# PHOTOCHEMICAL MODELING OF AN INDUSTRIAL CITY IN QATAR

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## 1. INTRODUCTION

The Ras Laffan Industrial City (RLIC) is located 80 km north of Doha and forms the heart of Qatar's natural gas industry (see **Figure 1**). Covering 106 $km^2$, RLIC is home to major companies such as RasGas and Qatargas and is assigned to host additional companies in the future. In recent years, monitoring has indicated that ozone concentrations in communities downwind of RLIC are exceeding standards set by the State of Qatar. Therefore, as a permit condition for expansion at RLIC, Qatar's Supreme Council for the Environment and Natural Reserves (SCENR) required that a photochemical grid modeling analysis be performed to assess RLIC's contributions to ozone concentrations in the region.

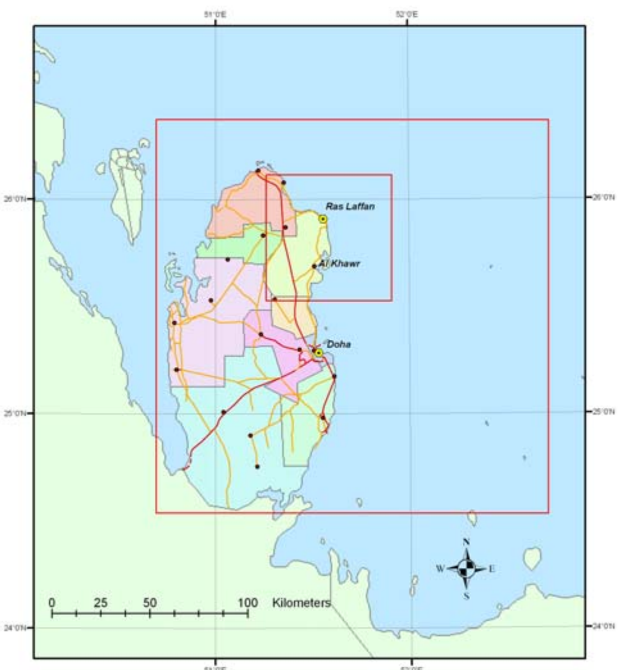


Fig 1. Map of Qatar.

## 2. APPROACH

Two periods were selected for analysis. The first period selected was August 23-30, 2004, which included two days when peak observed 1-hr ozone concentrations approached the state standard of 120 ppb at Ras Laffan City site (RLAC) — 113 ppb on August 26 and 119 ppb on August 29. The highest ozone concentrations observed in August and September occurred on these two days. No unusual temporal fluctuations were observed in the ozone or oxides of nitrogen ($NO_x$) concentrations, indicating that this episode should be representative of the days in which local controls could be effective. However, observed ozone concentrations were not available from the Al Khor site (ALKH), leaving only one site with ozone measurements against which to evaluate model performance.

November 25-28, 2004 was the second period. On November 27, 2004, the peak 1-hr ozone concentration reached 108 ppb at ALKH. While measured ozone concentrations were higher during several October episodes (including an exceedance of the 1-hr standard on October 14), data from a new background site at Al Shamal (ALSH) were only available starting the second week of November. Modeling the November 25-28 period provided an opportunity to address some of the issues with respect to establishing boundary conditions.

### *2.1 Data Analysis*

Air quality data from two sites in the Ras Laffan region, RLAC and ALKH, were available for the August 23-30, 2004, episode. The RLAC site is located in the southeastern portion of the RLIC. The ALKH site is located on the north side of the city of Al Khor at the edge of a housing community. The data were initially provided from these sites for August and September 2004. However, data from the first week of August were suspect.

The ALSH site is located in the park at Al Shamal. Data became available for this site in the last week of November 2004 and was available for the second period investigated.

The air quality measurements available at each of these three sites are summarized in **Table 1**. These data along with available meteorological data were analyzed to gain a better understanding of high ozone days in the Ras Laffan area

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Table 1. Air quality data availability.

| Site | Measurements |
|---|---|
| RLAC | $O_3$, NO, $NO_2$, $SO_2$, $H_2S$, $PM_{10}$, $CH_4$, NMHC |
| ALKH | $O_3$, NO, $NO_2$, $SO_2$ |
| ALSH | $O_3$, NO, $NO_2$, $SO_2$, TRS, $PM_{10}$, CO, $CH_4$, NMHC |

## *2.2 Meteorological Modeling*

Meteorological modeling was performed with the Pennsylvania State University/National Center for Atmospheric Research Mesoscale Model, Version 5 (MM5) (Grell et al., 1994) on the three domains shown in **Figure 2**. The outer domain consisted of 93 x 63 36-km cells. The intermediate domain consisted of 79 x 79 12-km cells. The inner domain consisted of 73 x 79 4-km cells. Each domain had 34 vertical levels extending from the surface to approximately 14 km.

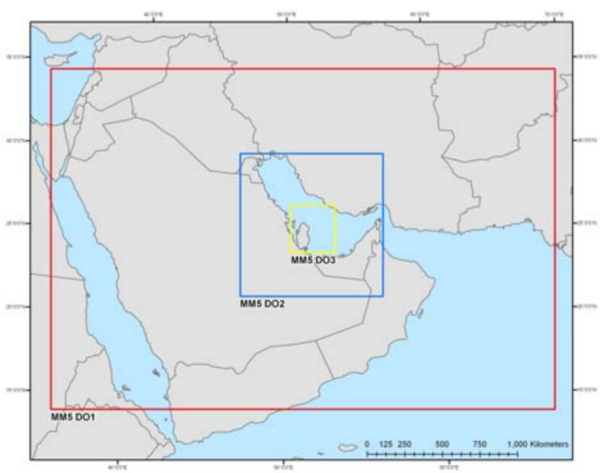


Fig 2. Meteorological modeling grids for the Ras Laffan modeling study.

The following model physics options were used:

- Radiation Scheme – Cloud radiation cooling
- Cumulus Parameterization – Grell (36 km), Kain-Fritz-2 (12 km), no parameterization (4 km)
- Explicit Moisture Scheme – Dudhia simple ice
- Planetary Boundary Layer Scheme: Gayno-Seaman
- Surface Scheme – Blackadar force/restore

Synoptic observations and analysis data from the Global Data Assimilation System (GDAS) were obtained from the University Center for Atmospheric Research (UCAR) for use in initialization, establishing boundary conditions, and preparing nudging analyses for MM5.

Four-dimensional data assimilation was used in the simulations. Two techniques (analysis nudging and observation nudging) were used together on the 12-km domain. Only analysis nudging was used on the 36-km domain, and only observation nudging was used on the 4-km domain.

## *2.3 Emission Inventory*

Stationary source emissions data were obtained from the inventory developed by URS Corporation (2004a). URS provided an emission inventory spreadsheet designed to calculate atmospheric emissions from stationary sources in the region surrounding RLIC and Al Khor. The spreadsheet was populated with existing information about stationary sources and allowed users to enter new sources, modify existing sources, and generate graphical and tabulated emissions summaries from a selection of sources, facilities, and regions. The inventory included current and planned emissions sources.

URS Corporation (2004b) also prepared a mobile source emission inventory for RLIC. The mobile source inventory was intended to estimate emissions from mobile sources in the Ras Laffan air shed. The air shed generally covers the area between Al Khor and RLIC. The mobile source emission inventory was one part of an extensive air quality study conducted for the RasGas facility and was designed, in conjunction with stationary sources inventories and area source inventories, to be used in dispersion and photochemical modeling. The majority of the mobile sources identified in this study were believed to be associated with operations inside RLIC. However, other sources were included if their activity data could be characterized and estimated.

The mobile source emission inventory was separated into four parts: on-road vehicle emissions, marine vessel emissions, fishing vessel emissions, and emissions from construction equipment. The inventory was created to represent the activities of mobile sources in the area during 2003. The inventory was designed to be easily updated with more current information as the expansion of the area continues.

For the periods modeled, day-specific information was obtained from RasGas and Qatargas. These data included the dates, times, and quantities of condensate and liquid natural gas (LNG) loaded into ships and information about any process upset conditions.

The emission inventory was processed into CAMx-ready inputs using the Sparse Matrix Operator Kernel Emissions Modeling System (SMOKE) processing system (Coats, 1996; Houyoux and Vukovich, 1999; Houyoux and Adelman, 2001).

### 2.4 Photochemical Modeling

Photochemical modeling was performed with the Comprehensive Air Quality Model with Extensions (CAMx) (ENVIRON International Corporation, 2004).

The photochemical domain covered the entire State of Qatar as shown in Figure 1 and was defined to cover an area of 248 km x 264 km with 49,104 4-km cells. The domain included a large portion of the Arabian Gulf and was made as large as possible without extending into other countries. The domain was defined in Lambert Conformal coordinates to ensure compatibility with the MM5 meteorological model. The CAMx domain had 12 vertical layers with each CAMx layer consisting of one or more MM5 layers.

The CAMx model was configured with the options summarized in **Table 2**. The plume-in-grid submodel was used in this model application, and all stationary sources with significant plume rise were treated with this method.

Table 2. CAMx model configuration for the RLIC ozone modeling study.

| Option | Configuration |
|---|---|
| Model version | 4.11s (December 6, 2004, release) |
| Horizontal advection solver | Piecewise Parabolic Method (PPM) |
| Chemistry solver | Chemical Mechanism Compiler (CMC) |
| Chemical mechanism | Mechanism 3 (Carbon Bond IV) |
| Treat chemistry | Yes |
| Treat dry deposition | Yes (Wesley) |
| Treat wet deposition | No |
| Gridded emissions | Yes |
| Point source emissions | Yes |
| Plume in grid submodel | Yes |
| Maximum puff length | 2,000 m |
| Maximum puff age | 18 hours |
| Tropospheric ultraviolet-visible radiation model | Madronich et al. |
| Radiative transfer scheme | Pseudo-spherical two-stream delta-Eddington |

In addition to the base-case simulations, a series of sensitivity simulations were performed to gain a better understanding of the effects of boundary conditions and emission changes on local and regional air quality. Emission sensitivity simulations included across-the-board reductions of volatile organic compounds (VOC) and $NO_x$.

## 3. RESULTS

### 3.1 Data Analysis

**Figure 4** is a scatterplot of $NO_x$ concentrations by wind direction at the ALSH monitor for the second modeling period. Four clusters appear to be $NO_x$ concentrations. The lowest $NO_x$ concentrations are associated with winds from the northwest (315 degrees). Three other clusters show higher $NO_x$ concentrations: when the winds were from (1) the west-northwest (285 degrees), (2) from the southwest (210 degrees), and (3) the southeast (140 degrees). These clusters are annotated on Figure 4. When vectors are drawn to ALSH from these directions, as shown in **Figure 5**, the relationships between known source regions and $NO_x$ concentrations measured at ALSH become apparent: cluster 1 is associated with sources in Bahrain (and possibly sources in Saudi Arabia), cluster 2 is associated with sources in the industrial city of Dukhan, and cluster 3 is associated with sources in the RLIC.

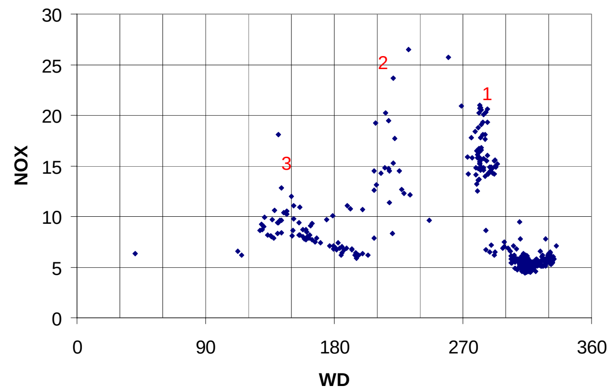


Fig 4. Scatterplot of $NO_x$ concentrations (ppb) at the ALSH monitor by wind direction (WD).

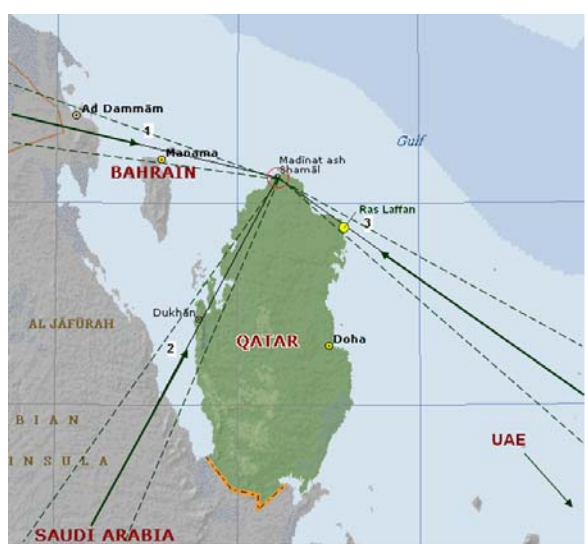


Fig 5. Source-receptor relationships in northern Qatar.

### *3.2 Photochemical Modeling*

Peak 1-hr ozone concentrations predicted by CAMx are compared to observed concentrations in **Table 3**. It is clear from these comparisons that peak 1-hr ozone concentrations are significantly underpredicted on the days with the highest observed concentrations.

Table 3. Comparison of observed and predicted peak 1-hr ozone concentrations for the days modeled.

| Date | Peak 1-hr Ozone Concentrations (ppb) | | | | |
|---|---|---|---|---|---|
| | Observed | Hour | Site | Predicted | |
| | | | | At Site | Hour |
| 8/23/04 | 43.6 | 10 | RLIC | 33.6 | 9 |
| 8/24/04 | 66.9 | 21 | RLIC | 44.4 | 10 |
| 8/25/04 | 58.2 | 9 | RLIC | 45.5 | 9 |
| 8/26/04 | 112.5 | 14 | RLIC | 47.3 | 11 |
| 8/27/04 | 45.2 | 12 | RLIC | 48.5 | 9 |
| 8/28/04 | 22.3 | 9 | RLIC | 47.1 | 9 |
| 8/29/04 | 119.1 | 17 | RLIC | 50.7 | 9 |
| 8/30/04 | 83.2 | 10 | RLIC | 44.5 | 11 |
| 11/25/04 | 50.6 | 16 | ALKH | 36.7 | 13 |
| 11/26/04 | 61.6 | 14 | ALKH | 43 | 15 |
| 11/27/04 | 108.8 | 14 | ALKH | 38.7 | 14 |
| 11/28/04 | 47.9 | 12 | ALKH | 36.8 | 13 |

For the three highest ozone concentration days modeled, contour plots of peak predicted ozone concentrations were prepared. **Figure 6** shows the spatial distribution of ozone at 1400 LST on August 26. The peak predicted ozone was 64.2 ppb in the northeast corner of the modeling domain. **Figure 7** shows the predicted pattern of ozone at 1400 LST on August 29. The peak predicted ozone was 66.8 ppb just northeast of RLIC. **Figure 8** shows the spatial distribution of ozone at 1500 LST on November 26, when the predicted peak ozone was 48.1 ppb approximately 135 km east of RLIC.

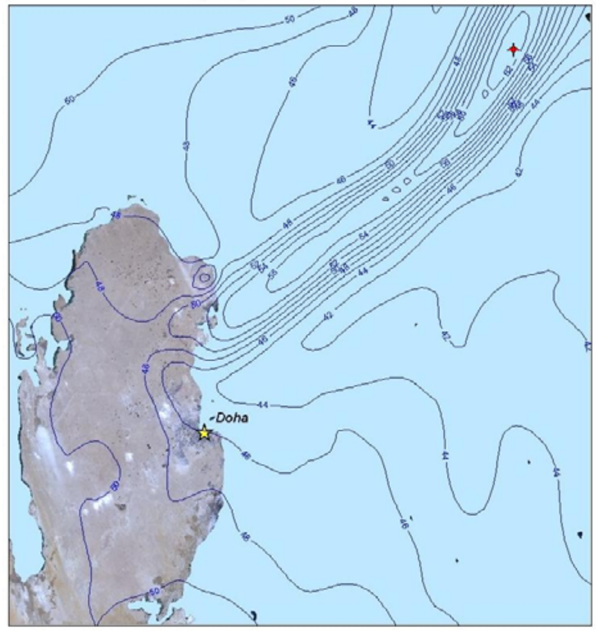


Fig 6. Peak predicted 1-hr ozone on August 26, 2004, at 1400 LST.

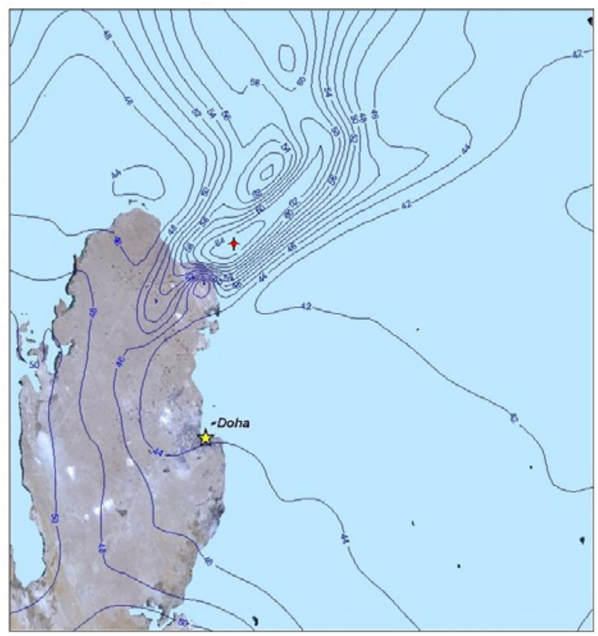


Fig 7. Peak predicted 1-hr ozone on August 29, 2004, at 1400 LST.

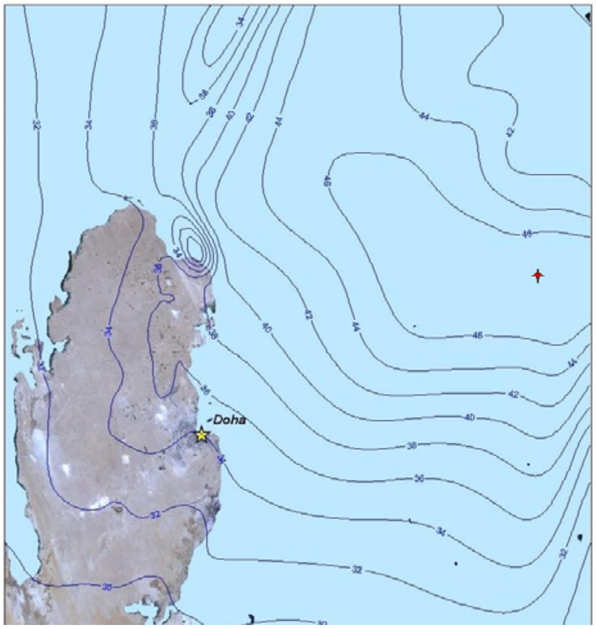


Fig 8. Peak predicted 1-hr ozone on November 27, 2004, at 1500 LST.

## 4. SUMMARY AND FINDINGS

Two episodes were modeled with the MM5-SMOKE-CAMx modeling system. Additional monitoring and data analysis were used to supplement the modeling analysis and help the SCENR understand ozone formation in the Arabian Gulf region. Based on the data analysis and modeling performed in this study, several important findings were noted.

### *4.1 Data Analysis Findings*

- Both the 1-hr and 8-hr ozone standards are exceeded in the Ras Laffan area. The 8-hr standard appears to be exceeded more often than the 1-hr standard. During the periods reviewed (which unfortunately did not include July 2004), one 1-hr and eight 8-hr ozone standard exceedances occurred.
- Background ozone concentrations (i.e., when winds are persistently from the north) measured at the ALSH monitoring site can exceed the 8-hr standard, which implies that there may be significant regional contributions to observed ozone concentrations. During February 2005, a 1-hr ozone concentration of 103 ppb and an 8-hr concentration of 99 ppb were observed at ALSH.
- $NO_x$ concentrations at the ALSH were often above 5 ppb under northerly winds, which indicated that air upwind of Qatar is not clean.
- $NO_x$ concentrations at ALSH show a correlation with wind direction. The highest concentrations were observed when the winds were from the direction of Dukan but, on average, the concentrations were higher when the winds were from northern Bahrain and Ad Dammam. The third highest concentrations were observed when the winds were from the direction of Ras Laffan. The correlation between $NO_x$ concentrations in northern Qatar and transport from known emission source areas highlights the importance of expanding the emission inventory for photochemical modeling.
- Transport distances of 100 to 200 km per day were observed during ozone episodes; thus, the potential for regional contributions to ozone is significant. Based on analysis of observed winds, transport distances of 100 km or more per day were likely during the August episodes and more than 200 km per day were likely during the November episode.

### *4.2 Photochemical Modeling Findings*

- Ras Laffan area emissions alone contribute only a small portion of total observed ozone. Photochemical modeling of the RLIC emissions only produced peak concentrations that were 12 to 15 ppb above background (boundary) concentrations.
- Modeling to date does not account for the total observed ozone. The modeling system was only able to predict concentrations that were about 56% of those observed.
- Ozone is underpredicted by the modeling system, in part, because of the domain size. On several of the days modeled, it was evident that emissions reached the modeling domain boundary before winds reversed and brought emissions and ozone back to the RLIC area.
- Ozone is underpredicted by the modeling system, in part, because not all emissions sources in the domain are included in the model. It is evident from the modeled transport that emissions from areas outside RLIC may contribute to the formation of ozone that eventually affects the RLIC area.
- Ozone is underpredicted by the modeling system, in part, because transport of ozone and ozone precursors were not modeled completely and could not be addressed through boundary conditions alone. Without specific measurements at many locations along the modeling domain boundary, adjusting boundary conditions to represent sources outside the domains tends to result in under- or overpredictions.
- Emission sensitivity simulations with the photochemical model indicate that doubling $NO_x$ emissions will usually decrease peak ozone

concentrations and doubling VOC emissions will increase peak ozone concentrations.

- Based on the RLIC emission inventory, the Ras Laffan area would appear to be VOC-limited, and VOC reductions will likely be most effective in reducing ozone concentrations. The response of the modeling system to VOC and $NO_x$ reductions indicates that the modeled atmosphere is VOC-limited, which is consistent with the large $NO_x$ emissions in the RLIC inventory.
- $NO_x$ reductions will likely increase ozone unless very high levels of $NO_x$ reduction are obtained. However, smaller $NO_x$ reductions may be effective at reducing regional ozone concentrations downwind of the RLIC. In VOC-limited atmospheres, $NO_x$ reductions tend to increase ozone near the source area due to reduced ozone titration. However, $NO_x$ provides the "building blocks" for ozone, and $NO_x$ reductions, even under VOC-limited conditions, will reduce ozone concentrations at some distance downwind of the source.
- Inclusion of other regional sources may significantly change the conclusions of this study. It is apparent that significant amounts of $NO_x$ are being transported into northern Qatar. If $NO_x$ is the only ozone precursor being transported into the region, we expect that the conclusions about emission controls will prevail. However, if significant amounts of VOCs are being transported into the region, the conclusions may differ.

## 5. ACKNOWLEDGEMENTS

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