

## A FORWARD AND ADJOINT NEIGHBORHOOD SCALE AIR QUALITY MODEL

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### 1. INTRODUCTION

The nonlinear chemistry of ozone formation can easily be misrepresented by air quality models used in ozone attainment demonstrations, which typically employ horizontal resolutions of about 4 km. Henderson et al. (2010) showed that regions with concentrated petrochemical industrial activity have high ozone production rates that can only be properly simulated with grid cell sizes  $\leq 1$  km. Coarser models could thus bias regulatory decisions by erroneously calculating the efficacy of control strategies. In addition, official emission inventories in highly industrialized areas can suffer from 1-2 orders of magnitude of uncertainty, due to temporal variability and other physical reasons.

In this paper, we review some very recently published results from a new air quality model intended to provide fine resolution simulations of ozone plumes in industrial neighborhoods. We then introduce an adjoint version that can be used for inverse modeling of reactive chemical species, and use it to infer historical flare emissions of formaldehyde in the vicinity of Lynchburg Ferry in Baytown, Texas during the 2006 Second Texas Air Quality Study (TexAQS II). Finally, we indicate how the adjoint model can facilitate Computer Aided Tomography (CAT) of chemically reactive pollution plumes based on Differential Optical Absorption Spectroscopy (DOAS).

### 2. MODEL DESCRIPTION

The Houston Advanced Research Center (HARC) neighborhood air quality model is a fine (~200 m) horizontal resolution 3D Eulerian chemical transport model (Olaguer, 2012a,b). While it employs transport solvers commonly used in the Community Multi-scale Air Quality (CMAQ) model, it has a customized chemical mechanism consisting of 47 gas-phase reactions selected for near-source applications. The model presupposes ambient NO mixing ratios  $> 0.5$  ppb so that chemical equilibrium can be assumed for HO<sub>x</sub> species for temporal resolutions of ~20 s. The

Euler Backward Iterative (EBI) scheme (Hertel et al., 1993) is then used for the chemical group consisting of NO, NO<sub>2</sub> and O<sub>3</sub>, while a simpler backward Euler scheme is employed for longer lived species such as CO. Altogether, there are 16 transported species in the HARC model, including isoprene and several highly reactive olefins (ethene, propene, 1,3-butadiene and butenes); the radical precursors, formaldehyde (HCHO) and nitrous acid (HONO); and the aromatics, toluene and xylenes. Less reactive “background” organics, such as alkanes and higher aldehydes, are lumped together and assigned a total OH reactivity, denoted by  $r_{BVOC}$ .

### 3. CHEMICAL MECHANISM EVALUATION

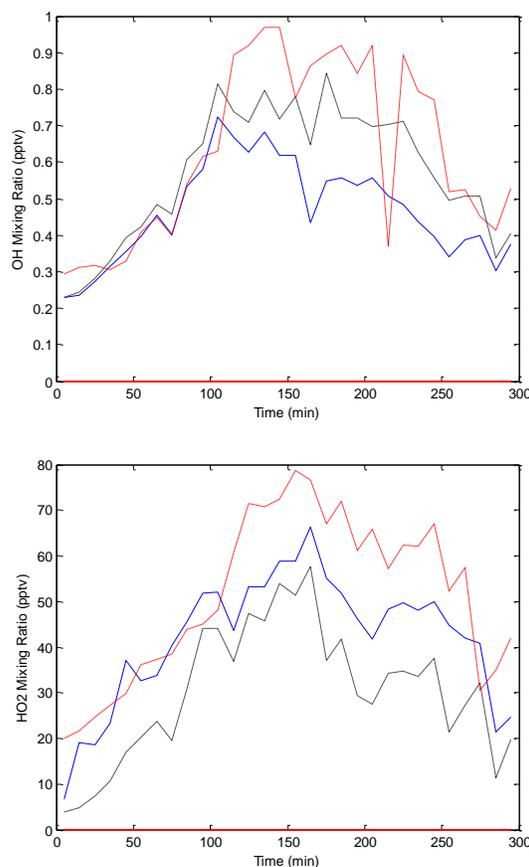


Fig. 1. Mixing ratios of OH (upper) and HO<sub>2</sub> (lower) at 10:00 – 15:00 CST, 9/14/06 for  $r_{BVOC}=0$  (black),  $r_{BVOC}=\text{observed}$  (blue), and TRAMP measurements (red).

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The HARC mechanism's predictions of HO<sub>x</sub> radical concentrations were evaluated against observations from the 2006 TexAQS II Radical and Aerosol Measurement Project (TRAMP). Results of the evaluation, as performed by Olaguer (2012a), are shown in Fig. 1. Note that chemical interferences have recently been found in the Laser Induced Fluorescence (LIF) detection method used to measure HO<sub>x</sub> during TRAMP (Mao et al., 2012), so that the discrepancy between model predictions and true HO<sub>x</sub> concentrations are not as large as they appear in the figure. In any case, the HARC mechanism behaves very similarly to established mechanisms such as CB05 and SAPRC also evaluated against TRAMP data (Chen et al., 2010).

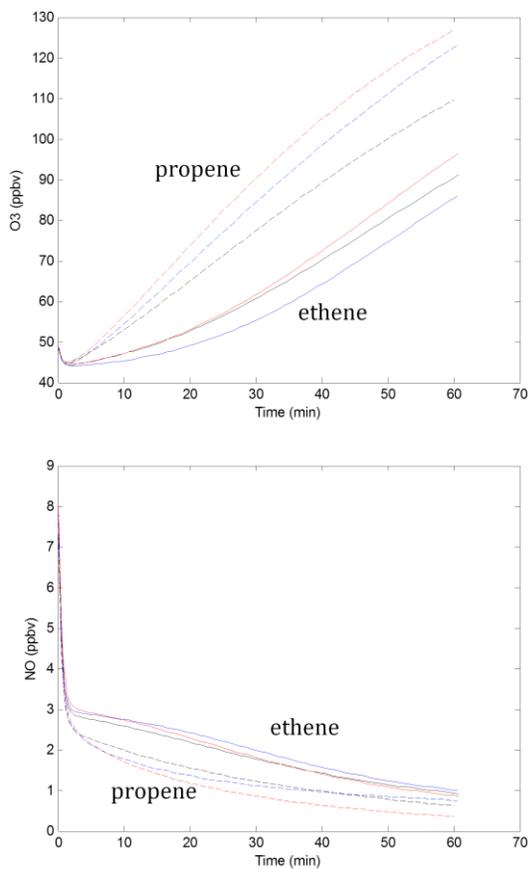


Fig. 2. Mixing ratios of O<sub>3</sub> and NO predicted by OZIPR model for the CB05 (black), SAPRC97 (red), and HARC (blue) mechanisms, with an initial 100 ppb olefin plume consisting of either ethene or propene. CO and NO are initially set at 200 ppb and 10 ppb.

Olaguer (2012a) also compared ozone simulations using the OZIPR model and the HARC, CB05 and SAPRC97 mechanisms. Ozone and NO results for 1-hr simulations of NO<sub>x</sub>-olefin

plumes are shown in Fig. 2. The HARC propene chemistry is somewhat more reactive than that of CB05, possibly because CB05's lumping scheme for olefins higher than ethene underestimates the ozone formation potential of propene.

#### 4. FORWARD SIMULATION OF OZONE FROM A LARGE OLEFIN FLARE

Olaguer et al. (2012b) simulated a historical emission event in the Houston Ship Channel based on reported routine and flare event emissions, in which >1400 lbs/hr of ethene were released. The simulation was conducted over a domain of 12 km × 12 km (horizontal) × 1 km (vertical) for 9:30 am – 12:30 pm CST, 10/7/06, with a spatial resolution of 200 m × 200 m (horizontal) × 50 m (vertical) × 20 s (temporal). A uniform hourly-varying horizontal wind was assumed based on meteorological measurements at the nearest downwind monitoring station. In addition, a HCHO:CO molar ratio of about 8% was assumed in the flare based on the results of the 2010 TCEQ Flare Study (Allen and Torres, 2011).

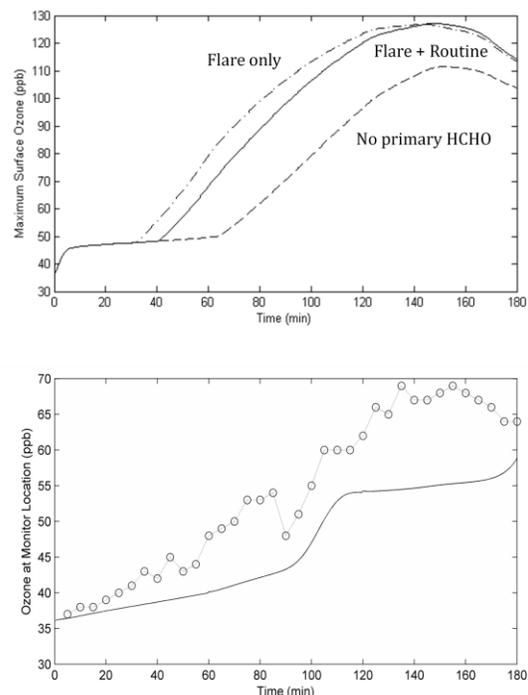


Fig. 3. Top: Evolution of peak O<sub>3</sub> in model domain during simulated emission event. Bottom: HARC model O<sub>3</sub> predictions vs. observations at the closest monitor downwind of the flare.

Simulation results are presented in Figs. 3-4. Note how the model predicts a rapid rise in peak

ozone (> 40 ppb/hr) as a result of the flare, and that the presence of primary HCHO substantially accelerates O<sub>3</sub> production. Moreover, degrading horizontal resolution from 200 m to 1 km artificially diffuses the O<sub>3</sub> plume induced by the flare.

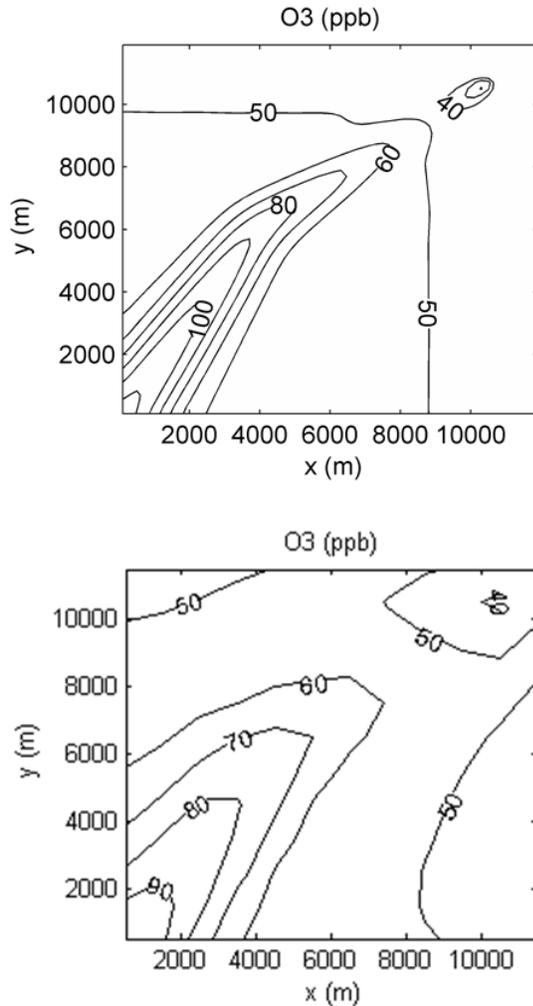


Fig. 4. Flare-induced O<sub>3</sub> plume predicted at 200 m (upper) and 1 km (lower) resolution.

## 5. INVERSE MODELING OF FLARE EMISSIONS OF FORMALDEHYDE

The largest ambient HCHO concentrations ever observed in Houston (up to 52 ppb) were measured at Lynchburg Ferry (LF) during TexAQS II on September 27, 2006 (Eom et al., 2008). We constructed an adjoint version of the full chemistry transport model and used it to perform 4Dvar inverse modeling of flare emissions of HCHO, CO and olefins from a sequential planned shutdown of

a facility about 8 km upwind of LF during a 1.5 hr period when the highest HCHO concentrations were measured. Flare emissions were inferred from LF observations (Table 1) using a model horizontal domain size and grid resolution of 8 km x 8 km and 400 m.

Table 1. Lynchburg Ferry measurements (ppb) used to drive adjoint model.

Species	8:00-9:00 LST	9:00-9:30 LST
NO	7.3	4.9
NO <sub>2</sub>	42.6	13.6
ozone	54	65
formaldehyde	See Fig. 5	See Fig. 5
ethene	5.46	7.49
propene	17.58	10.29
1,3-butadiene	1.92	1.53
1-butene	5.26	0.60
2-butene	7.51	0.57

The simulation included routine point source emissions from industrial facilities within the model domain, as well as link-based traffic emissions from the MOVES model provided by the Houston Galveston Area Council. Meteorological observations were obtained from the regulatory monitoring station (CAMS 35) closest to the flare emission event.

Inverse modeling was conducted for two cases: 1) a control run, in which the inflow boundary condition for HCHO was set at 4 ppb, and 2) a sensitivity run in which the HCHO boundary condition was set at 31.5 ppb to simulate an incoming plume of secondarily formed HCHO transported from outside the model domain. In both cases, large emissions of primary HCHO were inferred from the shutdown flare event: 282 kg/hr for the control run, and 239 kg/hr for the sensitivity run. The inferred emissions from the control case are roughly 50 times larger than HCHO emissions from flares used in routine operations, as inferred from remote sensing and/or real-time in situ measurements during the 2009 SHARP campaign (Wood et al., 2012).

Fig. 5 shows the resulting ambient HCHO concentrations at LF predicted by the forward model with the inferred emission rates, and compares them to the corresponding LF measurements. The model sensitivity experiment demonstrates that the LF observations cannot be explained by long range transport of secondarily formed HCHO as hypothesized by Parrish et al. (2012), as opposed to a large nearby source of primary HCHO and olefins.

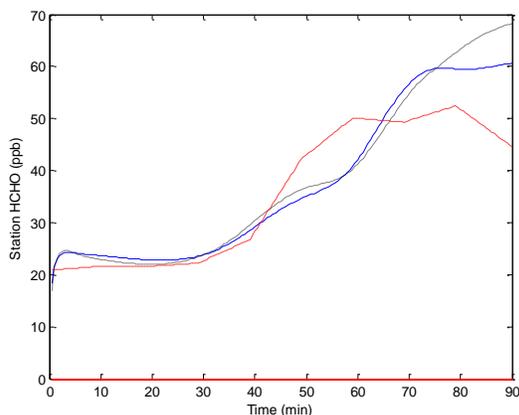


Fig. 5. Model-predicted HCHO mixing ratio at Lynchburg Ferry for the control run (blue line) and sensitivity experiment (black line) vs. corresponding ambient measurements (red line).

## 6. TOMOGRAPHIC RECONSTRUCTION OF REACTIVE PLUMES

Olaguer (2011) used a passive tracer version of the HARC model to demonstrate a new method for performing Computer Aided Tomography (CAT) scans based on Differential Optical Absorption Spectroscopy (DOAS). The method relies on 4Dvar inverse estimation of the horizontal turbulent diffusion coefficient and local emissions based on remote sensing measurements over multiple intersecting light paths. The forward version of the transport model with optimized turbulence and emission parameters is then used to reconstruct pollution plumes within the remotely scanned domain.

While Olaguer (2011) demonstrated the method for unreactive species, the full chemistry transport model can be used to extend the CAT-4Dvar technique to reactive species such as O<sub>3</sub>, NO<sub>2</sub>, HCHO, HONO and SO<sub>2</sub>, all of which can be measured by DOAS. The size of the horizontally scanned domain can be expanded to ~10 km in length if a UV/visible light source is placed at the end of the light path opposite the detector, so that retro-reflector mirrors are not used to fold the light paths in two.

## 7. REFERENCES

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