Supporting Information

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

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AURAMS Description

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

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

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of Equation (6) ($\boldsymbol{S}$=0.012+0.000137*THC$^{2.53}$) where uptake has units of kg organic particle per kg sulfate and GTHC has units of μg m^{-3}). A Newton iteration method was used to calculate the equilibrium solution with a 1% convergence criteria for the GTHC vapour. Gas-phase loss by oxidation with OH, NO_3 and O_3 was calculated with rate coefficients of 1.2E-11, 1.2E-14 and 6.7E-18 cm^3 molec^{-1} sec^{-1}, respectively. These rate coefficients are reactivity-weighted averages from the individual species rate coefficients in the VOC emissions profile for gasoline exhaust.

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

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

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

In this study, a lumped monoterpene species was separated from the original ADOM-II anthropogenic long-chain alkene species and assigned the $OH/O_3/NO_3$ kinetics of α-pinene. A lumped sesquiterpene species was added to the mechanism and modelled with β-caryophyllene OH/ O_3/NO_3 kinetics. Benzene was separated from the original ADOM-II lumped species, propane (sum of propane, acetylene and benzene), and reacted in the modified mechanism with OH kinetics. The overall organic aerosol yield approach was applied to the following VOC precursor species: isoprene (ISOP), monoterpenes (PINE), sesquiterpenes (SESQ), benzene (BENZ), mono-substituted aromatics (TOLU), multi-substituted aromatics (AROM), long chain anthropogenic alkenes (ALKE), long chain anthropogenic alkanes (ALKA) and intermediate volatile organic compounds (IVOC). Aerosol yields were calculated for low and high NO_x limits as a function of existing organic aerosol loadings (sum of primary and secondary) and temperature. Updated α_i and K_i values were based on recent literature studies (ISOP, Kroll et al. (2006) and Lane et al. (2008); PINE, Pathak et al. (2007), Griffin et al., (1999) and Zhang et al. (2006); SESQ, Lane et al. (2008); BENZ, Ng et al. (2006); TOLU, Hildebrandt et al. (2009); AROM, Ng et al. (2007); ALKE, Lane et al. (2008); and ALKA, Lane et al. (2008); IVOCs, Pye and Seinfeld, (2010)). An incremental increase in SOA mass was calculated from decreases in precursor VOC concentrations for a given time step under both low and high NO_x conditions. A linear interpolation between the low NO_x and high NO_x incremental SOA mass was performed based on the fraction of the RO2 radicals that react with HO_x vs NO_x (Presto and Donahue, 2006; Henze et al., 2008). An organic particle density of 1.5 g cm^{-3} was assumed for conversion of normalized aerosol yield data. The particle size distribution is represented in the CTM by 12 size bins ranging from 0.01 to 40.96 μm in Stokes diameter, with the 8 lower bins corresponding to sizes below 2.5 μm. Particle composition is represented by nine chemical species (sulfate, nitrate, ammonium, black carbon, POA, SOA, crustal material, sea salt, and particulate water), which are assumed to be internally mixed within each size bin (*14*). Condensation of the SOA to the particle size distribution is described by a modified Fuchs-Sutugin equation as described by equation A14 in Gong et al. (2003).

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

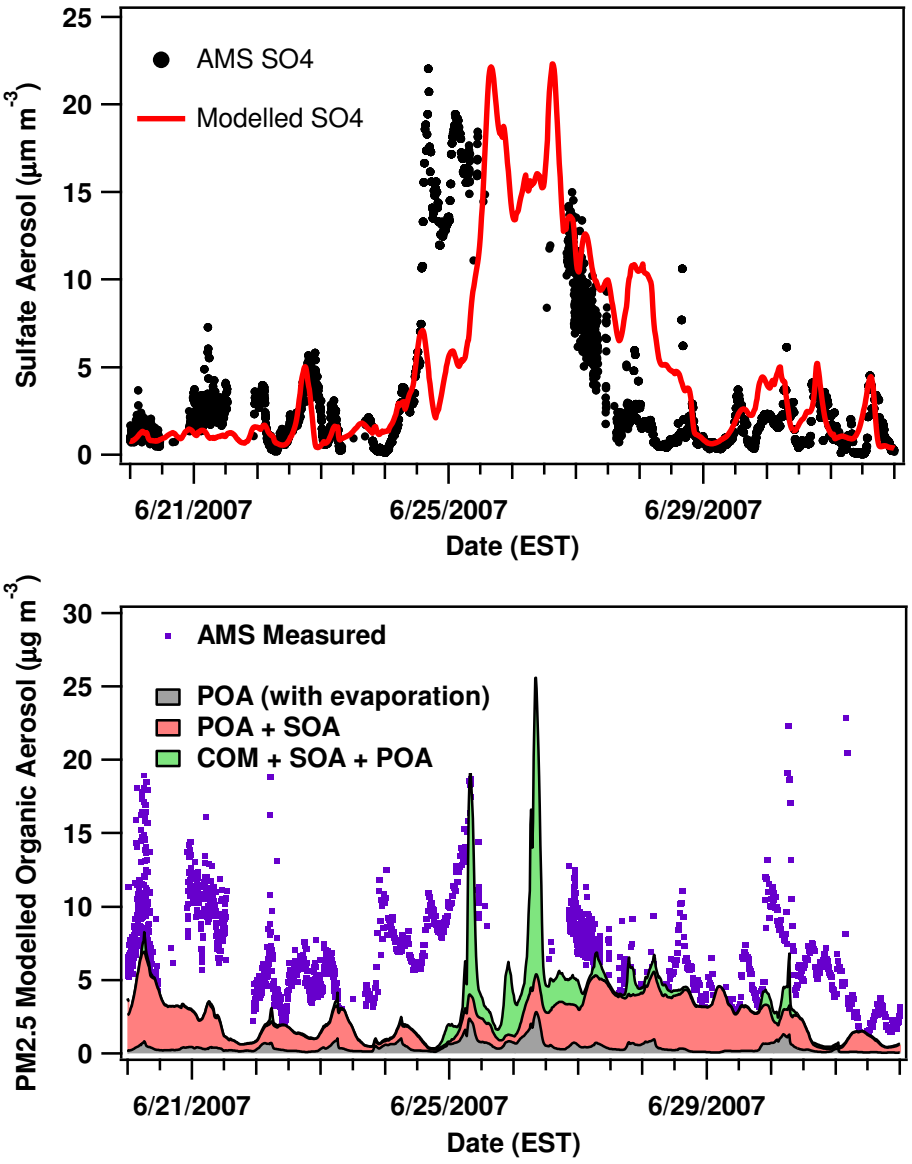

Figure S1. Windsor time series for measured and modelled sulphate aerosol (top panel) and organic aerosol (bottom panel, traces for POA, SOA, and COM stacked).

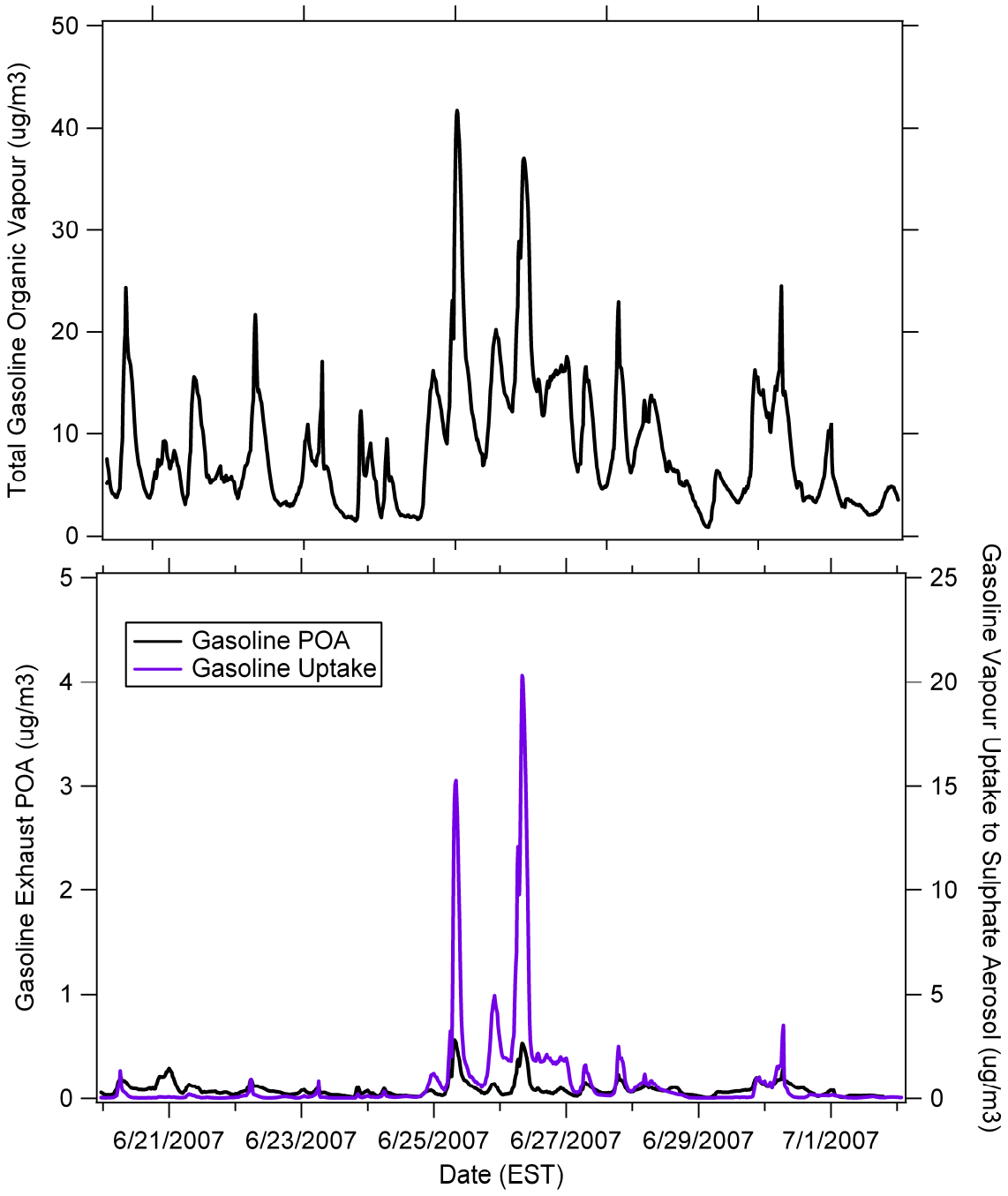

Figure S2. Windsor time series for total gasoline organic vapour (top panel), gasoline exhaust primary organic aerosol (bottom panel) and gasoline vapour uptake to sulphate aerosol (bottom panel).

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