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**Influence of NO_x on Secondary
Organic Aerosol and Ozone**

Executive Summary

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COORDINATING RESEARCH COUNCIL, INC.

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Influence of NO_x on Secondary Organic Aerosol and Ozone

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EXECUTIVE SUMMARY

The major objectives of this project were to determine the contributions of US anthropogenic sources to secondary organic aerosol (SOA) and ozone in the Houston region and to evaluate how the concentrations of SOA and ozone and the source contributions depend upon NO_x emissions.

We addressed the objectives by using the Comprehensive Air Quality model with Extensions (CAMx) and a September 2013 modeling database developed for the Texas Commission on Environmental Quality (TCEQ). During this period, the measured maximum daily average 8-h (MDA8) ozone in the greater Houston area varied from 12 ppb to 104 ppb and averaged 38 ppb. Particulate matter $\leq 2.5 \mu\text{m}$ in diameter (PM_{2.5}) and organic carbon (OC) were both measured at one site in central Houston. At this site, 24-h PM_{2.5} varied from 3 $\mu\text{g}/\text{m}^3$ to 16 $\mu\text{g}/\text{m}^3$ during September. Using a standard factor to convert OC to organic aerosol (OA), 24-h OA varied from 1.0 $\mu\text{g}/\text{m}^3$ to 5.5 $\mu\text{g}/\text{m}^3$, and OA as a fraction of PM_{2.5} averaged 25% with a range of 7% to 37%.

Simulations were conducted for September 2013 and 2028 on a nested grid of 36-km, 12-km and 4-km domains, the latter domain covering the greater Houston area. The 2013 emissions are those prepared by TCEQ, and the 2028 emissions were developed by calculating reduction factors for the major emission sectors from EPA's national emissions for 2011 and 2028 and applying the factors to the 2013 emissions. We also conducted a background simulation without US anthropogenic emissions and used it to determine the anthropogenic increment to ozone and SOA, the anthropogenic increment being the difference between concentrations in the 2013 or 2028 simulation and the background simulation.

The 1.5-Dimensional Volatility Basis Set (1.5-D VBS) scheme was used to represent organic gas-aerosol partitioning and oxidation. SOA formation in the 1.5-D VBS scheme is driven by the atmospheric concentration of the hydroxyl radical (OH) and emissions of primary organic aerosol (POA), NO_x, and certain volatile organic compounds that form SOA (VOC(SOA)). The Path-Integral Method (PIM) was extended to include the 1.5-D VBS scheme and used to apportion the anthropogenic increment of ozone and SOA to 6 emission source categories: onroad vehicles, nonroad vehicles, oil and gas operations, other area sources, point sources and cooking activities.

We compared modeled and measured MDA8 ozone concentrations during September 2013 at TCEQ's monitoring sites on the 4-km and 12-km domains, and the model's performance is quite good. Normalized mean bias (NMB) is 2.7% and 0.3% for the 4-km and 12-km grids, respectively, and normalized mean error (NME) is 17% and 13%. We also evaluated the model's performance for OC at EPA's sites on the 12-km domain. This performance is also good

considering the current state of the science. NMB is 20% and -3% at IMPROVE and CSN sites, respectively, and NME is 43% and 32%.

The PIM requires integration of sensitivity coefficients, and we used the same numerical procedure for SOA as previously used for ozone in CRC Projects A-90 and A-99. The accuracy was checked for SOA by comparing the sum of the source contributions to the anthropogenic increment, and the agreement is excellent ($R^2 > 0.999$ and root mean square error $< 0.025 \mu\text{g}/\text{m}^3$ for 24-h POA and SOA concentrations). We concluded that the PIM is readily generalized from source apportionment of ozone to apportionment of OA and its components.

We selected 21 of TCEQ's Continuous Ambient Monitoring Station (CAMS) sites in the greater Houston area and calculated source apportionments at individual sites as well as 21-site averages. Figure ES-1 gives the 21-site averages for SOA and ozone in 2013 and 2028. (The SOA concentration for an individual site is the monthly average of the 24-h concentration, and the ozone concentration is the monthly maximum MDA8 concentration.)

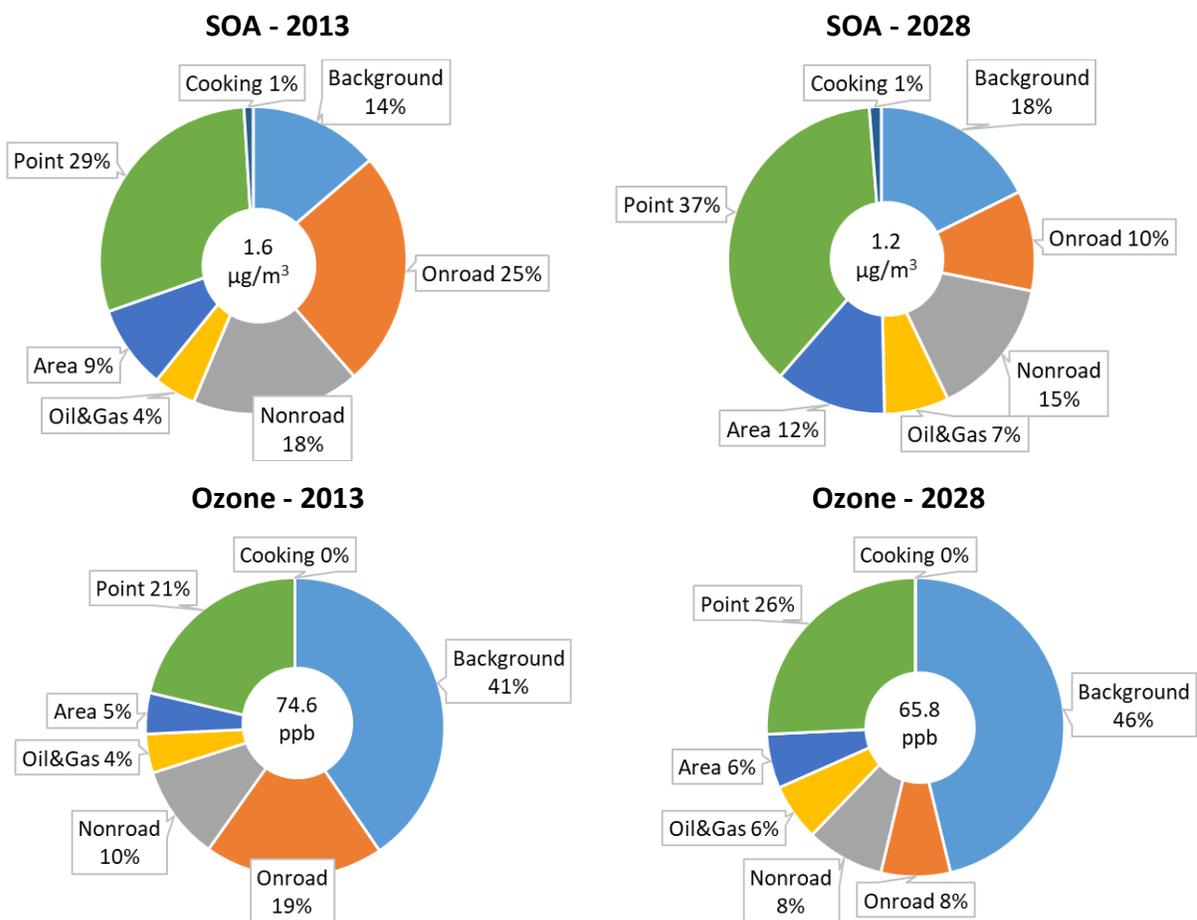


Figure ES-1. The SOA and ozone concentrations in Houston in 2013 and 2028 and the contributions of the background and anthropogenic sources to the concentrations. Results are averages over 21 sites in the Houston area for the September average 24-h SOA and the monthly maximum MDA8 ozone concentrations.

Of the anthropogenic sources, point sources make the largest contribution to SOA and ozone in both years. After point sources, onroad and then nonroad sources have the largest contributions to SOA and ozone in 2013. In 2028, nonroad, area, and onroad sources make the next largest contributions to SOA after point sources, and nonroad, onroad, oil and gas and area sources have similar, relatively small contributions to ozone. Cooking emissions make only small contributions to SOA, and negligible contributions to ozone. The background concentrations are significantly more important for ozone than SOA.

There is some variation in the results for individual Houston sites, but the results for the individual sites generally agree with the 21-site averages in Figure ES-1. Over the 12-km domain, the relative importance of the sources to monthly maximum MDA8 ozone is generally the same as for the 21-site Houston averages. However, for monthly average 24-h SOA, onroad vehicles are more important than point sources in most areas of the 12-km domain in 2013 and oil and gas operations are more important than area sources in some parts of the domain.

From 2013 to 2028, the anthropogenic NO_x emissions in the 4-km domain decrease by 46%, VOC emissions contributing to ozone ($\text{VOC}(\text{O}_3)$) by 15%, $\text{VOC}(\text{SOA})$ emissions by 31%, and POA emissions by 10%. The 21-site average SOA decreases by 23% from 2013 to 2028 but ozone by only 12%. The ozone response is muted in comparison to the SOA response likely due to the larger percentage contribution of the background to ozone.

The PIM incorporates the direct and indirect effects of all the emissions of a source in determining the source's contribution to the atmospheric concentration of a pollutant. This is important for ozone because both VOC and NO_x emissions promote ozone formation. This is also the case for SOA because, though it is the $\text{VOC}(\text{SOA})$ and POA emissions of a source that form the actual aerosols, the NO_x emissions affect the atmospheric chemistry and thereby the oxidation rate of the VOCs and volatilized POA. The importance of the NO_x emissions to SOA formation in Houston is clear from Figure ES-2. For both 2013 and 2028 there is a strong correlation between the fractional contribution of a source to the anthropogenic SOA increment and the source's fractional contribution to anthropogenic NO_x emissions. On the other hand, there is not a strong correlation to a source's $\text{VOC}(\text{SOA})$ emissions in Figure ES-2 (b), likely because anthropogenic $\text{VOC}(\text{SOA})$ emissions are only 10% and 7% of total $\text{VOC}(\text{SOA})$ emissions in 2013 and 2028, respectively, in the 4-km domain.

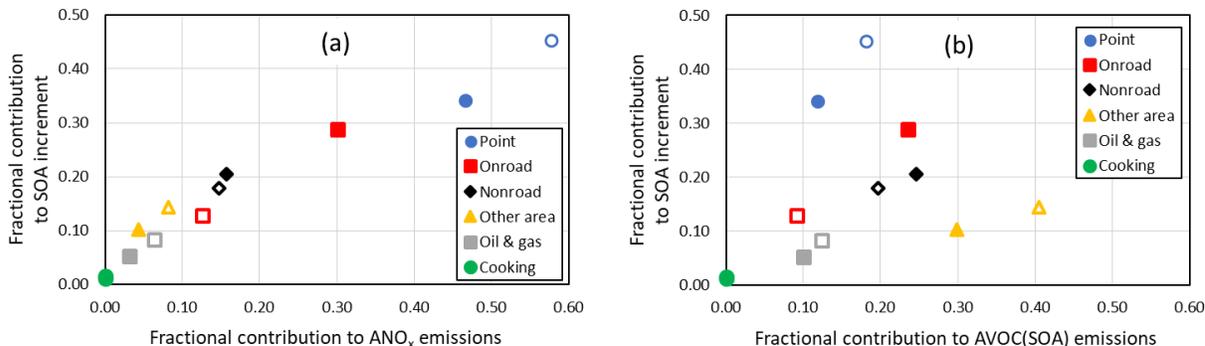


Figure ES-2. Fractional contributions of sources to the anthropogenic SOA increment vs. their fractional contributions to (a) anthropogenic NO_x or (b) anthropogenic VOC(SOA) emissions. The 24-h SOA concentrations are averaged over September and 21 sites in the Houston area and the emissions are those in the 4-km domain. Closed symbols denote 2013; open symbols, 2028.

Some previous experimental and modeling studies have concluded that anthropogenic emissions enhance the formation of OA from biogenic emissions, and we estimated this effect using our simulations. Figure ES-3 gives the total monthly 24-h OA averaged over the 21 Houston sites and the contributions of the background, OA from the biogenic emissions enhanced by the anthropogenic emissions, and OA from the anthropogenic emissions alone. The biogenic enhancement is 46% and 48% of the total OA concentration in 2013 and 2028, respectively, and is the largest fraction of the total. The source apportionment of the biogenic enhancement indicates again that point sources make the largest contribution, followed by onroad sources in 2013 and area sources in 2028. This work is apparently the first effort to ascribe the biogenic enhancement to source categories, considering all the VOC, NO_x and POA emissions of each category and the direct and indirect effects of the emissions.

Our results indicate the importance of NO_x emissions for formation of SOA (and OA) in areas of large biogenic VOC emissions. However, the average SOA concentration did not respond proportionately to the reduction in anthropogenic NO_x emissions from 2013 to 2028 (25% reduction in SOA in Figure ES-1 vs. the 46% reduction in anthropogenic NO_x emissions in the 4-km domain) nor did the enhancement of OA from biogenic emissions (15% reduction in Figure ES-3 (a)). Also, the average total OA in Houston decreased by only 19% from 2013 to 2028. The SOA and OA concentrations in 2013 respond to the emission reductions projected for 2028, but the percentage reductions in concentrations are smaller than the percentage reductions in anthropogenic NO_x or VOC(SOA) emissions.

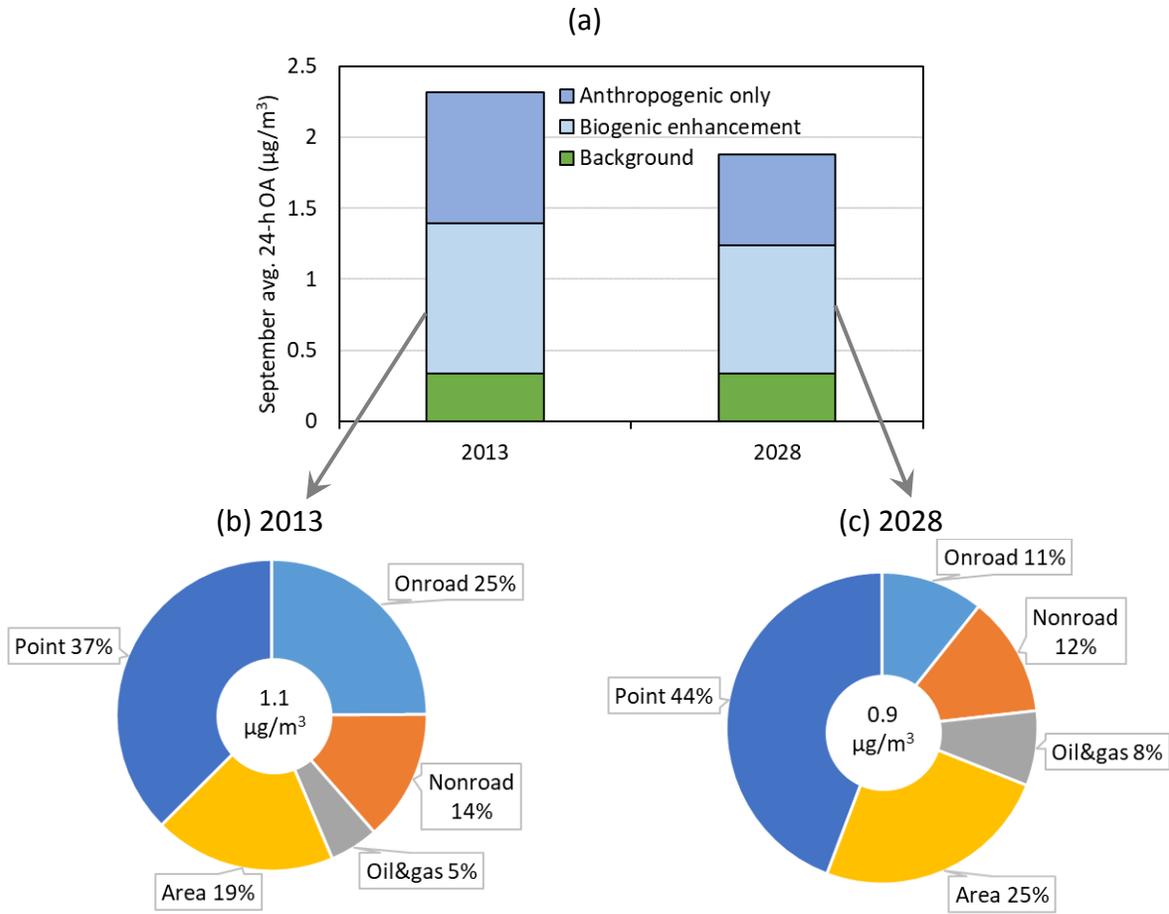


Figure ES-3. Components of the total OA concentration in Houston (a). The enhancement of OA from biogenic emissions due to U.S. anthropogenic sources and the contributions of the sources to it for (b) 2013 and (c) 2028. Results are September averages of the 24-h concentrations, averaged over 21 sites.