

1 Supporting Information

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3 **Condensational Uptake of Semivolatile Organic Compounds in Gasoline**
4 **Engine Exhaust onto Pre-existing Inorganic Particles**

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22 **AURAMS Description**

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24 AURAMS (version 1.4.0) is an off-line chemical transport model (CTM) that is
25 driven by the Canadian operational weather forecast model, GEM (Global Environmental
26 Multiscale model). GEM (version 3.2.2) was used to produce meteorological fields with a
27 15-km horizontal grid spacing. GEM was run for 12-hr periods from reanalysis files with
28 a 6-hr spin-up and 6-hr of simulation stored for the CTM. AURAMS was run with a 15-
29 km horizontal grid spacing for a domain covering the northeastern U.S. and eastern
30 Canada and using climatological chemical boundary conditions.

31 Gridded hourly anthropogenic point, area and on-road mobile emissions files were
32 prepared for the CTM with the 2005 Canadian and 2005 U.S. national criteria-air-
33 contaminant emissions inventories and version 2.2 of the SMOKE emissions processing
34 system. Total gasoline exhaust organic vapour was treated as an additional gas-phase
35 species in the on-road mobile emissions stream of the emissions processing system. This
36 species was emitted, transported, lost by gas-phase chemistry and allowed to reach an
37 equilibrium partitioning with sulphate aerosol based on the effective uptake coefficient fit

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38 of Equation (6) ($S=0.012+0.000137*THC^{2.53}$) where uptake has units of kg organic
39 particle per kg sulfate and GTHC has units of $\mu\text{g m}^{-3}$). A Newton iteration method was
40 used to calculate the equilibrium solution with a 1% convergence criteria for the GTHC
41 vapour. Gas-phase loss by oxidation with OH, NO₃ and O₃ was calculated with rate
42 coefficients of 1.2E-11, 1.2E-14 and 6.7E-18 cm³ molec⁻¹ sec⁻¹, respectively. These rate
43 coefficients are reactivity-weighted averages from the individual species rate coefficients
44 in the VOC emissions profile for gasoline exhaust.

45 Gasoline exhaust primary organic aerosol emissions were also modelled in
46 AURAMS as a separate tracer aerosol species. A sensitivity run was performed with
47 POA evaporation assuming that the modeled POA emissions had the volatility
48 distribution described in Robinson et al. (2007). As an example, this corresponds to POA
49 reductions by a factor of ~3.8 for dilution to ambient conditions at organic aerosol
50 concentrations of 10 $\mu\text{g/m}^3$ and a temperature of 298 K. IVOC emissions were
51 parameterized from the POA emissions in the NEIs, as in Robinson et al. (2007).

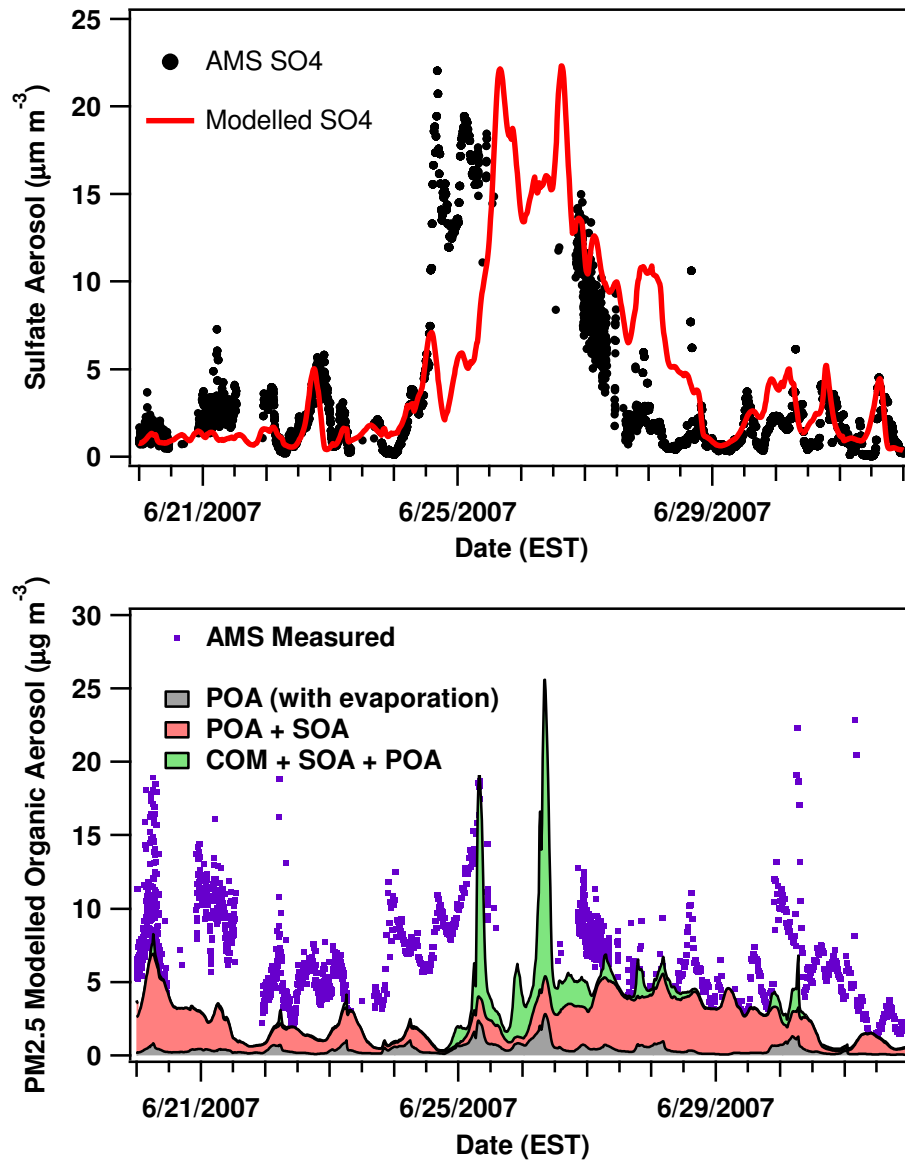
52 Biogenic emissions were calculated on-line by AURAMS using BEIS version
53 3.09, the Biogenic Emissions Landcover Database (BELD3) vegetation data set (30 tree
54 species, 20 crop species), and meteorological fields (temperature and irradiance) from
55 GEM. Biogenic VOC emissions are speciated into four groups: isoprene; monoterpenes;
56 sesquiterpenes; and "other VOCs". Monoterpene emissions for pine and spruce trees
57 were updated based on recent satellite LAI retrievals and ground survey measurements of
58 leaf area densities during the BOREAS field program in the Canadian boreal forest
59 (http://www.iwaqfr-2010.ca/presentations/Stroud_final_Emissions.ppt). Sesquiterpene
60 emissions were calculated by scaling monoterpene emissions, as described in Helmig et
61 al., (2007) (e.g., sesquiterpene emissions were a factor of 0.16 lower than monoterpenes
62 at 30C).

63 The gas-phase mechanism in AURAMS is an updated version of the ADOM-II
64 mechanism (Lurmann et al., 1986; Stockwell et al., 1989; Kuhn et al., 1998) that is solved
65 using a vectorized version of the rodas3 solver (Sandu and Sander, 2006). A detailed
66 description of the ADOM-II VOC lumping scheme can be found in Stroud et al. (2008).

67 In this study, a lumped monoterpene species was separated from the original ADOM-II
68 anthropogenic long-chain alkene species and assigned the OH/O₃/NO₃ kinetics of α-
69 pinene. A lumped sesquiterpene species was added to the mechanism and modelled with
70 β-caryophyllene OH/ O₃/NO₃ kinetics. Benzene was separated from the original ADOM-
71 II lumped species, propane (sum of propane, acetylene and benzene), and reacted in the
72 modified mechanism with OH kinetics. The overall organic aerosol yield approach was
73 applied to the following VOC precursor species: isoprene (ISOP), monoterpenes (PINE),
74 sesquiterpenes (SESQ), benzene (BENZ), mono-substituted aromatics (TOLU), multi-
75 substituted aromatics (AROM), long chain anthropogenic alkenes (ALKE), long chain
76 anthropogenic alkanes (ALKA) and intermediate volatile organic compounds (IVOC).
77 Aerosol yields were calculated for low and high NO_x limits as a function of existing
78 organic aerosol loadings (sum of primary and secondary) and temperature. Updated α_i
79 and K_i values were based on recent literature studies (ISOP, Kroll et al. (2006) and Lane
80 et al. (2008); PINE, Pathak et al. (2007), Griffin et al., (1999) and Zhang et al. (2006);
81 SESQ, Lane et al. (2008); BENZ, Ng et al. (2006); TOLU, Hildebrandt et al. (2009);
82 AROM, Ng et al. (2007); ALKE, Lane et al. (2008); and ALKA, Lane et al. (2008);
83 IVOCs, Pye and Seinfeld, (2010)). An incremental increase in SOA mass was calculated
84 from decreases in precursor VOC concentrations for a given time step under both low and
85 high NO_x conditions. A linear interpolation between the low NO_x and high NO_x
86 incremental SOA mass was performed based on the fraction of the RO₂ radicals that
87 react with HO_x vs NO_x (Presto and Donahue, 2006; Henze et al., 2008). An organic
88 particle density of 1.5 g cm⁻³ was assumed for conversion of normalized aerosol yield
89 data. The particle size distribution is represented in the CTM by 12 size bins ranging
90 from 0.01 to 40.96 μm in Stokes diameter, with the 8 lower bins corresponding to sizes
91 below 2.5 μm. Particle composition is represented by nine chemical species (sulfate,
92 nitrate, ammonium, black carbon, POA, SOA, crustal material, sea salt, and particulate
93 water), which are assumed to be internally mixed within each size bin (14). Condensation
94 of the SOA to the particle size distribution is described by a modified Fuchs-Sutugin
95 equation as described by equation A14 in Gong et al. (2003).

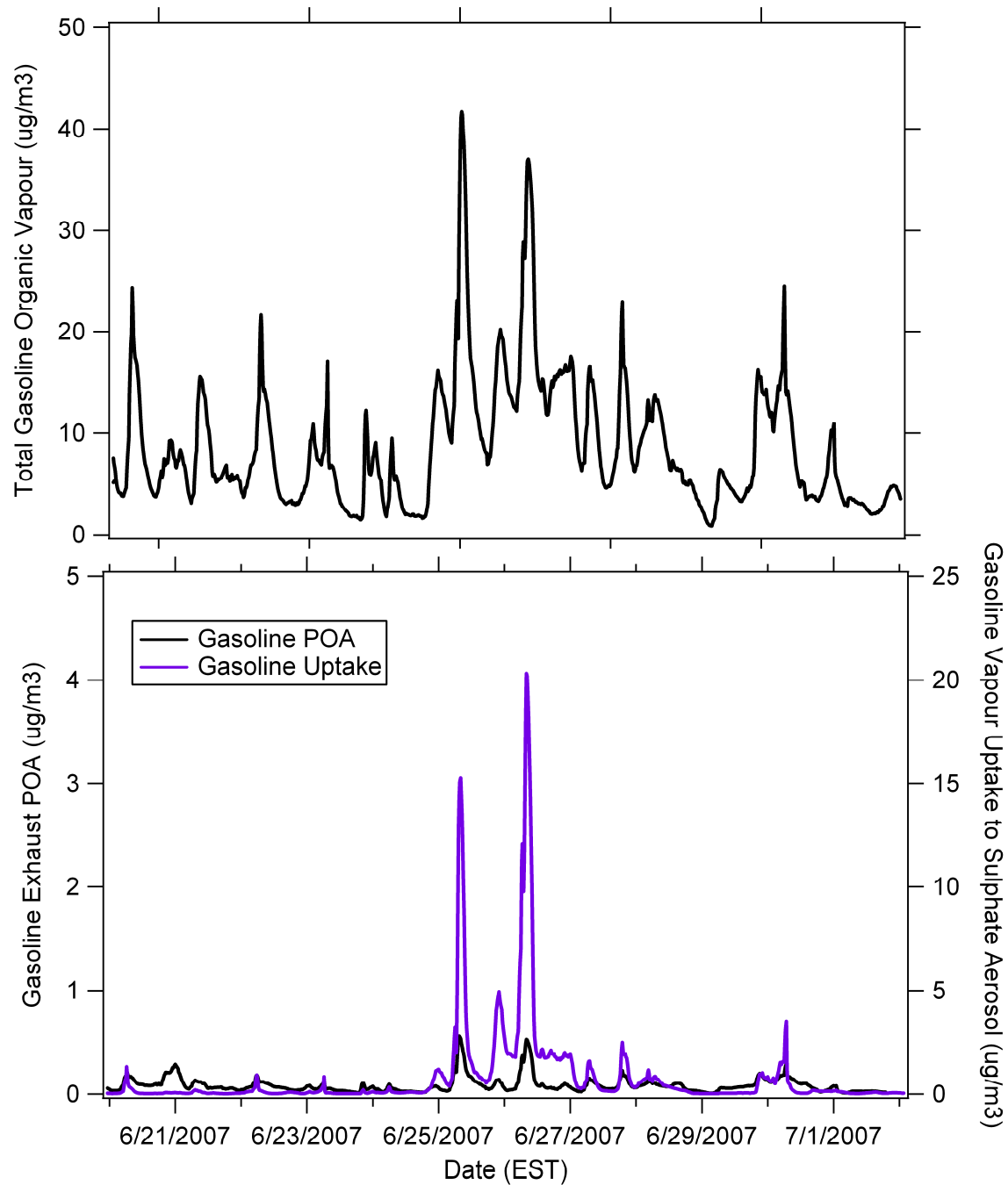
96 Figure S1 illustrates the model and measured time series at Windsor, ON for
97 sulfate and organic aerosol. Sulfate is modeled reasonably well compared to the measured
98 sulfate in terms of maximum for the 12 day period and diurnal cycles with the exception
99 of the model underestimate for the afternoon on June 25 to the following afternoon on
100 June 26. Panel b includes traces for POA (from the evaporation sensitivity run), SOA
101 (traditional method with updated monoterpene emissions for pine and spruce trees) and
102 the gasoline vapour uptake to sulfate aerosol. Good organic aerosol closure is achieved
103 for the mid-morning June 25 maximum comparing the sum of the three modeled traces
104 and the AMS organic aerosol measurements. Unfortunately, AMS data were missing for
105 the June 26 modeled maximum. For other times, model organic aerosol predictions were
106 still underpredicted. Figure S2 illustrates the gasoline vapour mixing ratio (panel a) and
107 the gasoline exhaust POA compared to the gasoline vapour uptake to sulfate aerosol
108 (panel b). The gasoline uptake to sulfate was considerably higher than the gasoline
109 exhaust POA in the NEIs.

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Figure S1. Windsor time series for measured and modelled sulphate aerosol (top panel) and organic aerosol (bottom panel, traces for POA, SOA, and COM stacked).



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Figure S2. Windsor time series for total gasoline organic vapour (top panel), gasoline exhaust primary organic aerosol (bottom panel) and gasoline vapour uptake to sulphate aerosol (bottom panel).

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