Tropospheric photochemistry modeling: 1. Global impact of isoprene nitrate  2. Ozone and secondary species in Mexico City  3. Ozone and reactive mercury

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1. Global modeling: Impact of aromatics and isoprene nitrates

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Overview

A global-scale chemistry/transport model has been exercised to test the effect of extended photochemistry. The model base case uses the GEOSCHEM mechanism (Fiore and Jacob, 2003). The expanded model includes the following additions to chemistry and emissions:

- Explicit representation of hydroxyalkyl nitrates formed from isoprene and isoprene reaction products (represented by HNO3 in the base chemistry)
- Aromatic hydrocarbons (chemistry and emissions added)
- Terpenes (chemistry and emissions added)
- Direct emission of methanol, phenol, acetic acid and formic acid from biomass burning (Ito and Penner, 2002)
- Emissions, transport and photochemical production of acetone replacing prescribed values. The model is IMPACT (Rozanov et al., 2004) with a modified solution for photochemistry (Sillman, 1991).

Meteorological fields are from NASA DAO GEOS-STRAT. Resolution is 4° latitude × 5° longitude horizontally and 30 vertical layers.

Results

The effect of including expanded chemistry causes the following changes vs. base chemistry:

- O3 increases by 20% in both polluted regions and the remote troposphere
- PAN increases by 40% (see Figure 1)
- NOx increases by 20% in the remote troposphere
- OH increases by 10%

Model performance does not improve or degrade in comparison with measurements from Emmet al. (2000) (see Figure 2).

The increased O3 is driven by the increased NOx in the remote troposphere, which is caused by the enhanced rate of PAN as a transporter of NOx.

The increased PAN is largely to the isoprene nitrates. Because these are relatively short-lived, they react to release NOx and organics.

2. Secondary species and O3-NOx-VOC indicators in Mexico City

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Overview

Previous results (Sillman and He, 2002) have suggested that secondary species (reactive nitrogen and peroxides) can be used to evaluate ozone photochemistry in polluted regions. Correlations and ratios among secondary species show characteristic patterns if O3 is primarily sensitive to NOx and a different pattern if O3 is primarily sensitive to VOC. It has been suggested that ratios among secondary species (e.g., O3/NO3, NOy/HNO3) can be interpreted as "indicators" for O3/NO3 VOC sensitivity.

Here, results are shown from a model for ozone formation in Mexico City (West et al., 2004). Mexico City has many features that differ from other locations. Model results for secondary species in Mexico City are compared with results found elsewhere.

The model is the U.T. model with SAPHIR 99 chemistry, applied to pollution events in Mexico City during March, 1997, previously published by West et al. (2003).

Results

The ratio O3/NO4 is higher in Mexico City than elsewhere, and ambient HgII is lower, based on model predictions (Figure 3). In contrast to other cities, the ratio O3/HNO3 does not correlate well with NOy/VOC sensitivity. VOC-sensitive locations in Mexico City have high NOx and NOy, low NO4, but they have low HgII and high O3.

The ratio O3/PAN predicted to be lower in Mexico City than elsewhere, and PAN concentrations are higher. O3/PAN is correlated with temperature, but is not correlated with NOx VOC sensitivity.

O3 vs NOy (Figures 4 and 5) is correlated with NO2-VOC sensitivity in Mexico City, as elsewhere, for a different reason. VOC-sensitive locations in Mexico City have high NOx; other cities VOC-sensitive locations have high HgII.

Figure 6 shows NOy (ppb) at four locations: Mexico, O3, O3 (special emissions/36-41 March 1997), and Vancouver (O3 (special emissions/36-41 March 1997).

Speculation: Temperatures are lower during high-ozone events in Mexico City than elsewhere. This causes higher PAN formation: PAN acts as a sink for NOy and HgII, and its formation reduces the potential to form HNO3, NOy, and ozone.

3. Ozone and reactive mercury: Results from a regional-scale model

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Overview

A regional-scale chemistry/transport model (CMANC) has been modified to represent the chemistry of elemental and reactive mercury. The modifications include implementation of a new solver for photochemistry (Sillman, 1991), Barth et al., 2003; Feng et al., 2004) that provides an integrated solution for gas-phase and aqueous reactions. The model includes the chemistry of O3, NOx, organics, sulfates, chlorine, bromine and mercury.

The model has been used to simulate 15 days in June, 2000, for a domain that includes the eastern U.S. and large parts of the Atlantic Ocean. Results are compared with aircraft measurements in south Florida. Reactive mercury (HgII) is formed by photochemical conversion from elemental mercury (HgI), and is also emitted directly.

Results

The model predicts that high concentrations of reactive mercury form at 3000 m over the Atlantic Ocean. High mercury is apparent in episodic patches that correspond to cloud-free periods (see Figure 6). Gas-phase chemistry converts HgI to HgII; aqueous chemistry converts HgII back to HgI. The elevated HgII at 3000 m is consistent with aircraft observations in south Florida.

The model predicts that HgII concentrations are significantly increased during pollution events with elevated O3 in the northeastern and midwestern U.S. HgII is predicted to correlate with O3 during these events. If anthropogenic NOx and organic emissions were eliminated, ambient HgII would decrease by a factor of 2-3 during pollution events (see Figure 8).

Figure 7: Concentration of HgII (ppb) in the model at 2000 m, valid for 3pm June 13, 2000. The symbols represent different sensitivity regimes: blue asterisks, representing locations dominated by transport from outside the model boundary in this case). Locations are identified as follows: light green, 40-80 pg m-3; orange, 240-280 pg m-3; red, 280-320 pg m-3; light green, 20-40 pg m-3; storage, all values < 20 pg m-3.