Technical challenges involved in implementation of VOC reactivity-based control of ozone

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Summary:

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ADDITIONAL METRICS FROM AQMS

While one-dimensional box models provide the MIR, MOIR, and EBIR metrics, three-dimensional air quality modeling yields additional metrics to describe VOC reactivity (*1*). Table S1 describes seven different metrics than can be derived using AQMs. These represent a range of conditions, such as average conditions, low VOC/NOx ratios (similar to MIR conditions), high ozone concentrations, and those relying on least-squares summaries of the data.

OZONE SENSITIVITY CALCULATIONS USING AQMS

To study the sensitivity of ozone formation to individual VOCs, the CMAQ modeling system (*2*) version 4.3 with the Direct Decoupled Method (*3*) implemented (CMAQ-DDM) was applied for a continental domain. The grid spacing was 32 km in the horizontal, resulting in 178 by 124 grid cells and used 21 vertical layers. The CMAQ implementation of the SAPRC-99 chemical mechanism (*4*) was used to describe the chemistry and meteorological inputs were obtained from the MM5 meteorological model (http://box.mmm.ucar.edu/mm5/) version 3.6.1. Anthropogenic emissions were based on the 1999 National Emissions inventory (NEI) (http://www.epa.gov/ttn/chief/net/1999inventory.html). Biogenic emissions were calculated with BEIS v3.12 (www.epa.gov/asmdnerl/biogen.html). Emissions were processed with SMOKE v.2.0 (http://cf.unc.edu/cep/empd/products/smoke/index.cfm). The model was run on a Linux cluster for an episode of July 1-14, 1999, with 7-day spinup prior to the episode.

The other two AQMS considered in this analysis include the Urban-to-Regional Multiscale Model (URM) previously reported by Hakami et al. (*5*), and the CAMx model˙ previously reported by Carter et al. (*1*). The URM application results presented in Figure 4 consisted of an episode from July 1-9, 1999. A multiscale grid was used with 192-, 96-, 48-, and 24-km grid cells calculated as one continuous domain, and the finest (24-km) grid was placed over major source regions. Gas-phase chemistry from a modified version of the SAPRC-99 mechanism was used, and the Regional Atmospheric Modeling System (RAMS) (*6*) provided the meteorology. More information on this model and application is available in Hakami et al. (*5*).

The CAMx application covered the period July 12-15, 1995, with a 5-day spinup period and the CB4 chemical mechanism (*7*) to describe the gas-phase chemistry. The application consisted

of 36-, 12-, and 4-km nested grids, with the 4-km resolution centered on the New Jersey/New York metropolitan area. The meteorology was developed using MM5. More information on the model can be found in Carter et al. (*1*).

Both the URM and the CAMX model applications also calculated ozone sensitivities using the DDM.

CITY-TO-CITY VARIATION OF MIR

Figure S1a shows the range of MIRs for each chemical in Table 1 across the 39 cities reported by Carter (*8*). In Figure S1b, the MIR for each chemical is ratioed to the MIR of the base VOC mixture. In this case, the city-specific values show a large amount of variation, but when normalized to the base mixture in each city, the variation is minimized. The median values for all chemicals are well represented by the average MIR value.

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Table S1: Description of seven different three-dimensional regional metrics and the box model MIR, from Carter et al. (*1*)

| Metric	Definition	Characteristics
Regional Average Ozone	Calculated by summing up the incremental reactivity of a VOC over all cells, dividing by the incremental reactivity of the Base ROG summed over all cells.	Weighs effects of VOCs on ozone formation in all grids equally.
Regional Maximum Ozone	The reactivity of a VOC is based on the cell and time period where the highest ozone concentration occurs	Reflects effect of an individual VOC on the highest ozone level. Considers only one cell in deriving reactivities, thus has significant day to day variations.
Regional Average Ozone over Standard	A version of the regional average ozone metric but instead of summing the incremental reactivities over all cells, it only considers the cells where the ozone exceeds the air quality standards.	Similar to Regional Maximum Ozone, but considers all cells where ozone is greater than the standard.
Minimum Substitution Error Method 1 (MSE 1): Base ROG for VOC	Reactivity of a VOC is calculated by minimizing the error resulting from substituting base ROG for species VOC by a factor equal to amount of species times relative reactivity of the VOC.	Considers all cells, but is more influenced by VOC-sensitive cells.
Minimum Substitution Error Method 2 (MSE 2): VOC for Base ROG	The reactivity of a VOC is calculated by minimizing the substitution error resulting from replacing the base ROG with the species VOC multiplied by a reactivity-adjusted factor.	Considers all cells, but gives more influence to VOC-sensitive cells. More "realistic" than MSE1, but can give values that are not well defined in some situations.
Regional MIR	Based on impacts in the cell where base ROG has the highest incremental reactivity.	Represents the reactivity in only one cell for each episode.
Regional MIR to MOIR	A version of regional average ozone metric but instead of summing incremental reactivities over all cells, only considers cells in which daily maximum ozone has negative sensitivity to NOx and positive sensitivity to VOC.	Only reflects impacts in areas that can be categorized as having MOIR to MIR conditions, where VOC impacts are high and NOx controls may be counter-productive.
Box Model MIR	Based on box model calculations of maximum incremental reactivity using the 39-cities average conditions	Based on 1-day simulation and one data point
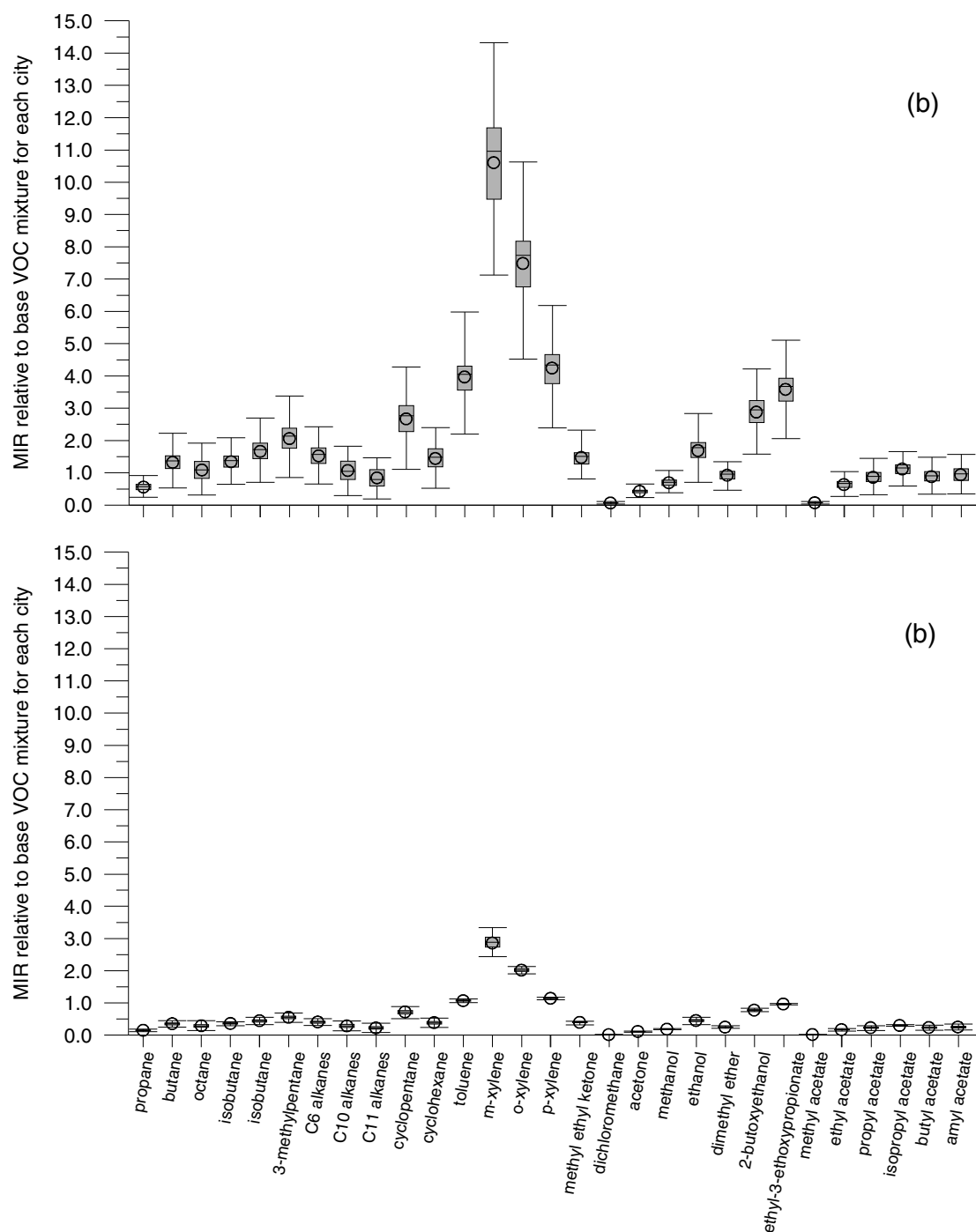
Figure S1. Median and range of the (a) 39 city-specific MIRs, and (b) 39 city-specific MIRs normalized by the MIR of each city's base (ambient) VOC mix. Circles indicate the value of averaged MIR normalized by the MIR of the averaged base VOC mix. The MIRs are as reported by Carter (*8*) using SAPRC-99 and a box model. Values are plotted for 29 chemicals that are components of aerosol coatings or proposed replacements.