, pyruvic acid) (*10*−*13*). Glyoxal and methylglyoxal are highly water-soluble compounds found widely in the atmosphere with anthropogenic and biogenic precursors (*14, 15*). Oxalic acid (usually measured as oxalate and predominantly present as the monoanion at typical cloud pH) is found widely in the environment, primarily in the particle phase (*16*); primary sources are not sufficient to explain observed concentrations (*17*). Positive correlations between atmospheric oxalate and sulfate have been documented in an array of field investigations; in-cloud formation provides the likely explanation (*18, 19*). Recent laboratory evidence confirms that oxalic acid and other low volatility species form in the aqueous phase during photo-oxidation of pyruvic acid (*13*), glyoxal (*20, 21*), and methylglyoxal (*22*). Aircraft measurements indicate elevated organic acid concentrations, with oxalic acid as substantial component, in layers above clouds, presumably as a consequence of aqueous chemistry (*23*−*25*).

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TABLE 1. Statistical Measures of CMAQ-Predicted OC and WSOC Measurements for ICARTT Flights[a]

	base CMAQ model	CMAQ with SOA_{cld}	flight
correlation (r)	0.77	0.78	3-Aug
	0.76	0.81	6-Aug
	0.15	0.19	11-Aug
	0.47	0.57	14-Aug
	0.92	0.93	15-Aug
normalized mean bias	−100%	−98%	3-Aug
	−59%	−49%	6-Aug
	−68%	−66%	11-Aug
	−64%	−15%	14-Aug
	−82%	−61%	15-Aug

	WSOC measurements	OC base CMAQ	OC With SOA_{cld}	flight
mean carbon ($<\mu g\ m^{-3}$)	2.4	0.7	0.8	3-Aug
	0.9	0.4	0.5	6-Aug
	3.4	1.0	1.0	11-Aug
	0.9	0.2	0.6	14-Aug
	1.5	0.3	0.5	15-Aug

[a] Note: Statistical measures for ICARTT comparisons are for layer-averaged CMAQ-predicted OC and PILS-measured WSOC.

Most notably, formation of SOA from cloud processing of isoprene oxidation products is predicted to affect air quality (*8*). However, SOA_{cld} modeling efforts remain to be validated with measurements. Reaction rate constants used in previous cloud chemistry models (*11, 12*) were chiefly developed from laboratory experiments that measured reactant disappearance; reaction mechanisms and products were mostly assumed from bond strength calculations. This represents a substantial knowledge gap. To validate and refine current cloud chemistry mechanisms, aqueous photochemical experiments with detailed product analysis were performed for pyruvic acid, glyoxal, and methylglyoxal with hydroxyl radical, the predominant aqueous phase atmospheric oxidant (*26*). Recent laboratory experiments demonstrate that previous aqueous phase mechanisms inadequately describe oxidation pathways, rates, and products (*13, 20−22*). The chemical transport modeling described in this paper makes use of yields from those laboratory photooxidation experiments.

Daily OC predictions from Community Multiscale Air Quality (CMAQ) model simulations (August 1−31, 2004) conducted with and without SOA_{cld} were compared with ground-based measurements of OC from two monitoring networks and with aircraft measurements of water soluble OC (WSOC). CMAQ model performance improved when SOA_{cld} was included. Addition of SOA_{cld} reduced the normalized mean bias between CMAQ OC predictions and ground level OC measurements from the Speciation Trends Network (STN; urban) and from the Interagency Monitoring of Protected Visual Environments (IMPROVE; rural/background) network. Correlations increased and bias was reduced when CMAQ OC predictions with SOA_{cld} were compared with WSOC concentrations aloft measured with a particle-into-liquid sampler (PILS) aboard the NOAA P3 aircraft (*27*) during the International Consortium for Atmospheric Research and Transformation (ICARTT) campaign.

Model Development, Application, and Limitations

An in-cloud SOA formation parametrization was included in a regional scale chemical transport model, the Models-3 Community Multiscale Air Quality (CMAQ), model version 4.6 (www.cmascenter.org). Simulations for August 1−31, 2004 were conducted for the eastern U.S. (12 km horizontal resolution, vertical extent from the surface to 100 mb) twice, once with and once without the in-cloud SOA mechanism. The meteorology for these simulations was developed using the MM5, version 3.6.3 model (Supporting Information). Addition of cloud produced SOA did not reduce SOA formation from other pathways because glyoxal and methylglyoxal are not precursors for other types of SOA in CMAQv.4.6 and $^{\bullet}OH$ is not an advected species (e.g., consumption occurs only for an individual time step). SOA precursors in CMAQv4.6 are monoterpenes, alkanes, xylene, creosol, and toluene. A detailed description of CMAQ aerosol processes and SOA formation is discussed in ref *28*. Additional CMAQ configuration and input details are in the Supporting Information.

Gas-phase concentrations of glyoxal and methylglyoxal were simulated as oxidation products of isoprene and aromatics using the SAPRC mechanism (*29*). Water-soluble fractions of glyoxal, methylglyoxal, and $^{\bullet}OH$ partitioned into the aqueous phase (according to Henry's Law) and reacted, consistent with measured reaction rates ($k_{GLY\text{-}OH} = 3E10$ (*21*), k_{MGLY} assumed to be the same). SOA_{cld} yields (1−10%) (molar) were applied stoichiometrically within the CMAQ aqueous chemistry module (aqchem) to the reacted fractions of glyoxal and methylglyoxal. Organic mass not retained as aerosol is assumed to oxidize to CO_2 and the yield value accounts for this loss. All gas-, aqueous-, and aerosol-phase species were subject to wet deposition.

Recent laboratory findings suggest SOA_{cld} yields range from 1 to 10% (molar) resulting from large, higher molecular weight compounds, in addition to monomeric carboxylic acids formed during aqueous photooxidation. The oxalic acid yield (mass) from aqueous photooxidation of glyoxal at 10 min of reaction time (typical of cloud contact time for one cloud cycle (*11*) has been reported as 1% (*21*). This yield was converted to a molar basis, and a 3% molar yield for higher molecular weight species was estimated from total organic carbon (TOC) measurements at 10 min (TOC minus sum of quantified species). Their sum (4%) is the total SOA_{cld} molar yield used in these simulations (further information provided in the Supporting Information), but molar yields can range from ∼1% for oxalic acid alone (from glyoxal) and ∼10% for oxalic acid and higher molecular weight species. Uncertainty arises when yields calculated from laboratory experiments conducted under controlled conditions (e.g., pH = 4.1−4.8 (*21*)) are extrapolated to the atmosphere. However cloud parcel modeling with explicit kinetic aqueous phase chemistry demonstrates little sensitivity in SOA_{cld} yields to pH; cloud contact time is the most sensitive parameter (*30*). To describe uncertainty in yield values, the range (1−10%) was used to provide bounds and describe uncertainty in model-predicted OC concentrations in Figure 1 (gray shading). When the glyoxal kinetic mechanism was explicitly incorporated into a cloud parcel model (*30*), the calculated SOA_{cld} yield from isoprene at VOC/NOx ratios ∼5, (typical of CMAQ-predicted ratios in these simulations at cloud-relevant altitudes), supports a higher yield *from glyoxal/methylglyoxal* than used here, suggesting these results are conservative.

CMAQ model evaluation was conducted using WSOC concentrations from five ICARTT flights (Table 1, Figure S-1,Supporting Information) and with a month of daily averaged OC concentrations from STN and IMPROVE. CMAQ OC predictions were calculated from organic aerosol mass predictions using organic matter-to-organic carbon (OM/OC) ratios for all organic aerosol species (*31*). It should be noted there is some difference between these metrics (i.e., WSOC represents only the water-soluble fraction of total OC). This difference is diminished however when SOA is a substantial contributor to OC because SOA is oxygenated/water soluble.

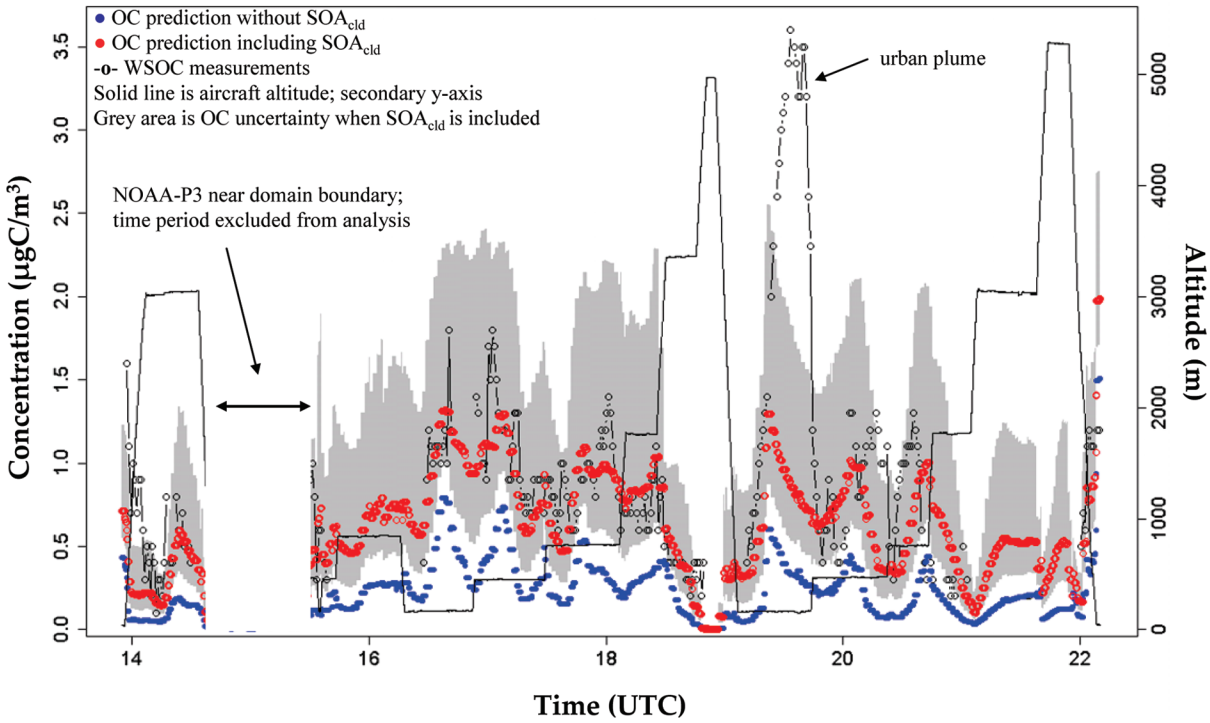

FIGURE 1. CMAQ-predicted OC and WSOC measurements (black) made from the August 14 NOAA-P3 flight during ICARTT. Base CMAQ OC predictions (blue) and CMAQ OC prediction including cloud-produced SOA (red) are plotted on the primary *y*-axis; plane altitude (solid line) is plotted on the secondary *y*-axis. Note agreement between measured WSOC and OC (when SOA$_{cloud}$ is included) in particular at elevated altitude. Gray area indicates uncertainty. The lower bound assumes a 2% mass yield (oxalic acid only) and the higher bound assumes a 32% mass yield (oxalic acid and higher molecular weight compounds).

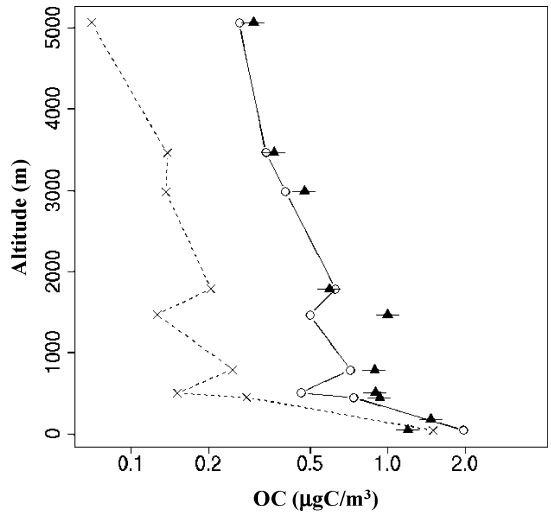

FIGURE 2. Layer-averaged vertical profiles of OC and WSOC on August 14, 2004. Normalized mean bias for layer-average values for this flight was reduced from −65% to −15% when SOA$_{cld}$ was included. Note: Dashed line and "×" indicates layer-averaged base CMAQ OC prediction. Solid line and "○" indicates CMAQ OC prediction with cloud-produced SOA included. WSOC observations, from the NOAA P3 flight are indicated with "▲". The *x*-axis is log scale.

Results

Model performance for predicting OC was enhanced when SOA$_{cld}$ was included, as demonstrated by reduced normalized mean biases and improved correlations for all five ICARTT P3 flights (Table 1). Agreement between predicted OC and measured WSOC was particularly improved for the August 14th cloud experiment NOAA P3 flight (Figures 1 and 2). The August 14th flight was selected for comparison because the flight was specifically designed to investigate clouds, whereas other flights typically focused on urban or power plant plumes (Figure S-1, Supporting Information); in addition, this flight did not appear to be impacted by wild fires (Figure S-2, Supporting Information). The time series (Figure 1) and layer-averaged values (Figure 2) demonstrate that the base CMAQ model drastically underpredicts OC. Predictions that include SOA$_{cld}$ show excellent agreement with WSOC measurements. Substantial enhancement of model performance is particularly noted aloft in the improved vertical OC profile (Figure 2). The normalized mean bias for *layer-averaged* OC predictions during the August 14 flight was reduced from −64% to −15% when SOA$_{cld}$ was included.

At ∼15 UTC (Figure 1), the NOAA P3 was flying within a cloud (RH measurements at ∼100%) not predicted by the model near the horizontal domain boundary. In addition, at this time, simulated concentrations near the horizontal domain boundaries were influenced by boundary conditions (which did not include SOA$_{cld}$) because there was inflow from outside the domain. Hence, at ∼15 UTC, CMAQ predictions of OC with and without SOA$_{cld}$ are excluded from the evaluation. At ∼19 UTC when the aircraft encounters an urban plume (strong covariance of CO and WSOC, Figure S-2, Supporting Information), CMAQ underpredicts OC in the plume even with SOA$_{cld}$ included.

Note that model predictions in the surface layer (<∼34 m) were also affected. Surface OC predictions were evaluated in urban areas with data from STN and in rural and background areas with data from the IMPROVE network. The monthly averaged August 2004 OC observations were 2.6 μg m^{-3} for STN and 1.9 μg m^{-3} for IMPROVE. Without SOA$_{cld}$, CMAQ predicted monthly averages were 2.0 μg m^{-3} for STN and 1.1 μg m^{-3} for IMPROVE. Monthly averages increased to 2.2 μg m^{-3} and 1.3 μg m^{-3} for STN and IMPROVE, respectively when SOA$_{cld}$ was included. Normalized mean bias calculated from the August daily averaged total carbon observations were reduced from −44% to −22% for IMPROVE

and from −33% to −16% for STN, when SOA_{cld} was included. Correlations at the surface between CMAQ predictions with and without SOA_{cld} did not improve for the daily averaged values at either surface network.

Cloud-produced SOA predictions varied in time and space, reflecting meteorology, for example, cloud fields, suggesting SOA_{cld} may be an episodic phenomenon, though regional signals were observed (Figure S-3, Supporting Information). On August 14th, predicted daily averaged SOA_{cld} concentrations are negligible in certain areas of the domain, while in others they are substantial. The August 14th maximum predicted 24-h average SOA_{cld} concentration was $\sim 5\ \mu g\ m^{-3}$, and for total SOA, it was $\sim 10\ \mu g\ m^{-3}$; these maxima occurred at different locations. The highest SOA_{cld} concentrations and fractions tended to be in areas with the most cloud cover. At certain locations SOA_{cld} was the dominant component of predicted SOA (Figure S-3, Supporting Information). This was particularly true over the ocean. While SOA_{cld} is predicted to have a low concentration over the ocean, other SOA species are predicted to be even lower, making the SOA_{cld} fraction large. Monoterpene SOA, for example, is not efficiently transported to the remote marine environment. In addition, isoprene SOA, which is expected to contribute to remote marine OC concentrations (*32*), is not included in this CMAQ version.

Discussion and Implications

Including SOA formed through cloud processing improved OC model and measurement agreement for all five P3 flights and most substantially for the August 14th cloud experiment flight. SOA from cloud processing of glyoxal and methylglyoxal substantially increased organic PM mass concentrations in areas influenced by clouds. Increases in OC concentrations are noted for all vertical model layers, especially aloft. Elevated OC concentrations aloft have been observed in several locations (e.g., in the Eastern U.S.) (*5, 33*) and in particular, in cloud-influenced air parcels (*23*). Other studies report ground-level SOA concentrations that are elevated when air from aloft is brought to the surface (*34, 35*). In addition to OC mass increases, improved correlation for compared modeled/measured organic aerosol for all five flights, suggests that inclusion of cloud processing may improve capture of OC variability, which is currently poor (*5*). Aqueous chemistry in fair weather cumulus venting to the free troposphere was identified as a source of nitric acid in the free troposphere during ICARTT (*36*). Similarly, cloud processing can result in substantial SOA aloft, potentially explaining elevated OC measurements in the free troposphere. SOA produced aloft can be transported long distances and thus can impact air quality regionally. On the basis of our findings, continued investigation of cloud-produced organic aerosol in three-dimensional atmospheric models is warranted.

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Supporting Information Available

P3 flight tracks, acetonitrile and CO oncentrations with cloud data for the August 14th flight, spatial profiles of predicted SOA_{cld} concentrations and fractions (of total SOA) in addition to carbon measurements from glyoxal experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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