OZONE SENSITIVITY ANALYSIS TO NOx AND VOC EMISSIONS AND THE IMPACT OF INTERNATIONAL ANTHROPOGENIC EMISSIONS IN MARICOPA COUNTY

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1. INTRODUCTION

Maricopa County make up a large portion of Phoenix-Mesa moderate nonattainment area (NAA) for the 2008 ozone National Ambient Air Quality Standard (NAAQS) and a marginal NAA for the 2015 ozone NAAQS (EPA 2022a and EPA 2022b). In the previous study at the Arizona Department of Environmental Quality (ADEQ) conducted in May 2020 to assess the ozone impacts of the stay at home order from COVID-19, we observed different ozone responses to emissions reductions in the spring and summer. Reducing nitrogen oxides (NOx) emissions led to ozone increase in the spring on some days and ozone decrease in the summer on all days. It was not well understood how ozone in Maricopa County responds to changes in local NOx or volatile organic compound (VOC) emissions under different conditions. In order to implement effective measures to bring the Maricopa County to attainment, it is critical to understand how ozone in this region responds to changes in the precursor emissions in the spring and summer.

The purpose of this study is to analyze how ozone in Maricopa County responds to changes in the local NOx and VOC emissions in the spring and summer months using the high order decoupled direct method (HDDM) and first-order DDM tool in the Comprehensive Air quality Model with extensions (CAMx) photochemical model (Ramboll 2021). In addition, we also quantified the contribution of international anthropogenic emissions to ozone in the Phoenix-Mesa NAA.

2. METHODOLOGY

2.1 2016 Modeling Platform

This study was based on the Environmental Protection Agency (EPA)'s 2016v1 modeling platform (EPA 2021). The EPA 2016v1 platform uses a 12-km continental US (12US2) domain embedded in a North America 36-km (36US3) domain which are shown in Figure 1.

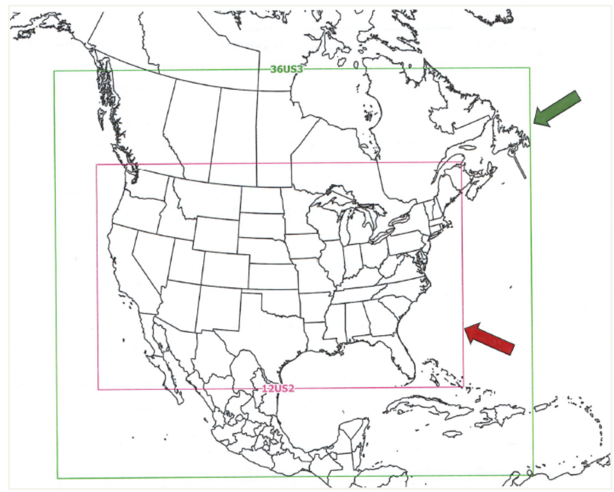

Figure 1. 12-km grid domain (red) and 36-km grid domain (green) used in this study.

2.2 Initial and Boundary Conditions

Boundary conditions (BC) for the CAMx most outer 36US3 domain (Figure 1) were based on output from a 2016 simulation of the hemispheric version of Community Multiscale Air Quality (CMAQ) modeling system (IWDW 2020). BCs for the 12US2 domain were provided from the 36-km domain simulation. The CAMx simulation used approximately 7 days of spin-up to wash out the effects of the Initial Concentrations (IC).

2.3 Other Model Inputs

The other CAMx model inputs include PPM advection solver (Colella and Woodward 1984) that was used for horizontal transport along with the spatially varying (Smagorinsky) horizontal diffusion approach. K-theory was used for vertical diffusion. The CB6r4 gas-phase chemical mechanism was selected for CAMx because it includes the latest chemical kinetic rates with halogen chemistry that affects ozone levels over the ocean (Emery et al. 2016). The latest aerosol mechanisms were used along with the standard wet and dry deposition schemes (Zhang et. al 2001 and 2003). We used a 240-sec time step for the meteorology data input to model temporal variability of the transport and the mixing behavior.

2.4 Sensitivity Analysis Setup

We grouped emissions inputs into two categories for sensitivity analysis purpose: anthropogenic and biogenic emissions. Anthropogenic emissions consisted of emissions from the following emissions sectors: on-road mobile, area fugitive dust, agricultural, nonpoint, nonroad, non-point oil and gas, point nonelectrical generating units, airports, point oil and gas, rail, residential wood combustion, point electric generating units, category 1 & category 2 commercial marine vessels, category 3 commercial marine vessels, point non-electrical generating units, point oil and gas, and agricultural fires. Biogenic emissions category consisted of plants and soil emissions developed using the Biogenic Emissions Inventory System version 3.61 (EPA 2021b) within the Sparse Matrix Operating Kernel Emissions (CMAS 2021).

Within CAMx, we used the DDM and HDDM tools to calculate the ozone sensitivity coefficients to anthropogenic and biogenic emissions in the Maricopa county. The sensitivity coefficients were tracked through a nested 36/12 km domain system, with the 36 km domain providing boundary conditions for the 12 km domain. We divided the modeling domain into three regions: Maricopa County, rest of Arizona, and rest of modeling domain. DDM sensitivity coefficient were calculated for emissions originating in Arizona while HDDM coefficients were calculated for emissions originating from Maricopa County. Figure 2 illustrates the regions used in this study.

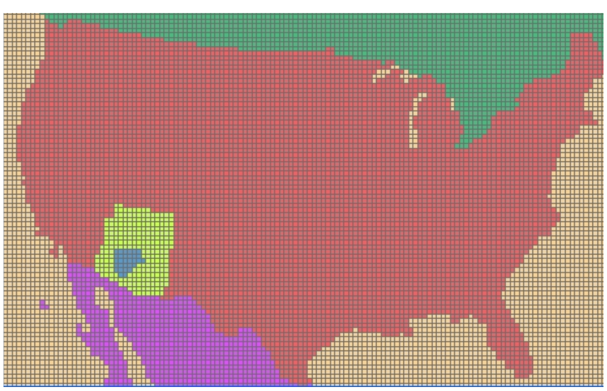

Figure 2. Emissions source regions within the 12US2 grid domain. DDM was performed in grid cells highlighted in blue and yellow while HDDM was performed in grid cells highlighted in blue. No sensitivity analysis calculation for other regions.

2.5 Modeling Period Selection

This modeling study was computationally intensive. We used OpenMP (OMP) parallelization to distribute the model run to multiple processors (CPU cores) and share the computational load on a shared-memory computer (OpenMP 2021). We used 32 out of 36 CPU cores available on our “Linux Box” to carry out this study. Even with this amount of computing resources, it took 16 hours to process one day of simulation for both the 36 km and 12 km domain. Therefore, a simulation from April to September could have taken about 4 months (122 days). Considering the timeline of this project, we decided to run the model during the periods of high measured ozone in the Maricopa County. These periods are: April 13-25, May 16-31, June 18-30, and July 13-31. These periods combine for 60 days with the first 7 days of each period used for spin up period. The model simulation took approximately 36 days.

2.6 International Anthropogenic Emissions Contribution

To estimate the international anthropogenic emissions contribution to ozone in the Phoenix-Mesa NAA, we run the model with (baseline) and without (scenario) anthropogenic emissions outside of the U.S. and then calculate the difference between the two model runs. For this run, we used EPA’s 2017 modeling platform (EPA 2021c). To calculate the ozone design values, we use the Software for the Modeled Attainment Test (SMAT) v1.6 tool (EPA 2021d) and update this tool with EPA’s published annual ozone design values (DV) from 2018 to 2020 (EPA 2020). EPA’s guidance recommends using DV based on 5-years of fourth highest maximum daily 8-hour average (MDA8) ozone data centered on the modeling year (EPA 2018), which is an average of the three DV from 2015-2017, 2016-2018, and 2017-2019 for this analysis.

3. MODEL PERFORMANCE EVALUATION

3.1 Ozone Monitoring Network

The model performance evaluation essentially consists of a series of analyses comparing the modeled data to monitored data. The monitored data for ozone in Maricopa County were downloaded from the Federal Land Manager environmental database (CIRA, 2021) which houses monitored data for several air monitoring networks, the Air Quality monitoring System (AQS) and the Clean Air Status and Trend Network (CASTNET) monitoring networks for ozone. Figure 3 shows the locations of selected ozone monitoring sites in Maricopa County.

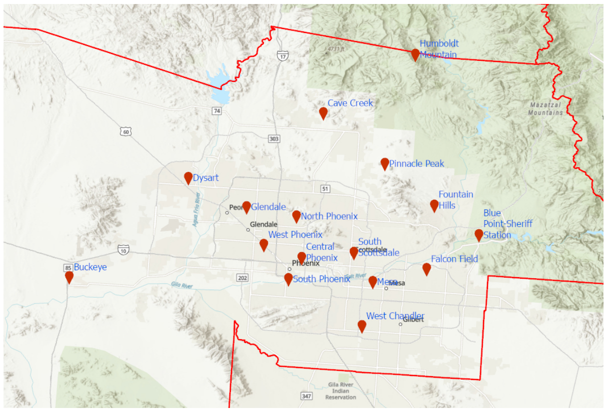

Figure 3. Locations of ozone air quality monitoring sites in Maricopa County

3.2 Comparison of Modeled and Monitored Ozone

Figure 4 displays time series of predicted and monitored hourly ozone concentrations at North Phoenix monitoring site. This monitoring site have had higher ozone concentrations in the past and its 2014-2018 DV was 75 ppb

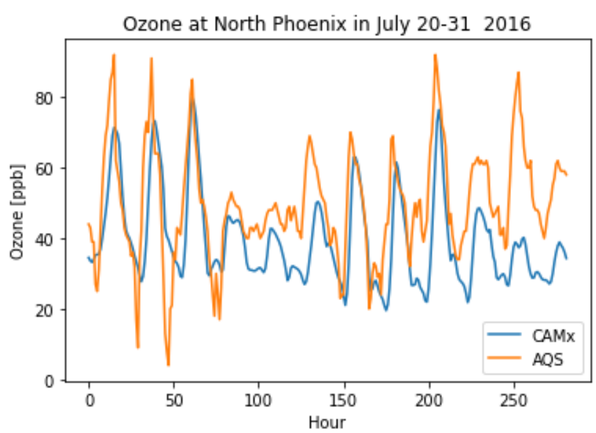

Figure 4. Time series of predicted and monitored hourly ozone concentrations at North Phoenix on high ozone days in July

CAMx prediction of the trend for hourly ozone in all study periods considered was good. The highlights of predicted and monitored ozone comparison are summarized below:

- In April, CAMx well predicted the monitored hourly ozone maxima, however, CAMx overpredicted monitored hourly ozone minima below 20 ppb.
- In May, CAMx struggled to predict the monitored ozone maxima and minima. CAMx underpredicted observed hourly ozone maxima above 60 ppb and minima above 30 ppb. CAMx also overpredicted minima below 20 ppb.
- In June, CAMx improved on the poor performance in May and well predicted observed hourly ozone maxima. However, CAMx still overpredicted hourly ozone minima below 20 ppb.
- In July, CAMx well predicted observed hourly ozone maxima most of the time. Similar to May, CAMx underpredicted hourly ozone minima above 30 ppb and overpredicted minima below 20 ppb.

3.2 Summary of Ozone Model Performance Evaluation

Normalized Mean Bias (NMB) and Error (NME) statistical metrics for hourly and maximum daily average 8-hour (MDA8) ozone averaged for all sites in the Maricopa County are shown in Table 1.

Table 1. Summary of CAMx performance statistics for hourly and MDA8 ozone for sites in Maricopa County. Red indicates that the statistic does not achieve the performance criteria

All Sites in Maricopa County				
Metric	NMB		NME	
Goal	≤±5%		≤15%	
Criteria	≤±15%		≤25%	
	Hourly		**MDA8**	
Month	NMB	NME	NMB	NME
April 20-25	1.7	21.9	-11.0	12.2
May 23-31	-11.1	22.6	-20.2	20.3
June 24-30	-7.1	23.4	-12.5	15.2
July 20-31	-15.8	23.3	-16.6	17.0

CAMx simulation on high ozone days achieves the ozone performance criteria outlined in Emery et al. (2017) for hourly and MDA8 NME in all periods simulated. Performance criteria are also achieved for hourly NMB in April, May, and June; and for MDA8 NMB in April and June. The NMB and NME hourly and MDA8 ozone statistics achieves the ozone performance criteria for 13 of the 16 conditions analyzed (81% of the time). CAMx slightly overestimate hourly NMB in April and underestimate ozone in all other conditions analyzed. The period simulated in May and July show a higher underestimation bias compared to the periods simulated in April and June both hourly and MDA8.

4. RESULTS

4.1 Sensitivity Model Run Output

In this study, three HDDM and two DDM sensitivity coefficients were produced. Equation 1 below was used to estimate the impact of change in NOx and/or VOC emissions on ozone in Maricopa County.

$$C(V_O + \Delta V, N_O + \Delta N) = C(V_O, N_O) + (\Delta V)S_V(V_O, N_O) + (\Delta N)S_N(V_O, N_O) + \frac{\Delta V^2}{2} S_{VV}(V_O, N_O) + (\Delta V)(\Delta N)S_{VN}(V_O, N_O) + + \frac{\Delta N^2}{2} S_{NN}(V_O, N_O) \quad (1)$$

Where $\boldsymbol{C}$ represents ozone concentration, $\boldsymbol{S_V}$ and $\boldsymbol{S_N}$ are the first-order sensitivity coefficients to anthropogenic VOC and NOx emissions, $\boldsymbol{S_{VN}}$ is the cross second-order sensitivity coefficient to anthropogenic NOx and VOC emissions, $\boldsymbol{S_{VV}}$ and $\boldsymbol{S_{NN}}$ are the second-order sensitivity coefficients to anthropogenic VOC and NOx emissions, $\Delta\boldsymbol{V}$ and $\Delta\boldsymbol{N}$ are the change in anthropogenic VOC and NOx emissions.

CAMx outputs the sensitivity coefficients in a separate file from the standard model output file for each grid domain used. We used CAMx support tools to combine the daily output files into a single file for each run period. Python was used to write a code that calculates the impact of emissions changes on ozone using the sensitivity coefficients from DDM and HDDM tools.

4.2 Ozone-NOx-VOC Isopleths

We developed MDA8 ozone-NOx-VOC isopleths using concentrations calculated from various NOx and VOC emissions changes and modeled sensitivity coefficients. Python was utilized to visualize, in a 2-dimension space, the impact of NOx and VOC emissions changes on ozone at various monitors in Maricopa County.

Figures 5 and 6 illustrate the average MDA8 ozone-NOx-VOC isopleth for all monitors in Maricopa County during high ozone periods in April and July, respectively. The isopleths in Figures 5 and 6 suggest a linear MDA8 ozone response to changes in anthropogenic NOx emissions in the spring and summer. Figure 5 also shows a minimal ozone response to anthropogenic VOC emission changes in the spring while Figure 6 shows no ozone response to anthropogenic VOC emission changes in the summer. In this case, reducing anthropogenic NOx emissions is more effective for ozone reduction in Maricopa County.

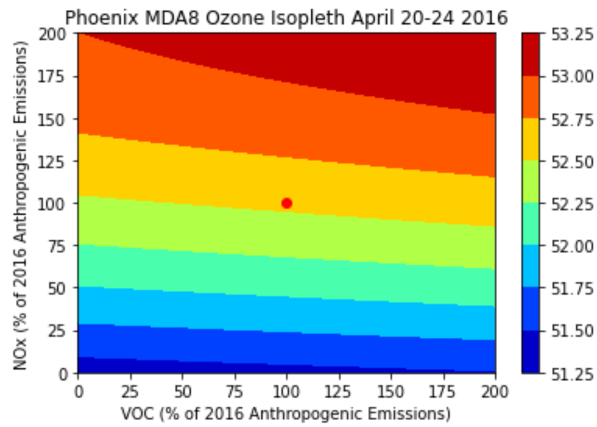

Figure 5. Average MDA8 Ozone-NOx-VOC Isopleth for all monitors in Maricopa County in April. The red dot indicates zero NOx and VOC emission changes from the baseline case

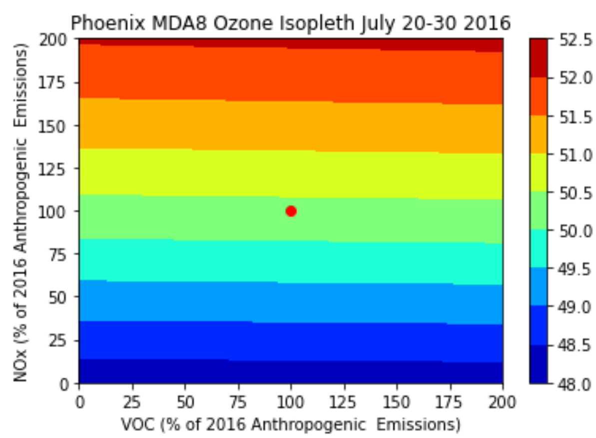

Figure 6. Average MDA8 Ozone-NOx-VOC Isopleth for all monitors in Maricopa County in July. The red dot indicates zero NOx and VOC emission changes from the baseline case

Note that only first order sensitivity coefficients were calculated for biogenic NOx and VOC emissions in Maricopa County. Therefore, MDA8 ozone-NOx-VOC isopleths for biogenic emissions indicates a linear response to biogenic VOC emission changes in the spring and summer. The ozone response to biogenic NOx emission changes is minimal.

Figures 7 and 8 present MDA8 ozone-NOx-VOC isopleth for Falcon Field monitor on measured ozone exceedance days (April 20 and July 22). Falcon Field demonstrates an example of an area in Maricopa County with a non-linear ozone response to anthropogenic NOx emission changes in the spring. In the summer, ozone response to anthropogenic NOx emission changes transitions to linear. Ozone response to anthropogenic VOC emissions changes in the spring is minimal and no ozone response to anthropogenic VOC emissions changes in the summer. The magnitude of ozone response to anthropogenic NOx emission changes increases from spring to summer. This trend suggests that local emissions contribute to ozone exceedance in the summer more compared to the contribution in the spring.

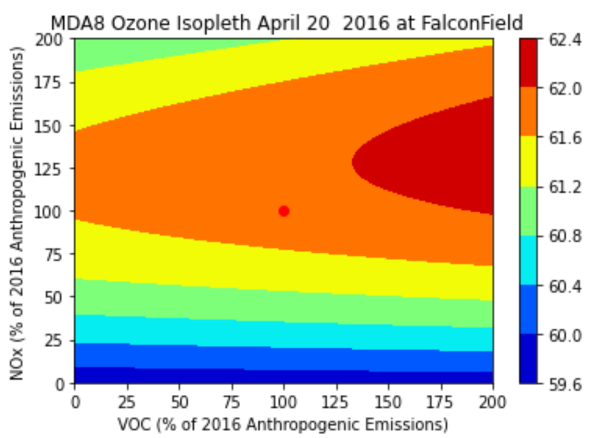

Figure 7. MDA8 Ozone-NOx-VOC Isopleth at Falcon Field monitor on selected ozone exceedance day (April 20).

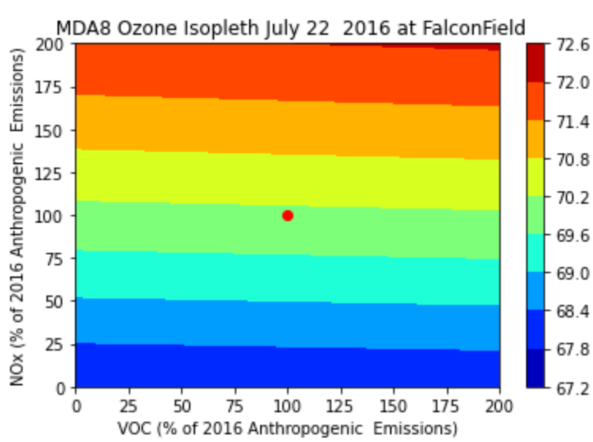

Figure 8. MDA8 Ozone-NOx-VOC Isopleth at Falcon Field monitor on selected ozone exceedance day (July 22).

The ozone response to changes in anthropogenic NOx and VOC emissions varied from one monitor to another and sometimes from morning to afternoon. This variability in ozone response makes the Maricopa County a complex area in terms of ozone control strategy.

The MDA8 ozone-NOx-VOC isopleth with changes in biogenic emissions show a strong response to biogenic VOC emissions changes which increases from spring to summer. This trend again emphasizes the increased contribution of local emissions to ozone exceedance days in the summer compared to the contribution in the spring. There was some unexpected ozone sensitivity behavior to biogenic emissions at Buckeye and Humboldt Mountain monitors on April 20 and July 22. Ozone transitions from strong response to changes in biogenic VOC emissions in the spring to minimal/no ozone response to changes in biogenic VOC emissions. It's not clear what's causing this shift in ozone response. Further investigations will be conducted in the future studies.

4.2 International Ozone Contribution

The results show that the average and median contributions from international anthropogenic emissions to 2017 ozone DV at monitors in the Phoenix-Mesa NAA is 4.0 and 3.9 parts per billion (ppb), respectively. The highest contribution occurs at Humboldt Mountain and Tonto National Monument (5.3 ppb) and the lowest contribution occurs at Buckeye (3.2 ppb).

The results show that without contributions from international anthropogenic emissions, the 2017 ozone DV at nine of fourteen monitors in the Phoenix-Mesa NAA would have attained the 2015 ozone NAAQS. The monitors at Mesa, North Phoenix, Falcon Field, Pinnacle Peak, and Red Mountain would not have attained the NAAQS.

Figure 9 illustrates the contribution from international anthropogenic emissions at each monitor in the Phoenix-Mesa NAA. Overall, the modeling results indicate a higher contribution from international anthropogenic emissions to ozone at high altitude areas and lower contribution at low altitude areas

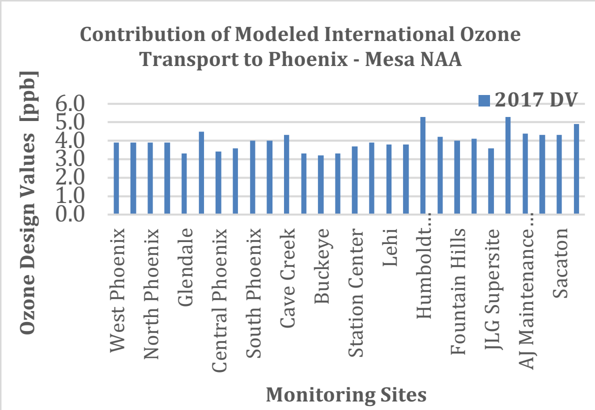

Figure 9. Ozone contribution from international anthropogenic emissions at each monitor in the Phoenix-Mesa NAA. Contribution determined using the 2017 DV.

5. SUMMARY AND CONCLUSION

ADEQ conducted a study to evaluate the impacts of changes in NOx and VOC emissions on ozone in Maricopa County. This study is critical to the effectiveness of emissions control strategies in Maricopa County, which account for most of the Phoenix-Mesa NAA. The objective of this study was to evaluate how ozone in Maricopa County respond to changes in NOx and VOC emissions within the county during spring and summer periods. We used HDDM and DDM tools within CAMx to carry out this study. In addition, we quantified the international anthropogenic emissions contribution to ozone at monitors in the Phoenix-Mesa NAA.

We ran the model for periods of high observed ozone in April (13-25), May (16-31), June (18-30), and July (13-31) to minimize the model simulation time to 36 days. The model performance evaluation in these periods indicated an overall acceptable CAMx prediction of monitored ozone, which was within the performance range of previous modeling studies. However, CAMx consistently overestimated observed ozone below 20 ppb. Given that ADEQ is interested in ozone chemistry during high ozone periods, the model performance when measured ozone is below 20 ppb is of secondary importance.

The sensitivity analysis showed a strong ozone response to changes in anthropogenic NOx and biogenic VOC emissions compared to a minimal/no response to changes in anthropogenic VOC and biogenic NOx emissions. The sensitivity analysis also showed a shift from non-linear ozone response to anthropogenic NOx emissions in spring, to a linear ozone response in summer for some monitors in Maricopa County. Unexpectedly, there was a shift from minimal ozone response to biogenic NOx emissions in the spring to significant response in the summer at Buckeye and Humboldt Mountain monitors. This behavior warrants further investigation in future studies.

The preliminary results of this study suggest that anthropogenic NOx emissions would be more effective for ozone reduction as biogenic VOC emissions cannot be regulated. A more detailed study should follow for the entire ozone season (April-September) to confirm the results outlined above. This detailed study should utilize the newly released 2016v2 EPA's model platform version (EPA 2021e), instead of the 2016v1 version used in this study. When comparing these modeling platforms for Arizona, biogenic VOC emissions decreased about 60%, biogenic NOx decreased more than 50%, and biogenic CO decreased about 20% from 2016v1platform to 2016v2 platform.

The analysis of the international ozone transport indicated a moderate (4 ppb) average contribution of international anthropogenic emissions to ozone in Maricopa County. Without international ozone transport, 15 out of 20 monitors would have attained the 2015 ozone NAAQS.

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