

# A Larger Pool of Secondary Organic Aerosol Precursors in Continental Air

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## I. Introduction

Measurements of aerosol in urban atmospheres and downwind of densely populated regions suggest production of secondary organic aerosol (SOA) cannot be explained by oxidation of organic gases that are routinely measured [de Gouw et al., 2005; Volkamer et al., 2006]. Laboratory experiments demonstrated exhaust from diesel-powered vehicles (DPVs) produced more SOA than the amount predicted from oxidation of volatile organic compounds (VOCs) in the emissions that are known precursors of SOA [Robinson et al., 2007]. A complex mixture of hydrocarbon-like, semivolatile organic compounds (HSVOCs) is suspected of producing the additional SOA. The HSVOCs and suspected oxidation products are not routinely measured in ambient air or are measured with insufficient temporal resolution to evaluate SOA formation rates. Here, gas-aerosol partitioning characteristics of the likely semivolatile precursors of SOA are evaluated, an HSVOC emission profile for a roadway tunnel is developed, and the annual contribution of vehicle-derived, semivolatile SOA precursors to SOA formation in the United States is estimated.

## II. Atmospheric Organic Matter C<sub>2</sub>-C<sub>31</sub>

Volatile SOA precursors are collected in treated stainless steel sampling canisters from which VOCs with vapor pressures less than ~190 Pa (the vapor pressure of *n*-C<sub>10</sub>) are incompletely recovered, or they are drawn directly into a gas chromatograph or proton transfer reaction-mass spectrometer that lacks sufficient sensitivity to quantify HSVOCs, occurring in continental air at mixing ratios of ~1 pptv. The HSVOCs are collected with a high-volume air sampler that incorporates a glass fiber filter to trap particles and an adsorbent bed downstream to preconcentrate gas-phase organic compounds. Levels of total volatile *n*-alkanes in urban air are typically present in the ten's of ppbv and mixing ratios of total semivolatile *n*-alkanes in background continental air are typically in the ten's of pptv and sub pptv in the gas- and aerosol-phases, respectively (Fig. 1). The unresolved complex mixture (UCM) is composed of a myriad of branched and cyclic aliphatic and aromatic hydrocarbons [Fryzinger et al., 2003].

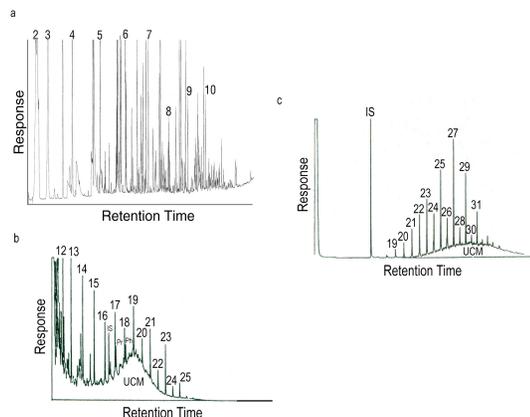


Figure 1. One-dimensional gas chromatograms of (a) VOCs in Mexico City, and (b,c) the aliphatic fractions of gas- and aerosol-phase HSVOCs during summer and winter, respectively, in a semireport forest [Doskey and Andren, 1986; Doskey, 2006]. (The *n*-alkanes are identified by the number of carbon atoms, IS, internal standard; Pr, pristane; Ph, phytane; UCM, unresolved complex mixture.)

## III. Gas-Aerosol Partitioning of HSVOCs in Vehicle Tailpipe Emissions

Tailpipe emissions from gasoline- and diesel-powered vehicles (GPVs, DPVs) contain a complex mixture of gas- and aerosol-phase HSVOCs including C<sub>11</sub>-C<sub>29</sub> *n*-alkanes, C<sub>14</sub>-C<sub>20</sub> isoprenoids (norfarnesane, farnesane, 2,6,10-trimethyl tridecane, norpristane, pristane, and phytane), C<sub>11</sub>-C<sub>25</sub> *n*-alkylcyclohexanes, C<sub>11</sub>-C<sub>13</sub> *n*-aldehydes, C<sub>8</sub>-C<sub>20</sub> *n*-alkanoic acids, polyaromatic hydrocarbons (PAHs), and a UCM [Schauer et al., 1999, 2002].

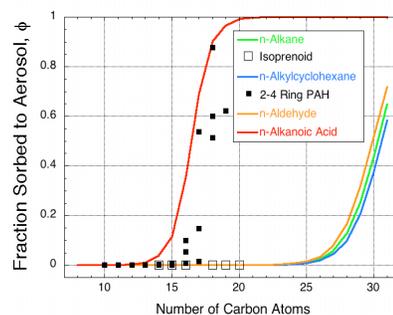
Gas-aerosol partitioning of organic substances is sensitive to the pure-component vapor pressure, aerosol concentration and chemical composition, and temperature [Pankow, 1994]. The fraction sorbed to aerosol ( $\phi$ ) can be estimated from the particle-air partition coefficient ( $K_{pa}$ ) and the total suspended particle concentration (TSP;  $\mu\text{g m}^{-3}$ ) by the following equation [Finizio et al., 1997]:

$$\phi = K_{pa} (\text{TSP}) / [1 + K_{pa} (\text{TSP})]. \quad (1)$$

Here  $K_{pa}$  is related to the octanol-air partition coefficient ( $K_{oa}$ ), which is simply the ratio of the octanol-water partition coefficient ( $K_{ow}$ ) and the dimensionless Henry's law constant ( $K_{aw}$ ).

## IV. Mixing Ratios and OH Reactivities of HSVOCs in an Urban Roadway Tunnel

Estimates of HSVOC levels in an urban roadway tunnel in Houston, Texas (i.e., Washburn Tunnel) indicate approximately 81% and 12% of the suspected SOA precursors emitted by DPVs and gasoline-powered vehicles (GPVs), respectively, are semivolatile. The magnitude of the OH reactivity of SOA precursor emissions from DPVs and GPVs are similar; however, approximately 82% and 15% of the OH reactivity from DPVs and GPVs, respectively, are contributed by HSVOCs. The HSVOCs contribute about 8% of the total OH reactivity. Similarities in the magnitude of the OH reactivity of volatile and semivolatile SOA precursors indicate they would contribute equally to SOA formation in and downwind of Houston. However, C:O ratios of aerosol diminished from ~3-1.5 downwind of Mexico City [Jimenez et al., 2009], which might indicate the reaction of OH with some HSVOCs is more rapid than the reaction of monoaromatics with OH.



## V. Composition of HSVOC-Derived SOA and Contribution to SOA Formation in Continental Air

In the high-NO<sub>x</sub> conditions of urban areas, HSVOC oxidation is likely to produce a complex mixture of hydroxynitrates, dinitrates, and hydroxycarbonyls [Lim and Ziemann, 2009]. Estimates of  $\phi$  for a C<sub>22</sub> alkyl and hydroxynitrate, which are first-generation oxidation products of *n*-C<sub>22</sub>, indicate nearly all of the nitrated products would be sorbed to aerosol. However, C<sub>22</sub> hydroxy and dihydroxycarbonyls would be partially sorbed to aerosol ( $\phi = 0.21$  and  $0.64$ , respectively). Aerosol mass spectrometric data indicate semivolatile oxygenated organic aerosol is correlated with ammonium nitrate and composes ~50% of aerosol in some urban areas [Jimenez et al., 2009]. The correlation suggests aerosol-phase organonitrates might also be present; however, they are poorly measured by current technology. Using transportation statistics on annual DPV and GPV mileage in the United States, the emission profile of HSVOCs in DPV and GPV exhaust, and the reported yield of SOA from photooxidation of diesel exhaust [85%; Robinson et al., 2007], the annual contribution of semivolatile SOA precursors to SOA formation in the United States is estimated to be about 20%.

## VI. Conclusions

The SOA precursors in tailpipe emissions from DPVs and GPVs in a Houston roadway tunnel were composed of 81% and 12% HSVOCs, respectively. Similarities in the OH reactivity of volatile and semivolatile SOA precursors in DPV and GPV emissions indicate they would contribute equally to SOA formation in and downwind of Houston. First-generation oxidation products are composed of hydroxynitrates and hydroxycarbonyls that partition between the gas and aerosol phases. The HSVOCs represent about 8% of the OH reactivity in the Houston airshed and might contribute as much as 20% to SOA production in the United States. The complex mixture of semivolatile SOA precursors and oxidation products are poorly measured by current technology; thus, current models under predict SOA production and SOA levels are likely greater than currently measured.

## VII. References

- de Gouw, J.A., A.M. Middlebrook, C. Warneke, P.D. Goldan, W.C. Kuster, J.M. Roberts, F.C. Fehsenfeld, D.R. Worsnop, M.R. Canagaratna, A.A.P. Pszenny, W.C. Keene, M. Marchewka, S.B. Bertman, and T.S. Bates (2005). Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002. *J. Geophys. Res.*, **110**, D16305. doi:10.1029/2004JD005623.
- Doskey, P.V. (2006). Volatile organic compounds in the atmosphere. In *Chromatographic Analysis of the Environment*, Third Edition, ed. Leo M.L. Nollet, pp. 617-644. CRC Press, Boca Raton, FL.
- Doskey, P.V., and A.W. Andren (1986). Particulate- and vapor-phase *n*-alkanes in the northern Wisconsin atmosphere. *Atmos. Environ.*, **20**, 1735-1744.
- Finizio, A., D. Mackay, T. Bidleman, and T. Harner (1997). Octanol-air partition coefficient as a predictor of partitioning of semi-volatile organic chemicals to aerosols. *Atmos. Environ.*, **31**, 2289-2296.
- Fryzinger, G.S., R.B. Gaines, L. Xu, and C.M. Reddy (2003). Resolving the unresolved complex mixture in petroleum-contaminated sediments. *Environ. Sci. Technol.*, **37**, 1653-1662.
- Jimenez, J.L. et al. (2009). Evolution of organic aerosols. *Science*, **326**, 1525-1529.
- Lim, Y.B., and P.J. Ziemann (2009). Effects of molecular structure on aerosol yields from OH radical-initiated reactions of linear, branched, and cyclic alkanes in the presence of NO<sub>x</sub>. *Environ. Sci. Technol.*, **43**, 2328-2334.
- Pankow, J.F. (1994). An absorption model of gas/particle partitioning in the atmosphere. *Atmos. Environ.*, **28**, 185-188.
- Robinson, A.L., N.M. Donahue, M.K. Shrivastava, E.A. Weitkamp, A.M. Sage, A.P. Grieshop, T.E. Lane, J.R. Pierce, and S.N. Pandis (2007). Rethinking organic aerosols: Semivolatile emissions and photochemical aging. *Science*, **315**, 1259-1262.
- Schauer, J.J., M.J. Kleeman, G.R. Cass, and B.R.T. Simoneit (1999). Measurement of emissions from air pollution sources. 2. C<sub>1</sub> through C<sub>30</sub> organic compounds from medium duty diesel trucks. *Environ. Sci. Technol.*, **33**, 1578-1587.
- Schauer, J.J., M.J. Kleeman, G.R. Cass, and B.R.T. Simoneit (2002). Measurement of emissions from air pollution sources. 5. C<sub>1</sub>-C<sub>22</sub> Organic compounds from gasoline-powered motor vehicles. *Environ. Sci. Technol.*, **36**, 1169-1180.
- 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.

