On the flux of oxygenated volatile organic compounds from organic aerosol oxidation

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Received 24 February 2006; revised 17 April 2006; accepted 12 June 2006; published 9 August 2006.

[1] Previous laboratory and field studies suggest that oxidation of organic aerosols can be a source of oxygenated volatile organic compounds (OVOC). Using measurements of atmospheric oxidants and aerosol size distributions performed on the NASA DC-8 during the INTEX-NA campaign, we estimate the potential magnitude of the continental summertime OVOC flux from organic aerosol oxidation by OH to be as large as ~70 pptv C/day in the free troposphere. Contributions from O$_3$, H$_2$O$_2$, photolysis, and other oxidants may increase this estimate. These processes may provide a large, diffuse source of OVOC that has not been included in current atmospheric models, and thus have a significant impact on our understanding of organic aerosol, OVOC, PAN, and HOX chemistry. The potential importance and highly uncertain nature of our estimate highlights the need for more field and laboratory studies on organic aerosol composition and aging.


1. Introduction

[2] Oxygenated volatile organic compounds (OVOC) comprise a large number of the species whose transport to the remote troposphere can impact radical budgets and sequester NO$_x$ in the form of nitrates [Singh et al., 1995; Wennberg et al., 1998; Muller and Brasseur, 1999]. In addition, they play a role in the formation of organic aerosols (OA) [Kanakidou et al., 2005, and references therein]. Field campaigns have noted large concentrations of OVOC throughout the troposphere, but their budgets are poorly understood [Singh et al., 2001, 2004; Wisthaler et al., 2002].

[3] Ellison et al. [1999] suggest that oxidation of OA may provide an OVOC source to the remote troposphere.

Field campaigns have established the ubiquity of OA throughout the troposphere [Murphy et al., 1998; Kanakidou et al., 2005]. Most aerosols contain both organic and inorganic components, though significantly, the organic fraction tends to be found on aerosol surfaces [Tervahattu et al., 2002a, 2002b, 2005, and references therein].

[4] Laboratory studies have demonstrated that organic surfaces can be oxidized by OH and O$_3$ [e.g., Rudich, 2003, and references therein; Thornberry and Abbatt, 2004; Molina et al., 2004]. Several of these studies have shown volatilization of OVOC resulting from organic surface oxidation. Molina et al. [2004], for example, report the full volatilization of a C$_{18}$ alkane monolayer following heterogeneous loss of 2–3 OH radicals to the surface, with many (though not exclusively) OVOC products. Evidence for such chemistry in the ambient environment include the demonstration by Grannas et al. [2004] that photooxidation of snow phase organic matter may explain the daytime flux of lightweight OVOC from snowpack to the boundary layer, and field observations that atmospheric OA becomes more oxidized with greater oxidant exposure and/or age [Gogou et al., 1996, de Gouw et al., 2005; Quinn et al., 2005; McFiggans et al., 2005; Robinson et al., 2006].

[5] Here, we use data collected on the NASA DC-8 aircraft during the INTEX-NA campaign (H. Singh et al., manuscript in preparation, 2006) to place constraints on OA oxidation’s potential contribution to continental summertime OVOC budgets. This campaign was designed to examine the transport and transformation of airmasses over continental scales. Most of the flights took place over the North American continent and the North Atlantic in the summer of 2004.

2. Method

[6] Aerosol size distributions, surface area, and volume for particles 10 nm to 3 μm in diameter were measured on the DC-8 using a differential mobility analyzer (DMA) and an optical particle counter (OPC) [Clarke et al., 2004]. Comparison of the DMA and OPC data to measurements of larger and ultrafine particles indicates that these instruments generally capture >90% of the total aerosol surface area except in a few select plumes. The aerosol size is quantified in conditions that are often dryer than the ambient atmosphere, so the aerosols may lose water (and thus mass) prior to measurement. Correcting for this effect is non-trivial, particularly for submicron particles, so we neglect it in our calculations. Based on the ratio of ambient to dry aerosol scattering coefficients, we believe the resulting underestimate of ambient surface area is significantly less than a factor...
where the factor of $\frac{1}{4}$ converts aerosol surface area to cross sectional area, $(8RT/\pi M)^{1/2}$ is the thermal speed of the oxidant (R is the universal gas constant, T is temperature, M is the oxidant molar mass), S the aerosol surface area, $[O_3]$ the concentration of oxidant (converted to a 24-hour average in the case of OH), and $f(D)$ the correction applied due to gas-phase diffusion limitations to large particles (for OH only) [Fuchs and Sutugin, 1971].

[8] For each point along the DC-8 flight track, we estimate a 24-hour average [OH] by scaling the observed [OH] by the ratio of the diurnally-averaged to instantaneous [OH] calculated from the highly-constrained NASA LaRC photochemical box model [Crawford et al., 1999]. The main source of uncertainty in determining the diurnal average is that cloud effects, which during INTEX-NA normally altered actinic flux ~20% relative to clear sky conditions, are assumed to be constant throughout the day, though they are generally transient. We expect that our large data set sufficiently captures the variability of cloud effects such that they will not significantly bias our estimate.

[9] Following the studies of Bertram et al. [2001] and Molina et al. [2004] we assume that each OH collision is reactive ($\gamma = 1$) and volatilizes 6 organic carbons. Although the alkane used in the Molina et al. [2004] study is not representative of all OA surfaces, long chain fatty acids may comprise a significant fraction [Tervahattu et al., 2002a, 2002b, 2005]. These parameters, which also assume full aerosol surface coverage by organic substrates, represent by far the largest uncertainties in our analysis. Because our assumptions imply a unity accommodation coefficient ($\alpha = 1$), we account for diffusion limitations in calculating the OH collision rate.

[10] Estimating the OVOC flux from aerosol collisions with $O_3$ and $H_2O_2$ is significantly more challenging and is not attempted here. While OH is highly reactive with many classes of organic compounds, $O_3$ reactivity and product yield are very substrate dependent [Rudich, 2003; Thornberry and Abbatt, 2004]; such selectivity also means that $\gamma_{O_3}$ would be time dependent as reactive sites are depleted [Poschl et al., 2001; Ammann et al., 2003]. Also, unlike for OH [Molina et al., 2004], $O_3$ reactivity with solid organic surfaces may depend on relative humidity [Poschl et al., 2001]. For $H_2O_2$, we found no experimental studies allowing us to constrain $\gamma$ or the product yield. For these oxidants, though, estimating the collision rate with aerosols is a first step for assessing their potential contributions to OVOC flux. We expect that the accommodation coefficients for these two oxidants are significantly less than unity – Berkowitz et al. [2001], for example, estimate $\gamma_{O_3} \sim 10^{-3}$ – and thus do not consider diffusion limitations for their collision rates.

Figure 1. Mean profiles of aerosol collision rates with (a) OH, (b) O$_3$, and (c) H$_2$O$_2$. Horizontal lines show the interquartile range and x’s are the elevation bin medians.

collisions = $\frac{1}{4} \times (8RT/\pi M)^{1/2} \times S \times [O_3] \times f(D)$

3. Results and Discussion

[11] Calculated 24-hour average collision rates are plotted as a function of elevation in Figure 1. For OH (Figure 1a) and $O_3$ (Figure 1b), most of the variability is driven by the (dry) aerosol surface area, which varies from ~10 $\mu$m$^2$ cm$^{-3}$ in the upper troposphere to ~150 $\mu$m$^2$ cm$^{-3}$ in the lowest elevation bin. For OH, we estimate the upper tropospheric collision rate to be ~1 x 10$^5$ collisions cm$^{-3}$ s$^{-1}$. Our assumption of carbon volatilization from Molina et al. [2004] thus yields an estimated OVOC source of ~70 pptv C/day in the upper troposphere. A significantly larger source
would exist in the lower troposphere (~500 pptv C/day in the lowest 2 km), but the contribution of this mechanism to OVOC concentrations will be less significant because of the much larger OVOC sources from gas phase oxidation of larger hydrocarbons in this region.

[12] Assuming a product yield for O3 similar to that of OH, the ratio of OH to O3 collisions gives a value of $g_{O3} \sim 10^{-6}$ necessary for the OVOC flux from O3 to equal that from OH. Achieving this value would require only ~0.1% surface coverage by typical alkene liquids ($g_{O3} \sim 3 \times 10^{-3}$ [de Gouw and Lovejoy, 1998; Rudich, 2003]). Thus, it is plausible that for certain aerosols reaction with O3 can be a significant oxidation mechanism. This is particularly true in the lower troposphere, where most primary (i.e., more unsaturated) OA is expected to reside. For H2O2 (Figure 1c), the equivalent $g_{H2O2}$ ranges from $\sim 10^{-5}$ in the lower troposphere to $\sim 10^{-2}$ in the upper troposphere, so H2O2’s contribution to OVOC flux is likely confined to the lower troposphere or in cloud. Because of clouds’ high aerosol surface area, increased actinic flux, and potential for aqueous phase chemistry, aerosol oxidation in clouds may warrant particular attention.

[13] Photolysis can, in principle, also lead to the decomposition of OA [Kieber et al., 1990]. To be competitive with the OH chemistry, however, photolysis rates would have to be relatively fast ($J \sim 10^{-6} \text{ s}^{-1}$), as photolysis is likely less efficient at degrading organic molecules in the condensed phase than in the gas phase: caging effects can stabilize the intermediates and aid their recombination or polymerization, preventing volatilization.

4. Atmospheric Implications

[14] A dispersed and previously unconsidered source of OVOC from OA oxidation may have important implications for tropospheric photochemistry. For example, measurements of acetaldehyde (CH3CHO) have repeatedly exceeded model predictions [Singh et al., 2001, 2004; Wisthaler et al., 2002]; this was also true during INTEX-NA (Figure 2a). For each acetaldehyde measurement, we divide the difference between measured and box model-predicted mixing ratios by the photochemical lifetime to estimate the flux necessary to reconcile the difference. We find that a source of ~90 pptv/day (~180 pptv C/day) is required to sustain the observed acetaldehyde concentrations in the upper troposphere. INTEX-NA also marked the first extensive airborne measurements of peroxyacetic acid (CH3C(O)OOH, PAA), which significantly exceeded model-predicted values in the upper troposphere as well (Figure 2b); a similar analysis for PAA yields an estimated missing source of ~20–200 pptv C/day (J. Crounse et al., manuscript in preparation, 2006). Even considering only acetaldehyde, oxidation by OH alone is likely too small to explain the upper tropospheric discrepancies between OVOC measurements and models; other oxidation mechanisms or alternative explanations are needed.

[15] A significant flux of OVOC from aerosol would have consequent impacts on HOx and peroxyacetyl nitrates. In fact, if the observations and our understanding of the subsequent chemistry of acetaldehyde are correct, peroxyacetyl nitrate (CH3C(O)OONO2, PAN) formation is very fast in the upper troposphere. Observations of PAN are not, however, consistent with those of acetaldehyde, based on current understanding of the chemistry that links these compounds [Staudt et al., 2003].

[16] A large OVOC flux from aerosol is also incompatible with current estimates of OA budgets. The Intergovernmental Panel on Climate Change [2001] estimate of OA production (and loss) is ~150 Tg “organic matter”/yr, or ~100 Tg C/yr. If our estimated OA oxidation rate from OH were representative of the entire atmosphere, the global flux of organic carbon from aerosol would be as large as ~150 Tg C/yr (integrating with bin median collision rates, ~100 Tg C/yr; interquartile range, ~50–200 Tg C/yr). This is clearly an upper limit due to the assumptions of unity $g$ and that the continental summertime conditions of INTEX-NA are representative. Nonetheless, even a fraction of this large flux would imply that oxidation may need to be included in OA models, which currently consider only deposition loss. From our carbon flux (and assuming internally mixed aerosols with density 1 g cm$^{-3}$ and organic carbon fraction 0.5), we estimate the median lifetime of aerosol organic carbon to be ~10 days, similar to estimates of carbonaceous aerosol lifetime against deposition of ~5–10 days [Kanakidou et al., 2005]; thus, oxidation may be an important sink, particularly in the upper troposphere and regions with minimal precipitation.

[17] Consideration of an additional significant sink of OA from oxidation would dramatically increase the required global OA production inferred from top-down analyses.
(generally calculated from measured OA burdens and estimates of the depositional loss rate). Bottom-up estimates, deduced from emission inventories and secondary organic aerosol (SOA) yields for precursor gases, may also be too low: Holzinger et al. [2005], for example, demonstrate that many biogenic SOA precursors are too short-lived to have been previously measured, and thus have been omitted from emission inventories. Furthermore, because of the diversity of SOA precursor gases, the photochemistry and SOA yield of only a few model compounds have been extensively studied; even for relatively well studied compounds, such as isoprene, estimates of SOA yields are undergoing significant revision upward [Limbeck et al., 2003; Claeys et al., 2004a, 2004b; Kanakidou et al., 2005; Kroll et al., 2005]. In addition, our understanding of other aspects of OA chemistry is poor. For example, Heald et al. [2005], considering only wet depositional loss, underpredict OA mass in the free troposphere 1–2 orders of magnitude, which they cannot attribute merely to OA flux underestimates.

5. Conclusions and Recommendations

Our estimate of the OVOC source and its atmospheric impact are highly speculative and uncertain due to the complexity of the processes involved and the paucity of laboratory and field data for quantifying key parameters. Continued identification of OA constituents and study of oxidant interactions with a wider range of substrates is necessary to better constrain OVOC flux from atmospheric aerosols. Of particular concern is that much of the OA in the atmosphere may actually consist of highly oxidized humic-like substances (HULIS) [Limbeck et al., 2003; Claeys et al., 2004a]; whether HULIS can be volatilized in a similar fashion as the aliphatic compounds usually studied in the laboratory must be investigated. De Gouw and Lovejoy [1998] find that O$_3$ reacts with liquid aldehydes and ketones ($\gamma \sim 10^{-3}$), presumably with the carbonyl moieties, but do not determine if any gas phase products form. An additional difficulty in applying laboratory studies is that they have utilized reaction parameters, such as low pressures and [O$_3$], and high [O$_3$] and [OH], which are not representative of the real atmosphere. Moise and Rudich [2000] find, for example, that $\gamma_{\text{O}_3}$ drops when O$_2$ instead of H$_2$ is used as a carrier gas in their experiments; also, Molina et al. [2004] propose that the carbon volatilization in their experiments would be reduced at atmospheric [O$_3$]. Other oxidants, such as NO$_3$ and – in certain areas such as coastal and polar regions – halogen atoms, may also play an important role in aerosol oxidation. Finally, our analysis assumes that all aerosols are completely covered with organic films; accurate parameterizations of surface coverage require more field studies of aerosol coatings. A full understanding of OA oxidation will only result from continued, multifaceted research endeavors.

Acknowledgments. We thank Jonathan Abbatt (University of Toronto) for reviewing a draft of this manuscript, Steven Howell (University of Hawai‘i at Manoa) for helpful discussions, Clyde Brown (NASA Langley Research Center) for preparing merged data files, and the NASA tropospheric Chemistry Program office for support of the INTEX-NA campaign (grant NNG04FA95G). This material is based upon work supported under a National Science Foundation Graduate Research Fellowship (AJK). This article was also developed under a STAR Research Assistance Agreement FP-91634301-2 awarded by the U.S. Environmental Protection Agency (JDC). It has not been formally reviewed by the EPA. The views expressed in this document are solely those of the authors and the EPA does not endorse any products or commercial services mentioned in this publication.

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