



Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected

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[1] The atmospheric chemistry of volatile organic compounds (VOCs) in urban areas results in the formation of ‘photochemical smog’, including secondary organic aerosol (SOA). State-of-the-art SOA models parameterize the results of simulation chamber experiments that bracket the conditions found in the polluted urban atmosphere. Here we show that in the real urban atmosphere reactive anthropogenic VOCs (AVOCs) produce much larger amounts of SOA than these models predict, even shortly after sunrise. Contrary to current belief, a significant fraction of the excess SOA is formed from first-generation AVOC oxidation products. Global models deem AVOCs a very minor contributor to SOA compared to biogenic VOCs (BVOCs). If our results are extrapolated to other urban areas, AVOCs could be responsible for additional 3–25 Tg yr⁻¹ SOA production globally, and cause up to -0.1 W m^{-2} additional top-of-the-atmosphere radiative cooling. **Citation:** Volkamer, R., J. L. Jimenez, F. San Martini, K. Dzepina, Q. Zhang, D. Salcedo, L. T. Molina, D. R. Worsnop, and M. J. Molina (2006), Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, *Geophys. Res. Lett.*, 33, L17811, doi:10.1029/2006GL026899.

[2] Anthropogenic air pollution poses an increasingly serious concern for public health [*Health Effects Institute*, 2000], agriculture [*Fuhrer*, 2003], and global climate [*Ramanathan et al.*, 2001]. In 2006, for the first time in human history, more people are predicted to be living in urban rather than rural areas on our globe [*United Nations Development Programme*, 2005]. Increasing amounts of VOCs, nitrogen oxides, and primary organic aerosol (POA) are emitted into the atmosphere from numerous anthropogenic and natural sources. SOA is formed from low volatility products of VOC oxidation. Recent field studies offer evidence that SOA is significantly more

abundant than state-of-the-art SOA models predict in large compartments of the troposphere [*de Gouw et al.*, 2005; *Heald et al.*, 2005; *Johnson et al.*, 2006]. The sources of these SOA enhancements remain highly speculative, and proved difficult to link unambiguously to anthropogenic influences. Further, the relative importance of first, second, and higher generation oxidation products contributing to anthropogenic SOA growth is virtually unknown [*Hurley et al.*, 2001; *Kroll and Seinfeld*, 2005]. Current estimates deem SOA responsible for about 10–40% of the global organic aerosol (OA) mass (sum of POA and SOA); this portion may be higher regionally. About 90% of SOA is currently believed to be due to biogenic VOCs (BVOCs) [*Kanakidou et al.*, 2005]. AVOCs have therefore not been included in most modeling studies that assess the relevance of SOA to climate forcing [e.g., *Chung and Seinfeld*, 2002].

[3] The chemical transformation of SOA-precursor VOCs was studied in the Mexico City Metropolitan Area (MCMA) during April 2003, as part of the MCMA-2003 field campaign, using data collected at the CENICA super-site in the south eastern part of MCMA [*de Foy et al.*, 2005]. Direct measurements of glyoxal (CHOCHO) by open-path Differential Optical Absorption Spectroscopy (DOAS) have recently become possible, and present novel means to constrain VOC oxidation processes [*Volkamer et al.*, 2005a]. Two open-path DOAS instruments directly measured time-resolved concentrations of gas-phase CHOCHO [*Volkamer et al.*, 2005a] and numerous aromatic SOA-precursor VOCs [see, e.g., *Volkamer et al.*, 1998] among other species, with a time resolution of few minutes. Further quantitative measurements of the size-resolved aerosol chemical composition of fine particles were carried out by Aerosol Mass Spectrometry (AMS) with a 4 minute time resolution [*Salcedo et al.*, 2006]. A recently developed analysis method for AMS organic spectra now allows the separation of ambient urban OA mass into hydrocarbon-like and oxygenated components (HOA and OOA), which in urban areas show strong correspondence with POA and SOA [*Zhang et al.*, 2005]. In addition, OH-radical concentrations were measured by Laser Induced Fluorescence (LIF) [*Shirley et al.*, 2006], and further VOC speciation was determined by GC-FID analysis of canister samples [*Lamb et al.*, 2004]. Concentrations of HOA, black carbon (BC), OOA, particle nitrate, and CHOCHO, plus the rate of VOC_{SOA} oxidation are shown together with meteorological parameters for April 9 2003 (Figures 1a and 1b). This specific day follows the arrival of a clean airmass, which led to very clean morning conditions, and is characterized by low wind speeds. Pollutants gradually accumulate in a planetary boundary layer (PBL) that remained low throughout the

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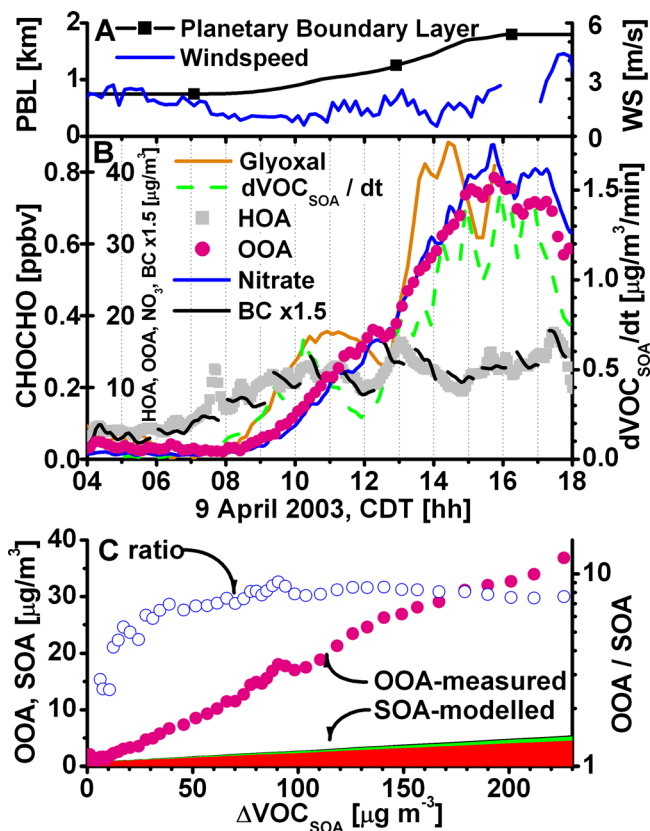


Figure 1. Measured and modeled SOA formation on April 9 2003. Time series of (a) meteorological parameters and (b) gas-phase CHOCHO, aerosol components HOA, BC, OOA, nitrate, and the rate of SOA-precursor-VOC oxidation; AMS HOA and OOA can be equated here to POA and SOA (see text). (c) Comparison of OOA and SOA. Data before 2pm is shown, when the flexible-top box-assumption (negligible pollution export from the MCMA) seems justified. Shaded areas indicate the calculated amount of SOA-mass: aromatics (red), alkenes (green), alkanes (black).

day. AMS HOA and OOA can be equated here to POA and SOA for the following reasons. The OOA time series follows other photochemical tracers, e.g., the particle nitrate, and is clearly not emitted by traffic in the early morning. OOA can neither be explained by the oxidation of HOA, i.e., due to the lack of apparent oxidation of HOA relative to BC, and because HOA oxidation provides insufficient mass to explain even a minor fraction of the OOA (Figure 1b). Finally, OOA during this day cannot have a significant contribution from biomass burning aerosol due to lack of fires or smoke transport in central Mexico (from satellite observations). SOA formation was calculated using a multicomponent gas-particle partitioning model that involves oxidation of 51 SOA-precursor VOCs (VOC_{SOA} ; 23 aromatics, 13 alkenes, 15 alkanes) to produce semi-volatile and non-volatile secondary organic gases (SOG) that partition into the aerosol phase as a function of temperature, volatility and available OA volume. The oxidized amount of VOC_{SOA} ($\Delta\text{VOC}_{\text{SOA}}$) is calculated directly from observations of OH-radicals, O_3 and VOC_{SOA} ; parti-

tioning of SOG employed SOA yields and VOC lumping from [Koo *et al.*, 2003; Odum *et al.*, 1996]. SOA dilution in the rising planetary boundary layer (PBL) is considered as the only SOA loss mechanism; three approaches to estimate PBL height (i.e., radiosondes, MM5 model [de Foy *et al.*, 2005], and a chemical tracer approach) gave consistent results. The temperature sensitivity of SOA yields was calculated using experimental values for the enthalpy of evaporation (ΔH) of SOA ($\Delta H_{\text{ARO}} = 36 \text{ kJ/mol}$, $\Delta H_{\text{BVOC}} = 85 \text{ kJ/mol}$). While the temperature sensitivity of alkane SOA is lower than that of aromatic SOA, a conservative estimate of ΔH_{ALK} was taken as that of ΔH_{ARO} [Offenberg *et al.*, 2006; Takekawa *et al.*, 2003]. Partitioning of SOG was assumed to occur into the total OA mass, i.e. to be equally efficient for both HOA and OOA mass, to derive an upper limit estimate for predicted SOA.

[4] HOA and BC from traffic emissions start rising around 6 am (local daylight savings time, UTC-5h), and account for essentially all measured aerosol mass ($\sim 10 \mu\text{g m}^{-3}$) until about one hour after sunrise (8 am), when the rise in CHOCHO indicates the start of VOC photochemistry [Volkamer *et al.*, 2005a]. OOA and CHOCHO are very low at night, and rise simultaneously in the early morning. OOA mass increases at a rate of $\sim 2 \mu\text{g m}^{-3} \text{ h}^{-1}$ (before 9:30am), $\sim 5.2 \mu\text{g m}^{-3} \text{ h}^{-1}$ in the later morning (9:30 am–12 pm), and reaches a maximum value of $\sim 8.2 \mu\text{g m}^{-3} \text{ h}^{-1}$ in the early afternoon (12 pm–3 pm), when total $\text{PM}_{2.5}$ mass peaks at $125 \mu\text{g m}^{-3}$. OA accounts for $\sim 55 \mu\text{g m}^{-3}$, of which OOA accounts for about 75% ($\sim 40 \mu\text{g m}^{-3}$). OOA is a major component of $\text{PM}_{2.5}$ mass in the afternoon. Inorganic sulfates, nitrates, chlorides, ammonium, soot and crustal material account for the remaining aerosol mass [Salcedo *et al.*, 2006]. The observed ratio of increase rates of OOA to O_3 for this day are in the range 0.2–0.65 $\mu\text{g m}^{-3}/\text{ppb}$, about an order of magnitude larger than the ratio reported previously for a relatively clean day in Pittsburgh ($0.038 \mu\text{g m}^{-3}/\text{ppb O}_3$) [Zhang *et al.*, 2005].

[5] The correlation between measured OOA mass and $\Delta\text{VOC}_{\text{SOA}}$ is excellent (Figure 1c, $R^2 = 0.96$). The amount of OOA measured in excess of the model predictions (“missing SOA”) increases towards larger $\Delta\text{VOC}_{\text{SOA}}$. The increase of OOA mass with $\Delta\text{VOC}_{\text{SOA}}$ is linear immediately after the onset of VOC oxidation, which demonstrates that primary (first generation) VOC oxidation products contribute efficiently to SOA growth. This is consistent with the simultaneous formation of CHOCHO and OOA, since about 80% of CHOCHO is formed from aromatic hydrocarbons during morning hours [Volkamer *et al.*, 2005b], and aromatics are known to form CHOCHO solely as a primary oxidation product [Volkamer *et al.*, 2001]. The aerosol yield for the VOC_{SOA} considered (i.e., the slope of Figure 1c) increases only slightly towards larger $\Delta\text{VOC}_{\text{SOA}}$ (from about 13% to 17%), indicating some minor additional OOA mass from higher generation oxidation products. The slope and ratio in Figure 1c may be biased low at extended oxidation times as our flexible-top box-model assumption does not account for mixing-in of cleaner air during pollution export from the MCMA ($\Delta\text{VOC}_{\text{SOA}} = 150 \mu\text{g m}^{-3}$ at 1:45pm). The amount of OOA formed is at least 8 times larger than predicted. Among the SOA mass accounted by partitioning theory, aromatics are the single most important SOA-precursor class in urban air (aromatics: 80% of

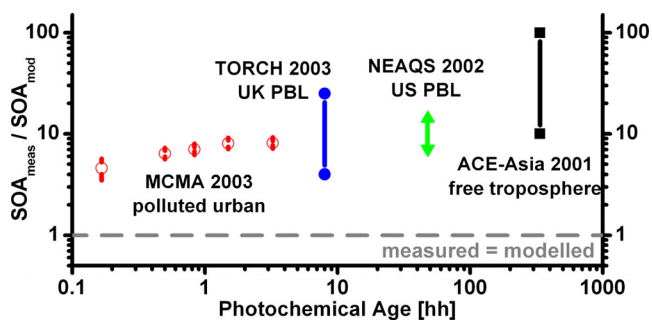


Figure 2. Comparison of the ratio of measured-to-predicted SOA from this study with other recent studies as a function of photochemical age. NEAQS-2002 refers to the study of [de Gouw *et al.*, 2005], ACE-Asia 2001 [Heald *et al.*, 2005], TORCH-2003 [Johnson *et al.*, 2006]. The photochemical age is calculated here as equivalent time assuming an OH-radical concentration $[OH] = 3 \times 10^6$ molec cm^{-3} , but use of any other OH-radical concentration would not alter the conclusions.

predicted SOA mass; alkenes 16%; alkanes 4%); similar models produced similar results in other urban atmospheres [Koo *et al.*, 2003]. The reactivity of OH-radicals in Mexico City is largely determined from reaction of OH-radicals with VOCs, and is accounted to within 20% from summation over individual measured sink terms [Shirley *et al.*, 2006]. VOC reactivity is overwhelmingly dominated by AVOCs in Mexico City (over 95% of the OH-reactivity), while isoprene and terpene-reactivity add less than 5%. Similar differences in measured-to-predicted SOA were found during MCMA-2003 for all other days studied. The contribution of BVOCs is expected to be higher downwind of the MCMA, as these may mix into the O_3 (and possibly NO_3) rich city plume. We conclude that the major SOA formation pathway is currently unaccounted for in urban air. It is unequivocally controlled by anthropogenic pollution factors in our study, and linked - though not limited - to primary oxidation products of reactive AVOCs.

[6] Our results are unique in extending existing evidence for a missing SOA source in large compartments of the atmosphere towards much shorter time-scales, and into the urban atmosphere (Figure 2). In the US PBL near the New England coast, ship observations [de Gouw *et al.*, 2005] show continued SOA formation after aging times of 2–3 days. The measured-to-modeled SOA-ratio of 14 could be biased high by up to a factor of two due to a somewhat uncertain role of BVOC in that study. Similar results were observed at slightly shorter oxidation time scales in the PBL downwind of London, UK [Johnson *et al.*, 2006]. Even larger differences are found in the free troposphere downwind of East Asia [Heald *et al.*, 2005]. Here models fall short in predicting SOA by one to two orders of magnitude. Recent estimates of global SOA from isoprene [Henze and Seinfeld, 2006] may explain a small fraction of these SOA enhancements, with the major fraction remaining unexplained. Isoprene certainly cannot explain SOA enhancements in Mexico City. Based on our results a tendency for increasing differences between predicted and measured SOA with photochemical age becomes apparent. The measured-to-predicted SOA-ratio is about 5 shortly after sunrise

and almost an order of magnitude after a few hours of oxidation. The atmospheric lifetime of first-generation oxidation products delays higher generation products to contribute to SOA (i.e. 30 min under conditions of Figure 2, assuming that primary oxidation products reacted at gas-collision rate with OH-radicals, i.e., $k_{OH} = 2 \times 10^{-10}$ cm^3 molec^{-1} s^{-1}). Thus, 10 mins after the onset of VOC oxidation only first-generation oxidation products can contribute to the factor of 5 higher “missing SOA”. This further corroborates our conclusion about the important role of first-generation oxidation products in SOA formation. The missing SOA source cannot be explained by contributions from BVOC (due to low concentrations of BVOCs), or cloud processing (higher than predicted SOA is observed during both cloudy and cloud-free mornings). Use of lower SOA yields found at elevated NO_x concentrations [Song *et al.*, 2005] would only increase the observed differences further. In addition, predicted SOA is fairly robust with respect to uncertainties in the PBL dynamics: for our case study predicted SOA mass is about 40% lower compared to the undiluted calculation at 3 pm, reflecting SOA is produced from an airborne source. Some uncertainty ($\sim 30\%$) exists in the exact value of enthalpy of evaporation. However, it is not possible to explain the measured SOA mass from model or measurement uncertainties.

[7] The SOA precursors and chemical pathways of SOA formation are presently not identified. This large missing SOA source is particularly surprising in urban air, as conditions in simulation chambers approximate the polluted atmosphere to the best possible extent with respect to VOC/ NO_x ratios, NO_x concentrations, temperatures, humidity, the pool of condensable species produced, OH-radical levels, and light conditions. Differences exist in the complex mixture of VOCs and pre-existing aerosols in urban air.

[8] Only two studies have quantified the global SOA production from AVOC to date [Tsigaridis and Kanakidou, 2003; Lack *et al.*, 2004]. These deem AVOC responsible for about 0.4–2.6 Tg yr^{-1} SOA or about 6 ± 2 % of the respective global SOA production. Based on these estimates the results from Mexico City extrapolate to 3–25 Tg yr^{-1} global SOA production from AVOC; one third of global SOA could be from AVOCs. Increased partitioning of SOG from AVOC and BVOC to aerosols due to additional global OA mass from SOA_{AVOC} will further increase global SOA production. The direct effect of SOA, i.e., to cool the atmosphere by increasing the scattering of radiation back to space, increases proportionally with the SOA burden [Maria *et al.*, 2004]; this additional SOA source could account for about -0.1 W m^{-2} top-of-the-atmosphere radiative cooling. Further, BC is quickly internally mixed with organic and inorganic aerosol components in Mexico City [Johnson *et al.*, 2005; Salcedo *et al.*, 2006]. The additional SOA source in urban air will enhance the absorption of BC [Jacobson, 2000], which heats the air by absorbing radiation, with implications for atmospheric stability and vertical motions, precipitation patterns, and the amount of radiation reaching the ground [Ramanathan *et al.*, 2001].

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