Analysis of Rising Ozone Concentrations in Maricopa County in 2011-2012

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ACRONYM LIST

ADEQ: Arizona Department of Environmental Quality

AVHRR: Advanced Very High Resolution Radiometer

AGL: Above ground level

CBSA: Core-Based Statistical Area

CDAS: Climate Data Assimilation System

CO: Carbon monoxide

CO_2: Carbon dioxide

CPC: Climate Prediction center

E0: Gasoline containing 0 percent by ethanol by volume

E10: Gasoline containing 10 percent by ethanol by volume

EDAS: Eta Data Assimilation System

EGU: Electric generating unit

EPA: Environmental Protection Agency

FINN: Fire INventory from NCAR

HMS: Hazard Mapping System

HYSPLIT: HYbrid Single-Particle Lagrangian Integrated Trajectory

LAI: Leaf area index

MAG: Maricopa Association of Governments

MEGAN: Model of Emissions of Gases and Aerosols from Nature

mb: Millibar

MDA8: Daily maximum 8-hour average ozone

MODIS: MODerate-resolution Imaging Spectroradiometer

MOVES: Motor Vehicle Emissions Simulator

NAAQS: National Ambient Air Quality Standards

NAB: North American Background

NCAR: National Center for Atmospheric Research

NCDC: National Climatic Data Center

NCEP: National Center for Environmental Prediction

NOAA: National Oceanic and Atmospheric Administration

NO: Nitric oxide

NOx: nitrogen oxides

OLR: Outgoing longwave radiation

PM: Particulate matter

PPB: Parts per billion

PPBC: Parts per billion carbon

PRB: Policy-relevant Background

PSI: Per square inch

RVP: Reid Vapor Pressure

SO_2: Sulfur dioxide

SST: Sea surface temperature

VOCs: volatile organic compounds

VMT: vehicle miles travelled

ω: vertical velocity

EXECUTIVE SUMMARY

The purpose of this project was to evaluate recent ozone trends in Maricopa County and determine the cause(s) of rising ozone concentrations in 2011-2012. We evaluated a number of hypotheses provided by the Maricopa Association of Governments (MAG) to explain increasing ozone in 2011-2012 that included both local and regional factors as well as long-range transport. These hypotheses are summarized as follows:

- Changes in emissions
  - Summer-time use of 10% ethanol gasoline blend fuel since 2011
  - Local/regional anthropogenic emissions
  - Local biogenic emissions
  - Local and regional wildfire activity
- Changes in importance of volatile organic compound (VOC)-limited ozone reactions in the urban core and the role of nitrogen oxide (NOx) emissions
- Changes in local and regional meteorological and climatic conditions
  - Temperature, winds, clouds/rainfall, El Nino phase, etc.
- Changes in background ozone concentrations and transport

The analyses performed in this study found that the 2008-2012 ozone trend observed at Maricopa County monitors is similar to ozone trends measured in other large metropolitan areas in nearby states in the western U.S. This suggests that regional-scale factors were important in determining 2011-2012 ozone levels in Maricopa County.

In Maricopa County, the May-June period preceding the summer monsoon tends to be associated with high ozone and variations in May-June cloudiness during 2008-2012 were consistent with Maricopa ozone trends. Satellite-derived measures of regional cloudiness and local Phoenix cloud cover data showed an unusually large amount of cloud cover in May-June 2009 and an unusually small amount of cloud cover in May-June 2011-2012. May and June were the two months with the largest number of high ozone days in Maricopa during 2008-2012.

Other factors that may have contributed to high ozone levels in 2012 were an unusually large number of high-temperature days in 2012, and more potential impacts from wildfire emissions in 2012 than in 2008-2011. No changes were evident in transport patterns or in the North American background ozone that would indicate that transport played a significant role in rising Maricopa ozone levels in 2011-2012.

Anthropogenic NOx and VOC emissions generally decreased during 2008-2011 in the Maricopa Non-Attainment Area. Modeling of on-road mobile sources using the U.S. Environmental Protection Agency's Motor Vehicle Emissions Simulator (MOVES) model indicated that vehicle emissions declined overall during 2008-2012, but do show an increase in VOC emissions after 2010 due to the use of 10% ethanol blend (E10) fuel.

Our evaluation of whether the Maricopa Non-Attainment area is NOx-limited or VOC-limited with respect to ozone formation showed that the suburban monitors to the northeast of the Phoenix urban core are NOx-limited. For these monitors, on-the-books NOx reductions should continue to bring ozone levels down. The Buckeye monitor, located to the southwest of the urban core, is clearly VOC-limited. Analysis of weekday/weekend ozone differences showed that from 2009-2012, monitors in the Phoenix urban core varied together by year between being NOx-limited and VOC-limited. These results indicate that the Phoenix urban area is in a transitional regime between being VOC-limited and NOx-limited with respect to ozone formation. The 2011 VOC/NOx ratio derived from the Maricopa Non-Attainment Area emission inventory indicated that the area was VOC-limited, while the weekday/weekend analysis showed all monitors except Buckeye to be NOx-limited in 2011. The VOC/NOx ratio of the emission inventory may be biased low.

MAG's Maricopa Non-Attainment Area emission inventory data for 2008 and 2011 indicate that NOx reductions have been larger than VOC reductions during 2008-2011. Recent Federal emissions control programs (e.g. reductions in highway and off-road vehicle emissions limits) have been primarily aimed at reducing NOx emissions. Wolff et al. (2013) note that, nationwide, a larger decline in NOx emissions than VOC emissions has pushed many areas from being VOC-limited to being NOx-limited. We conclude that the Maricopa area is in transition from being VOC-limited to becoming NOx-limited. This means the area may benefit from both NOx and VOC emission controls to reduce ozone in the short term, but that in the long term, NOx emissions controls are the best mechanism for decreasing Maricopa ozone levels.

Additional research could be conducted to bolster understanding of currently prevailing ozone formation conditions in Maricopa County. We recommend:

- Short duration canister sampling at the JLG Supersite during the 6-9 am period to determine the ambient VOC/NOx ratio in the morning when ambient measurements best reflect emissions. The VOC composition should be analyzed to investigate the contributions of on-road mobile evaporative emissions and other sources. The canister VOC samples should be analyzed for ethanol, if possible, to quantify the contribution of ethanol in gasoline.
- Further investigate a possible biogenic emissions "hot spot" near the North Phoenix monitor
- Evaluate high ozone day meteorological conditions as suggested by the ADEQ ozone forecasters.

1.0 INTRODUCTION

Maricopa ozone monitoring data are used to calculate the design values that determine whether the area is in compliance with the National Ambient Air Quality Standard (NAAQS) for ozone. The NAAQS for ozone is violated at a monitor if the annual fourth highest daily maximum 8-hour average concentration averaged over three consecutive years exceeds a threshold value. This threshold is currently 0.075 ppm (75 ppb). A single year of data is not considered sufficient to demonstrate attainment; instead, the fourth highest value in a given year is used in the calculation of the indicator of attainment status. Consequently, we refer to this statistic as the annual 8-hour design value.

Recent trends in the annual fourth highest daily maximum 8-hour average ozone concentration among all monitors in Maricopa County are shown in Figure 1-1. The dashed line in Figure 1-1 indicates the 1997 84 ppb NAAQS for ozone. In March 2008, the EPA promulgated a more stringent 8-hour ozone standard of 75 ppb. The 2008 NAAQS is shown as a solid red line in Figure 1-1. From 2000 through 2009, the overall trend in the annual fourth highest daily maximum 8-hour average concentration was downward. Although there are years where ozone increased (e.g. 2005, 2008), ozone decreased in the following year. From 2009 onward, ozone has increased each year, and has been above 75 ppb since 2010. In April 2012, the EPA designated part of Maricopa County to be a marginal non-attainment area using 2008-2010 ozone measurements. During 2011-2012, the Maricopa County air monitoring network continued to record increasing ozone concentrations.

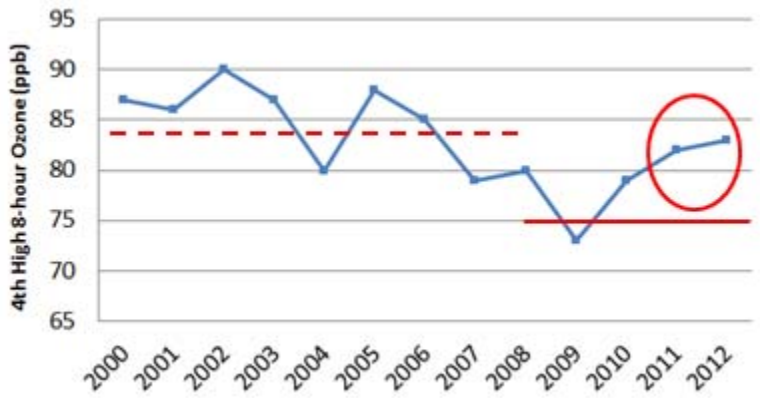

Figure 1-1. Maximum 4th highest daily maximum 8-hour ozone concentration among Maricopa County ozone monitors from 2000-2012. Data supplied by MAG.

The purpose of this project was to determine the cause(s) of rising ozone concentrations in Maricopa County in 2011-2012. We considered both local and regional factors as well as long-range transport.

We evaluated a number of hypotheses provided by MAG to explain increasing ozone in 2011-2012:

- Changes in emissions

- Summer-time use of 10% ethanol gasoline blend fuel since 2011 and associated production of aldehydes
- Local/regional anthropogenic emissions
- Local biogenic emissions
- Local and regional wildfire activity

- Changes in importance of VOC-limited ozone reactions in the urban core and the role of NOx emissions
- Changes in local and regional meteorological and climatic conditions
  - Temperature, winds, clouds, precipitation, El Nino phase, etc.
- Changes in background ozone concentrations and transport

This report is organized as follows: Section 2 is an analysis of local and regional emissions trends. In Section 3, we examine the relative importance of NOx and VOC emissions in limiting ozone formation in the Phoenix urban core and in outlying areas. Section 4 contains an analysis of the role played by local meteorological factors. In Section 5, we evaluate the importance of ozone transport in determining 2011-2012 ozone trends. In Section 6, we discuss the role of background ozone and regional-scale meteorological factors in setting Maricopa ozone levels in 2011-2012. Finally, in Section 7, we present conclusions and recommendations for further work.

2.0 EMISSIONS CHANGES

Increases in local and/or regional emissions are a potential cause of rising ozone concentrations in Maricopa. In this section, we analyze anthropogenic emission trends in the Maricopa Non-Attainment Area and trends in Arizona statewide emissions. We also analyze regional wildfire emissions and summarize MAG's analysis of local biogenic emissions.

2.1 On-Road Mobile Emissions Analysis

On-road mobile sources are an important local source of emissions in Maricopa County. These mobile sources include all highway motor vehicles—cars, pickups, heavy duty trucks, buses, and motorcycles. Motor vehicles emit ozone precursor pollutants VOC, carbon monoxide (CO) and NOx through fuel combustion and unburned VOC through gasoline evaporation.

ENVIRON performed several analyses of Maricopa's on-road emissions to determine whether they are likely to have contributed to rising ozone concentrations in 2011-2012. First, we analyzed the emission impacts of summertime use of gasoline blended with ethanol. Next, we calculated the on-road emissions trends of each pollutant during summer ozone seasons 2008-2012. Finally, ENVIRON reviewed ambient monitoring data to determine whether there is evidence of increased evaporative emissions during periods of high summer temperatures in Maricopa County that may not be captured by the EPA's MOVES on-road mobile emissions model.

2.1.1 Impact of Summer Use of 10% Ethanol Gasoline

The purpose of analyzing ethanol impacts on vehicle emissions was to determine whether use of this fuel caused an increase in overall on-road mobile VOC emissions. Ethanol blended gasoline was not used in Maricopa County during the ozone season prior to 2011, but was used in winter months in years prior to 2011. Starting in 2011, gasoline containing 10 percent by ethanol by volume (E10) became the primary fuel in Maricopa County, comprising 95% of the gasoline sales. Table 2-1 summarizes the shift in gasoline market share from conventional fuel (E0; gasoline containing no ethanol) toward E10 between 2008 and 2012.

Table 2-1. Ozone season E0 and E10 market shares in Maricopa County. Data provided by MAG.

Year	E0	E10
2008	100%	0%
2009	100%	0%
2010	100%	0%
2011	5%	95%
2012	5%	95%

Because the introduction of ethanol fuel coincided with an observed increase in Maricopa ozone (Figure 1-1), ENVIRON investigated the effects of E10 on VOC emissions. We used EPA's

MOVES model[1] with local data inputs provided by MAG[2] specific to Maricopa County. The MOVES runs covered the ozone season months April through September of 2008 through 2012 for purposes of calculating emissions trends (discussed in Section 2.1.2). The MOVES model requires local weather data as inputs, and ENVIRON obtained hourly temperature and humidity data for the 2008-2012 ozone seasons from data recorded at Phoenix Sky Harbor International Airport.

Based on Maricopa fuel survey data provided by MAG and discussions with MAG, ENVIRON determined fuel parameters for gasoline and diesel fuels by month and year for use in MOVES. Table 2-2 shows a gasoline parameter important in calculating VOC emissions: Reid Vapor Pressure (RVP), a measure of gasoline's volatility at 100°F. RVP varies by season (spring and summer) and fuel type (E0 and E10). E10 fuel used in spring is more volatile than the summer fuel used from May through September. Arizona Revised Statute Title 41-2083 limits Maricopa County RVP to 7 psi from May 31 to September 30. Federal regulations allow E10 a volatility waiver of 1 psi[3], whereas E15 is not currently granted such a waiver. There is a 1 psi volatility waiver for E10 for April and October only[2]. There is a rulemaking currently in public notice that will have the 1 psi waiver only apply in April, in order to not conflict with state statute.

Table 2-2. Reid Vapor Pressure (RVP) used in MOVES runs. Data provided by MAG, except E0 in 2011-2012.

Year	Spring Fuel RVP (psi) *April*		Summer Fuel RVP (psi) *May - September*	
	E0	**E10**	**E0**	**E10**
2008	7.8	*N/A*	6.5 - 7.1	*N/A*
2009	6.7		6.6 - 6.9	
2010	6.9		6.5 - 6.8	
2011	*7.9**	8.3	*7.0**	6.8
2012	*7.9**	8.4	*7.0**	6.7 - 7.0

*MOVES default for Maricopa County

In order to determine the impact of E10 fuel on on-road emissions, ENVIRON ran MOVES twice to simulate years 2011 and 2012; the only difference between runs was the ethanol content (E0 or E10) of the fuel used by Maricopa's gasoline-fueled vehicle fleet and the RVP as shown in Table 2-2. All other fuel properties, fleet activity, and ambient conditions were held constant between the runs.

The MOVES results showed that on-road total VOC emissions are higher when the gasoline-fueled fleet operates on E10. As shown in Figure 2-1, E10 causes an increase in emissions of VOC (12-13%), acetaldehydes (27-33%), and NOx (2-3%), but reduces CO emissions (-8 to -12%). Changes to formaldehyde and propionaldehyde emissions were relatively small (±1%).

[1] EPA, 2010. MOVES2010b with database version 'movesdb20120410.' http://www.epa.gov/otaq/models/moves/index.htm
[2] Personal communication with Matthew Poppen of MAG. April 2013.
[3] http://www.epa.gov/otaq/fuels/gasolinefuels/volatility/standards.htm

Although the acetaldehyde emissions exhibit the largest percent increase, their mass makes up only 1% of the total VOC emissions. Formaldehyde and propionaldehyde comprise approximately 2% and 0.1% of the VOC, respectively.

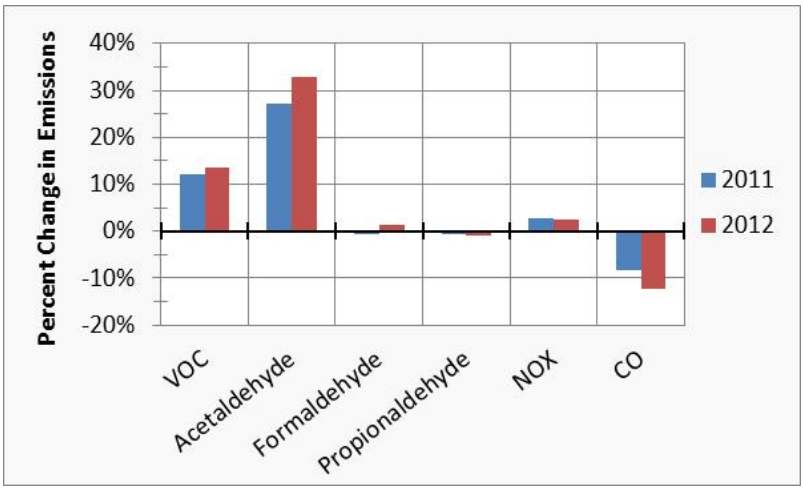

Figure 2-1. Ozone season emissions change resulting from E10 use in 2011 and 2012.

2.1.2 MOVES On-Road Mobile Emissions Trends

In general at most locations in the U.S., emissions from on-road vehicles show a decreasing trend year-over-year, despite an increase in vehicle miles traveled (VMT). The continued reductions in emissions are achieved through a fleet turnover effect whereby older, higher-emitting vehicles retire from the fleet as new vehicles with modern emission control technology enter. Federal regulations require that all new vehicles sold must meet emission standards that become increasingly stringent with the passage of time.

VMT in the United States typically grows year-by-year because the population is growing; this increases the total vehicle miles traveled. During recessionary periods however, VMT may remain stagnant or even decrease. Maricopa County VMT decreased by 2% from 2008 to 2009 and then fluctuated by ±1% from 2010 to 2012, as shown in Figure 2-2.

In ENVIRON's experience, seasonal VMT patterns typically exhibit highest activity during summer months with relatively low activity in winter. The effect is most pronounced in colder regions of the country such as the upper Midwest and the Northeast, but even default nationwide data contained in MOVES reflect this typical pattern. In sharp contrast, Maricopa County VMT trends show the lowest VMT occurring in July and August (Figure 2-2). Based on our discussions with MAG, the reasons for the low VMT in summer are that schools are on break, seasonal residents return to their home states in summer, and fewer special events are scheduled.

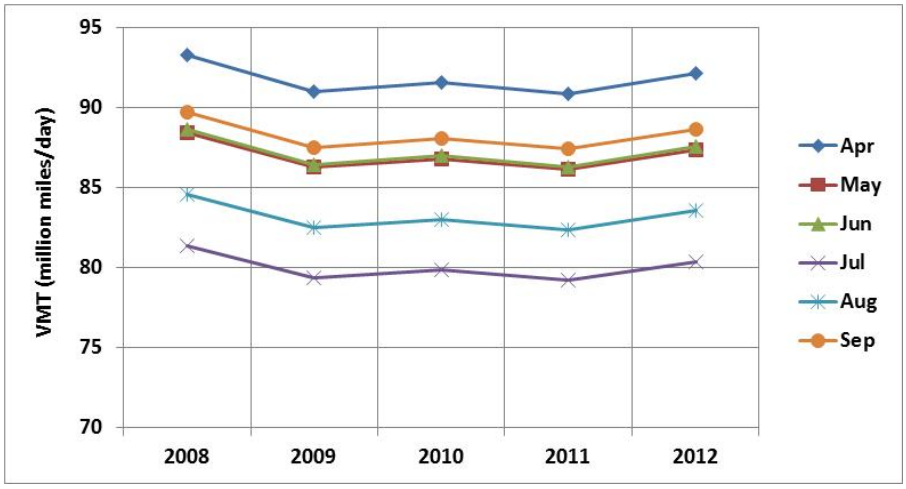

Figure 2-2. Maricopa County Vehicle Miles Traveled (VMT) trends by month.

Figure 2-3 though Figure 2-7 show trends in Maricopa County emissions—shown as an ozone season average or by month—for VOCs and the three aldehyde species that are calculated by MOVES. Beginning with VOC, Figure 2-3 shows trends by month. Overall, the VOC exhibits a downward trend from 2008 to 2012 due to fleet turnover. The fuel change to from 100% E0 in 2010 to 95% E10 in 2011 caused 2011 VOC emissions to increase relative to 2010 levels during the months May, June, August, and September.

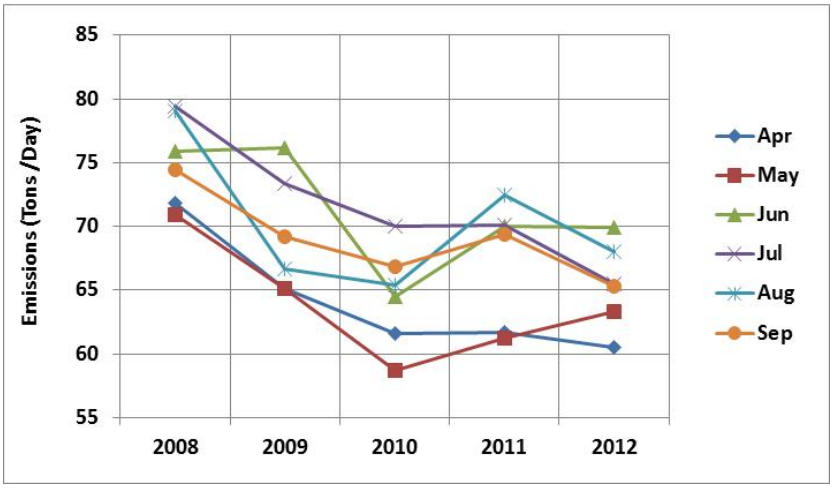

Figure 2-3. MOVES monthly on-road VOC emissions for Maricopa County.

Although the April and July VOC emissions did not increase in 2011, the ozone season average day VOC emissions (Figure 2-4) rose between 2010-2011. The total VOC emissions from on-road mobile sources decreased during 2008-2012 despite use of E10 in 2011 and 2012, due to lower VMT and lower average emission rates from fleet turnover.

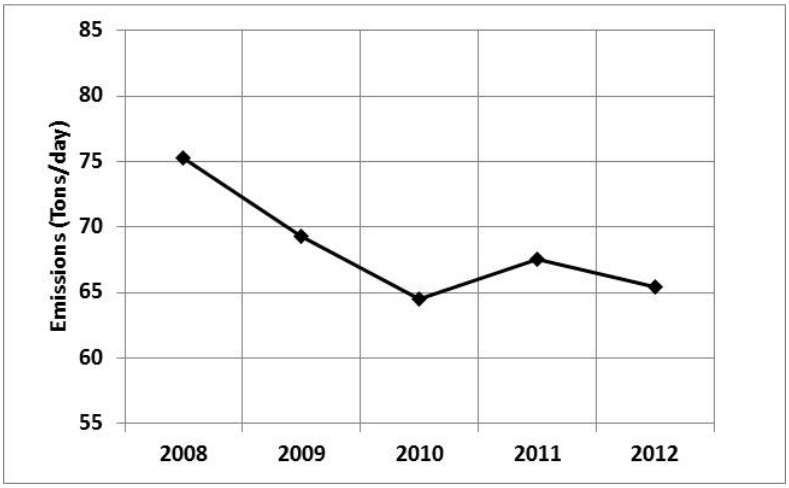

Figure 2-4. MOVES ozone season average on-road VOC emissions for Maricopa County.

MOVES estimates an increase in acetaldehyde emissions moving from E0 to E10 fuel. The acetaldehyde trend below tracks well with VMT from 2008 to 2010, but increases by approximately 30% in 2011 and 2012 due to use of E10 (Figure 2-5). The E10 effect on acetaldehyde is strong enough to cause an overall increase in acetaldehyde emissions over 2008-2012, although the total VOC trend is downward (Figure 2-4). Because the emitted acetaldehyde mass is small, these increased acetaldehyde emissions are expected to play a minimal role in ozone formation in Maricopa County.

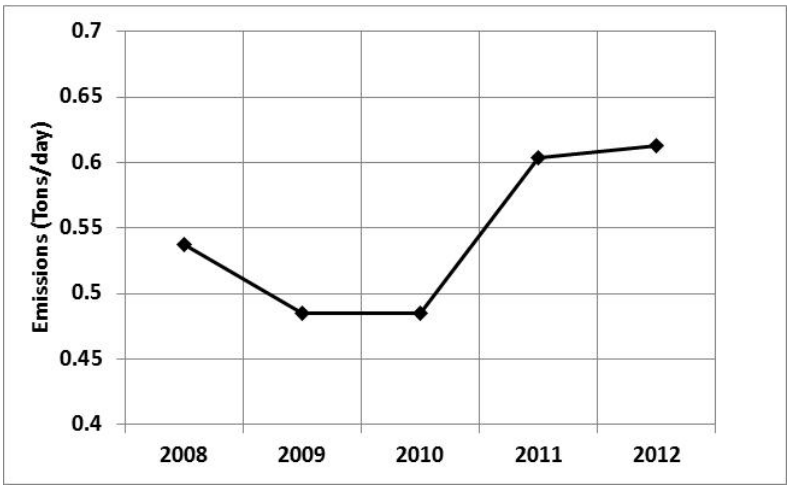

Figure 2-5. MOVES ozone season average on-road acetaldehyde emissions for Maricopa County.

Maricopa ozone season average emissions of formaldehyde and propionaldehyde decrease over 2008-2012, as shown in Figure 2-6 and Figure 2-7, respectively. Unlike total VOC and acetaldehyde emissions, formaldehyde and propionaldehyde emissions do not increase in 2011 in response to the introduction of E10 fuel.

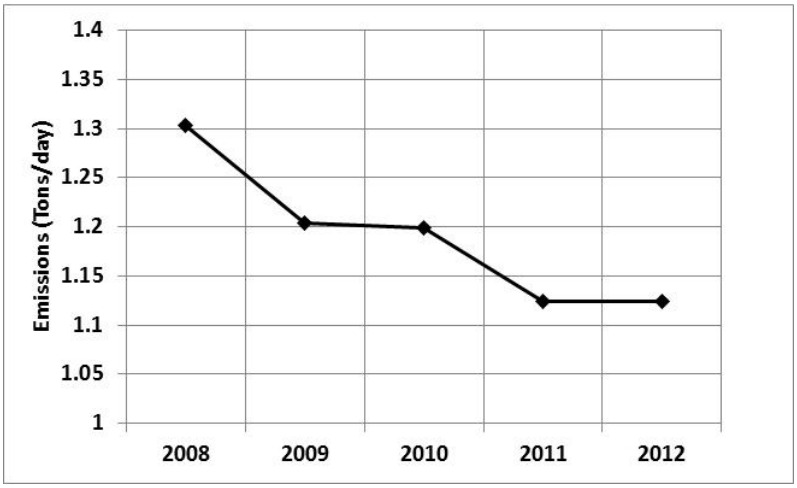

Figure 2-6. MOVES ozone season average on-road formaldehyde emissions for Maricopa County.

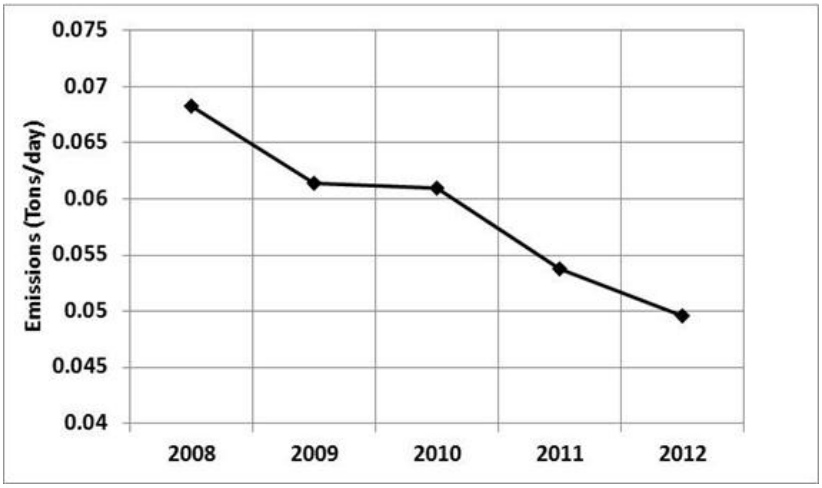

Figure 2-7. MOVES ozone season average on-road propionaldehyde emissions for Maricopa County.

In summary, the MOVES VOC emission trends for Maricopa County show that the introduction of E10 fuel in 2011 could have contributed to the observed ozone increase from 2010-2011. However, the VOC emissions decrease from 2011 to 2012 and show an overall decline in emissions from 2008-2012. Therefore, variations in on-road mobile emissions cannot explain the overall ozone trend from 2008-2012, nor the increase in ozone from 2011-2012. Acetaldehyde emissions increased from E10 use, although the amount of increased emissions is sufficiently small that it is unlikely to have caused a significant increase in ozone.

It should be noted that the model results are dependent upon the accuracy of MOVES, which may not accurately simulate running loss emissions at high temperatures (>96°F) and high RVP (>9). In order to further investigate this issue, ENVIRON analyzed ambient monitoring data from the Phoenix urban core.

2.1.3 Evaporative Emissions from Volatility

In a tunnel traffic study, Fujita et al. (2012) found that evaporative emissions of light hydrocarbons can exhibit a catastrophic increase at high temperatures, with non-methane hydrocarbon emission factors at temperatures of 101–102°F rising to about 3.5 times their values at cooler temperatures (71–72°F). Figure 2-8 shows an example of the variation in running losses with temperature from a Ford Escort automobile tested with its gas cap on (Lindhjem and Korotney, 1993). The vapor pressure, shown on the horizontal axis, is determined by fuel volatility and temperature.

At lower temperatures (22°C), the emissions are on the order of 2 g/test. When the temperature increased to 35°C, emissions increased dramatically, with one test showing emissions nearly two orders of magnitude larger than the tests performed at cooler temperatures.

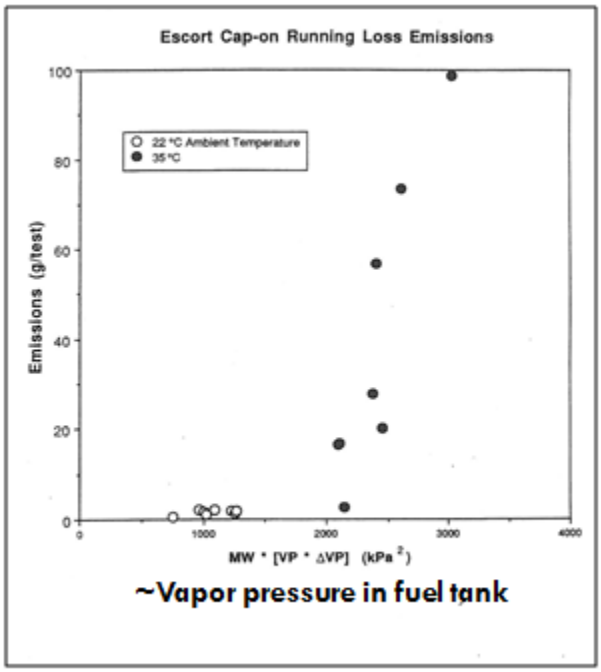

Figure 2-8. Variation of measured running loss emissions from a Ford Escort (Lindhjem and Korotney, 1993).

Emissions factors used in MOVES do not account for this increase in emissions at very high temperatures. Daily maximum temperatures in Maricopa County are frequently higher than 100 °F during the ozone season. It is therefore important to investigate whether this phenomenon of catastrophically increasing emissions occurs during episodes of high summer temperatures in Maricopa.

We used VOC and temperature data from the JLG Supersite in the Phoenix urban core to evaluate whether evaporative emissions show an abrupt increase at high temperatures. Data for the JLG Supersite were provided to ENVIRON by MAG. The JLG Supersite is located near

several large freeways and is expected to be strongly influenced by on-road mobile emissions. The VOC isopentane is a marker for evaporative emissions, as it is found in emissions from low RVP gasoline; butane is largely removed to attain an RVP of 7. We stratified measurements of isopentane by daily average temperature in order to determine whether there is a correlation between temperature and isopentane. The results for the 2010-2012 ozone seasons are shown in Figure 2-9. Figure 2-9 shows a lack of correlation between isopentane and temperature. Based on Figure 2-9, there is no evidence that fuel volatility affects ambient isopentane levels at the JLG Supersite, however, we note the following limitations of the data.

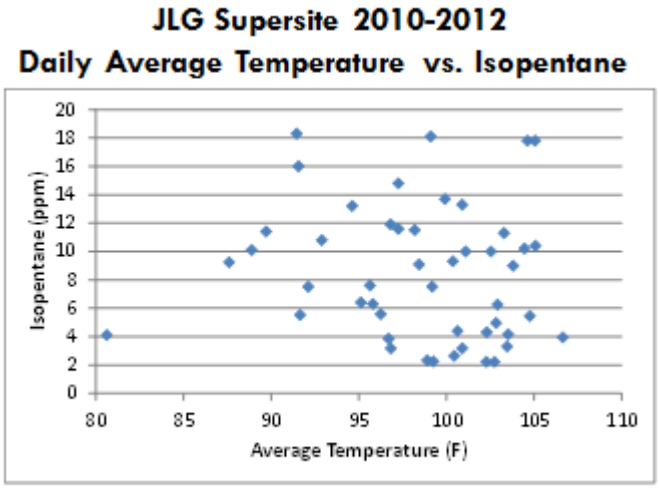

Figure 2-9. Daily average temperature plotted against isopentane concentration for the JLG Supersite (2010-2012).

VOCs are measured via canister sampling at the JLG Supersite, and the sampling occurs every 6 days with 24-hour duration (Arizona Department of Environmental Quality Air Quality Division, 2012). A sampling period extending from 6-9 am would be more useful for evaluating on-road mobile emissions. 6-9 am sampling provides the best characterization of on-road mobile emissions. The mixed layer is shallow and, for monitors located near major roadways, ambient concentrations of NOx and some VOCs such as isopentane are likely to be driven by fresh traffic emissions. Photochemical activity is minimal in the early morning. Evaporative emissions respond to the rate of change of temperature as well as to temperature itself. There is rapid expansion of vapor within car and truck engines as temperature rises rapidly in the early morning and this translates into an increased rate of emissions. In the afternoon, dilution and mixing are at a maximum, photochemical activity is high, and the temperature is falling; therefore afternoon does not allow for optimum sampling of on-road mobile emissions.

2.2 Regional Emissions Trends

We reviewed Arizona statewide emissions data from the U.S. EPA's National Emissions Trends Report (U.S. EPA, 2001; http://www.epa.gov/ttnchie1/trends/) to determine whether regional

emissions trends could be a cause of increased ozone in Maricopa in 2011-2012. If emissions of ozone precursors were increasing in Arizona as a whole during these years, it is possible that ozone transport into Maricopa could be a cause of rising ozone in 2011-2012. The EPA Trends Report lists many categories of emissions, but we have shown the categories with the largest emissions of NOx and VOC in Figure 2-10. The data are derived from the EPA's National Emission inventory, which is compiled every three years. For some source categories, data are available at three year intervals (e.g. industrial fuel combustion) while others are available at higher temporal resolution. For example, electric generating units (EGUs) measure emissions using in-stack continuous emissions monitoring devices, and hourly data are available for these sources. The EPA data are subject to potential year-to-year methodology changes, but can still provide an overview of statewide emissions trends that would serve as an indication that further analysis is warranted.

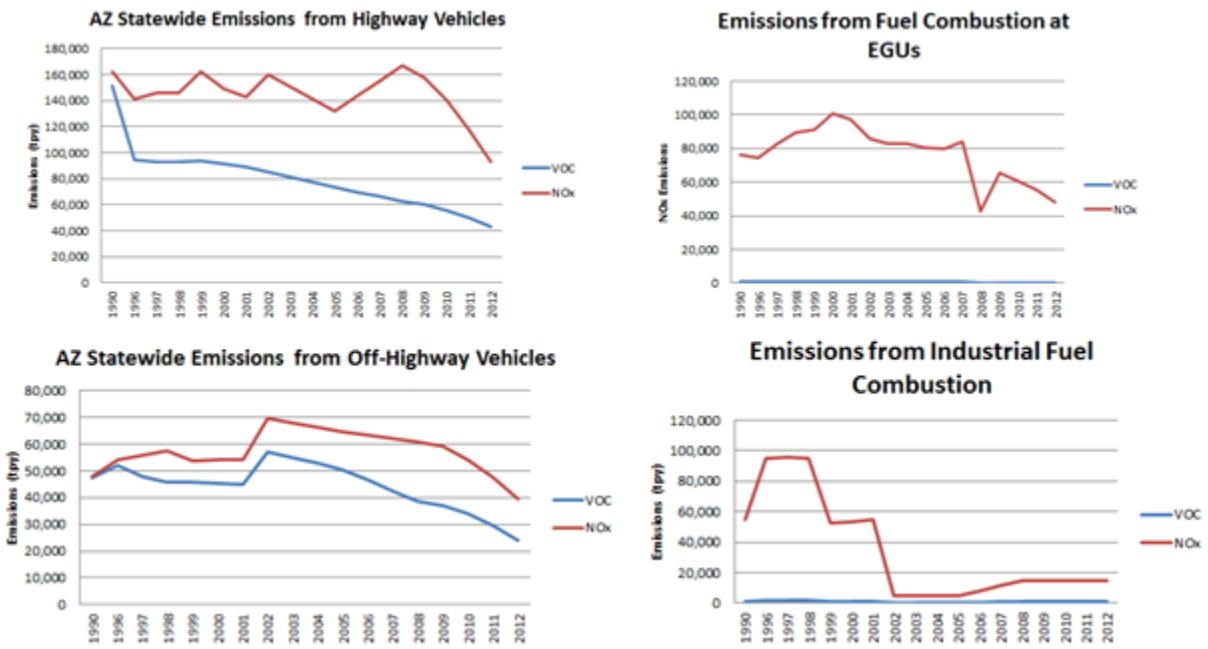

Figure 2-10. Arizona statewide emissions trends from EPA's National Emissions Trends Report.

The emissions data for the largest NOx and VOC emissions source categories show no evidence of increasing anthropogenic emissions during 2011-12 relative to previous years. Statewide emissions of both NOx and VOC for highway and off-highway vehicles decline during 2008-2012. For EGUs, NOx emissions decrease during 2008-2012. VOC emissions from EGUs are very small compared to NOx emissions and are not visible at the scale needed to see the NOx emissions; however, VOC emissions are flat during 2008-2012. NOx and VOC emissions from industrial fuel combustions are flat during 2008-2012. In summary, Arizona statewide emissions of NOx and VOCs are either flat or decreasing during 2008-2012 and during 2011-2012, and are not consistent with the ozone trends in Maricopa that show rising ozone during 2011-2012.

2.3 Maricopa Non-Attainment Area Emissions Trends

MAG provided 2008 and 2011 anthropogenic emission inventories for the Maricopa Non-Attainment Area. In the plots described in this section, ENVIRON used the emission inventories provided by MAG for all source categories except for on-road mobile. On-road mobile emissions were calculated by ENVIRON using MOVES 2010a as described in Section 2.1.

Figure 2-11 shows emissions trends in the Maricopa Non-Attainment Area from 2008 to 2011. Anthropogenic emissions of NOx and VOC decreased overall in 2011 relative to 2008. The total NOx reduction is larger than the total VOC reduction. The largest emissions reductions come from on-road mobile NOx and from area source NOx and VOCs. Non-road and point source emissions also decline from 2008 to 2011, but the magnitude of the decrease is smaller than for on-road mobile and area sources.

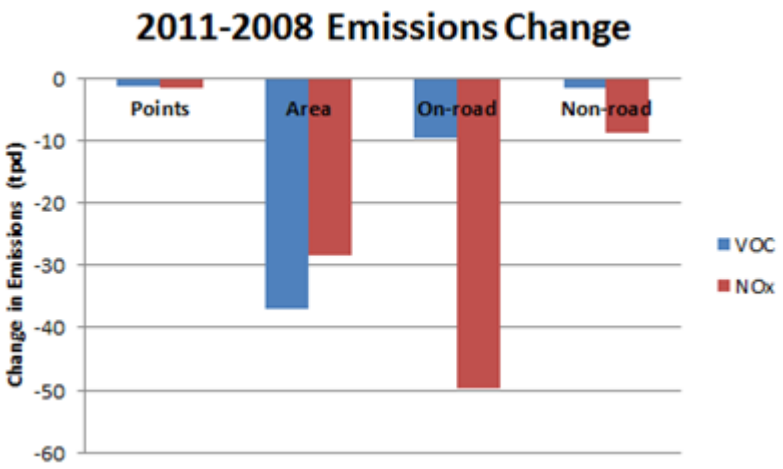

Figure 2-11. Emissions trends for Maricopa Non-Attainment Area: 2008 to 2011. Emission inventory data provided by MAG.

Figure 2-12 shows area source emission trends. The large decrease in area source VOCs shown in Figure 2-11 can be attributed to decreasing emissions from solvent use. For NOx, the 2008 to 2011 area source emissions reductions are to declining emissions from fuel combustion.

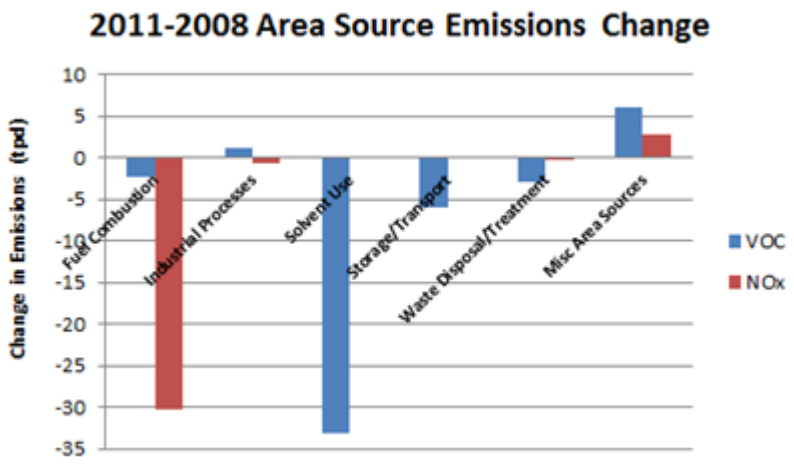

Figure 2-12. Area Source emission trends for Maricopa County: 2008 to 2011. Emission inventory data provided by MAG.

2.3.1 Wildfire Emissions

Wildfires can emit large quantities of trace gases and aerosols into the atmosphere, and these emissions undergo chemical and physical changes as they are transported away from the active fire region. Primary emitted species are depleted as they are deposited and/or chemically processed and secondary species such as ozone and secondary organic aerosols form within the plume. Both primary and secondary species can influence air quality at local and regional scales and can affect human health (e.g., Junquera et al., 2005; Jaffe et al., 2008, Hu et al., 2008.) Ozone and particulates formed in wildfire plumes can be transported to populated regions and can influence measured concentrations at air quality monitors.

In this section, we examine the possibility that emissions from wildfires in Arizona and nearby states could have contributed to rising ozone in Maricopa during 2011-2012. We begin by reviewing the fire emission inventory used to determine the location of fires during the ozone seasons of 2008-2012, and describe an analysis of potential fire emission impacts on all high ozone days in Maricopa during 2008-2012.

2.3.1.1 FINN fire data

For each day of the 2008-2012 ozone seasons, ENVIRON obtained estimates of fire emissions from the National Center for Atmospheric Research (NCAR) (Wiedinmyer, personal communication, 2008). These emission estimates are derived from analysis of fire locations determined by satellite-borne detectors. The MODerate-resolution Imaging Spectroradiometer (MODIS) instruments fly aboard two polar-orbiting satellites, Terra, and Aqua. These two satellites orbit the Earth, traveling from pole to pole while the earth rotates beneath them; a given area of the Earth will have an overpass from Terra and Aqua approximately twice a day. MODIS instruments detect fires as thermal anomalies (i.e. hot spots seen against a cooler background) at a spatial resolution of about 1 kilometer. Fire emissions derived from the MODIS data include NOx, CO, VOC, sulfur dioxide (SO_2) and particulate matter (PM) species, along with other compounds (e.g., mercury). The NCAR fire emissions inventory is described by Wiedinmyer et al. (2006, 2011).

Daily emissions from version 2 of the NCAR fire emissions model were available for most of North America for 2008-2012 period. September, 2012 fire emissions were not yet available at the time of the analysis, but this does not affect the analysis performed below because there were no high ozone days in Maricopa during September, 2012. The data record for each fire consisted of location (latitude and longitude), Julian date, acreage burned, biomass burned (fuel loading), and emission estimates. The acreage burned was set to 1 km^2 in almost every record, representing the size of a single satellite pixel. NOx emissions were extracted for the day-specific fire emission inventory and served as an indicator for fire location and intensity.

Figure 2-13 shows April-September total NOx fire emissions across the western US for each of the 5 years from 2008-2012. The data are shown at 36 km resolution. 2010 had the lowest fire emissions in the western half of the US; 2009 had the second lowest fire emissions.

Fires in Arizona and Surrounding Regions: 2008-2012

Figure 2-13 shows the locations of large fires in Arizona and vicinity during the ozone season for the years 2008-2012. In 2008 and 2010, there were fires to the east of Maricopa, but there were larger fires near the Arizona/New Mexico border in both 2011 and 2012. In 2011, the Wallow fire occurred in Apache, Navajo, Graham, and Greenlee Counties in Arizona and Catron County in New Mexico and burned from May 29-July 8, 2011[4]; it is the largest recorded Arizona wildfire. The Las Conchas fire was active from June 26-August 3, 2011 and burned approximately 150,000 acres near Los Alamos National Laboratory outside Albuquerque, New Mexico. In 2012, the Whitewater-Baldy Complex Fire burned in the Gila National Forest in New Mexico just east of the Arizona border. The fire began on May 9 and was 95% contained by July 23.The Whitewater-Baldy fire is the largest wildfire in New Mexico's history, surpassing the 2011 Las Conchas fire[5].

Figure 2-14 shows the same NOx emissions data as Figure 2-13, but the maximum value of the scale is reduced in order to show smaller fires. There are a number of smaller fires that occurred within and in the vicinity of Maricopa County. These smaller fires located closer to Maricopa are more likely to have had an impact on Maricopa ozone than the larger wildfires shown in Figure 2-13 that occurred to the east, which is generally downwind. In particular, the analysis described in Section 2.3.1.2 below showed that the 2012 fires circled in red in Figure 2-14 are likely to have had an influence on ozone in Maricopa County.

2.3.1.2 Fires on High Ozone Days: 2008-2012

We reviewed all days during the 2008-2012 ozone seasons that had a Maricopa monitor with daily maximum 8-hour average ozone (MDA8) > 75 ppb. We define MDA8>75 ppb as a high ozone day. For each Maricopa high ozone day, we prepared back trajectories from the time of highest 1-hour ozone for the monitor(s) with MDA8>75 ppb. On days where many monitors had MDA8>75 ppb, we selected one or two monitors that were centrally located among the group of exceeding monitors for back trajectory calculation.

The back trajectories were prepared using tools provided by the National Oceanic and Atmospheric Administration (NOAA) at http://www.arl.noaa.gov/ready/hysplit4.html. These tools are based on application of NOAA's HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler et al., 1997) with archived weather forecast model data from the National Center for Environmental Prediction's Eta Data Assimilation System (EDAS). The EDAS data have a horizontal resolution of 40 km. Note that back trajectories are a qualitative tool subject to theoretical and data limitations and can only provide approximate information regarding possible source regions for pollutants transported to a monitor. Back trajectories were calculated for three different heights: 2500 m, 1000 m and 500 m above ground level (AGL). Several heights were used in order to account for the potential for wind shear.

[4] http://www.inciweb.org/incident/2262/
[5] New York Times, July 26, 2012.

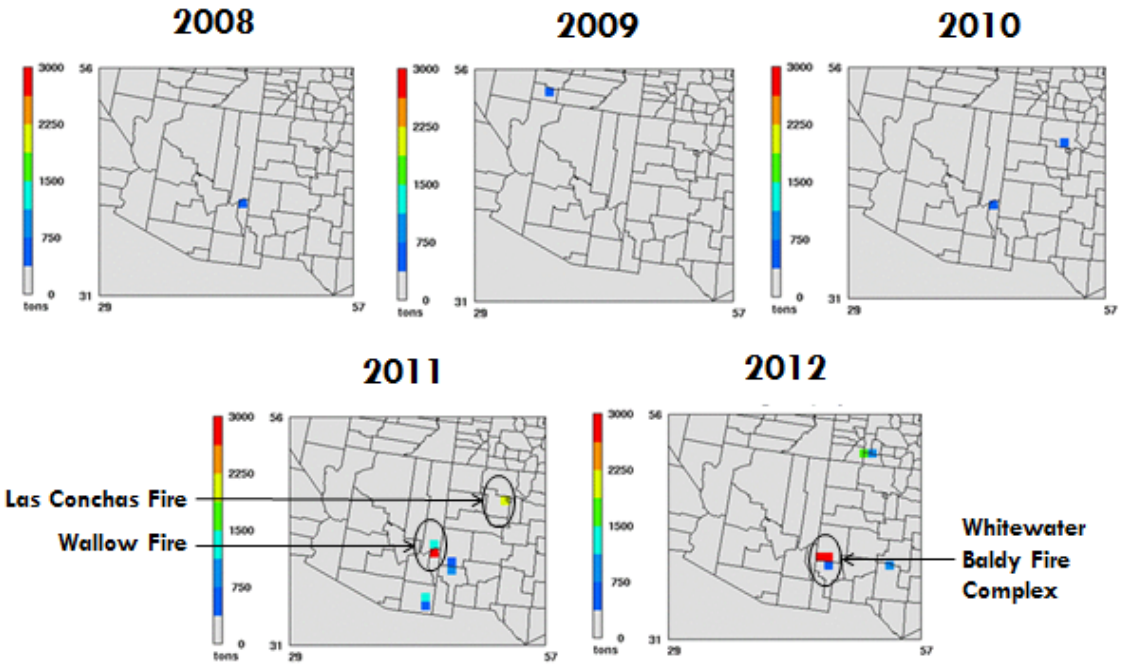

Figure 2-13. NOx emissions (tons/day) from fires in the vicinity of Arizona during ozone season from 2008-2012. Scale is set to show only the largest fires.

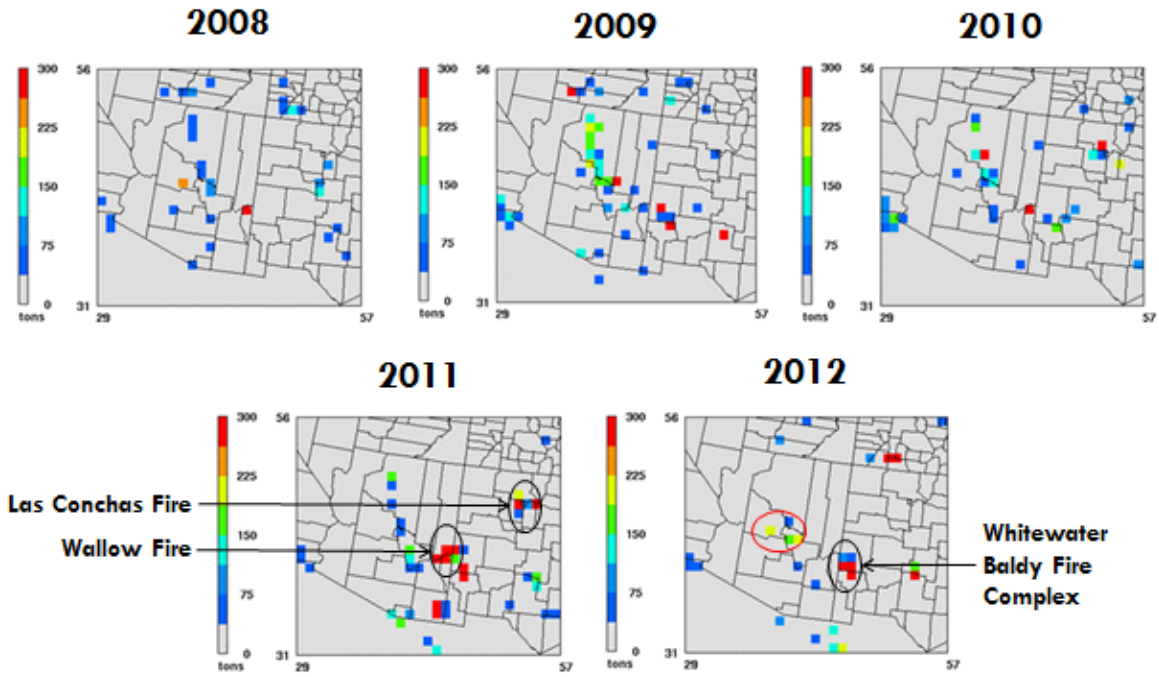

Figure 2-14. NOx emissions (tons/day) from fires in the vicinity of Arizona during ozone season from 2008-2012. Scale changed from Figure 2-13 to show smaller fires.

For each high ozone day during 2008-2012, we evaluated whether the HYSPLIT back trajectories cross the vicinity of wildfires shown on the NOx emissions plot for that high ozone day or on the previous day. Figure 2-15 shows an example of this procedure. On May 14, 2012, there were three fires burning to the north and northeast of Maricopa County: the Gladiator, Sunflower, and Bull Flat fires. MDA8 readings > 75 ppb were recorded at many Maricopa monitors on this day. Because the North Phoenix monitor is centrally located among the urban core monitors that exceeded 75 ppb, we used this monitor as the end point for the HYSPLIT back trajectories. The 24-hour HYSPLIT back trajectories for the North Phoenix monitor indicate that air arriving at the monitor during the period of high 8-hour ozone could have passed in the vicinity of the fires, so that emissions of ozone precursors from the fires could have contributed to high ozone at the monitor. News reports for May 14, 2012 indicate that health watches for air pollution were issued by the Maricopa AQD for this day and support the conclusions from the HYSPLIT analysis.

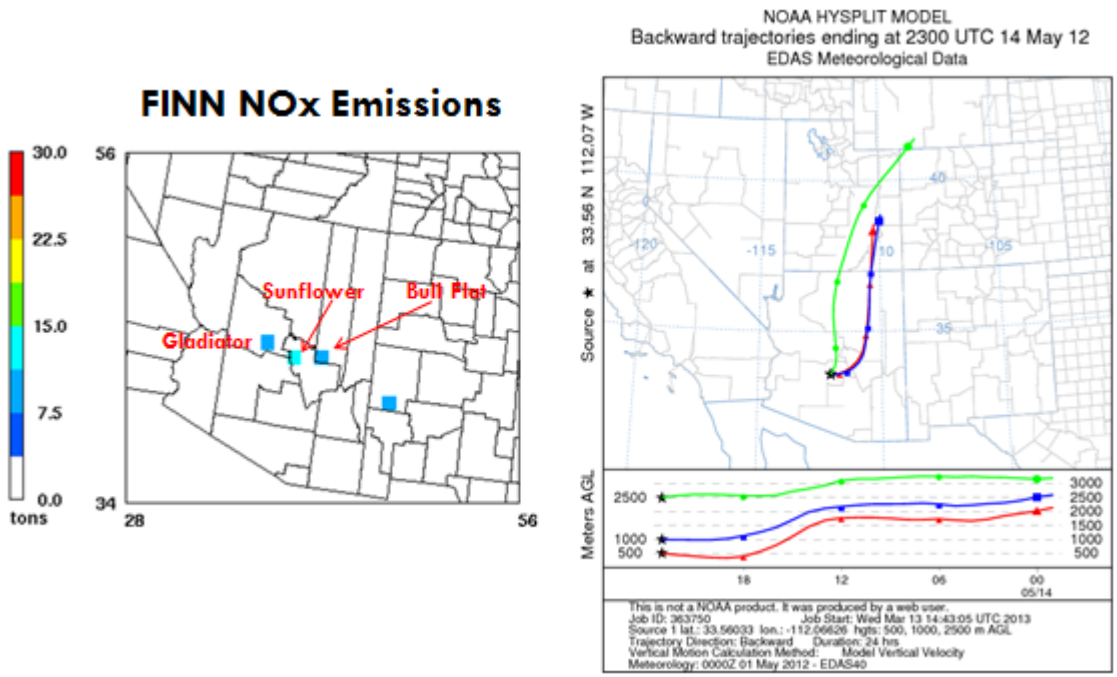

Figure 2-15. Example of High Ozone Day Fire Analysis: May 14, 2012. Left hand panel: NOx emissions from the NCAR FINN fire emission inventory for May 14. Right hand panel: HYSPLIT 24-hour back trajectories for 500 meters (m), 1,000 m, and 2,500 m ending at the North Phoenix monitor.

We note that the procedure described above for analyzing potential fire impacts is a screening method that serves only as a way of identifying days on which fire emissions could have had an impact on Maricopa ozone. In order to evaluate whether fire impacts played a significant role in high ozone in Maricopa, additional analysis would need to be performed that could include evaluation of ambient and satellite data, meteorological analysis, and photochemical modeling. Here, we use this screening procedure to determine how many high ozone days during the

2008-2012 ozone seasons were potentially influenced by fire emissions. The purpose of this analysis is to determine how the number of days with potential wildfire impacts varies by year and to assess whether the years 2011 and 2012 had more days than previous years in which fire emissions could have played a role in causing high ozone days.

Appendix A shows the HYSPLIT analysis for each high ozone day during 2008-2012. In Figure 2-16, we summarize the results of the fire impact screening procedure. 2012 has largest number of high ozone days as well as the largest number of days with potential fire impacts during 2008-2012. 2011 also has a large number of high ozone days, but has a relatively low number of potential fire impact days. Although the 2011 Las Conchas and Wallow fires were large, they were generally downwind of Maricopa County on high ozone days. 2009 had only three high ozone days, and there is no evidence that these were influenced by fire emissions.

The fire emissions analysis suggests that fire activity in the vicinity of Maricopa County could have played a role in the high ozone recorded at Maricopa monitors in 2012. The role of fire emissions is less important in 2011 in explaining high ozone in Maricopa.

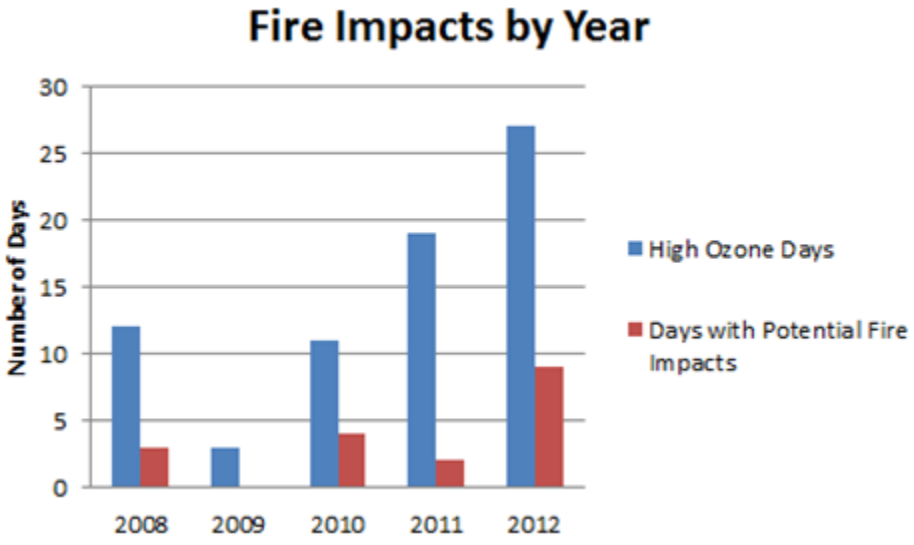

Figure 2-16. Number of high ozone days (MDA>75 ppb for one or more Maricopa County monitors) and number of high ozone days with potential ozone impacts from fire emissions during 2008-2012.

2.3.2 Biogenic Emissions

MAG has analyzed Maricopa ozone season biogenic emissions trends during the period 2008-2012. MAG's biogenic emissions modeling indicates that 2009 was the peak biogenic emissions year during the period 2008-2012, and that variations in local biogenic emissions cannot explain 2008-2012 ozone trends in Maricopa and, in particular, the increase in ozone during 2011-2012 (Matthew Poppen, MAG, personal communication, 2013). However, since there is uncertainty

in the biogenic modeling (e.g. land use inputs), it is not possible to rule out biogenic emissions altogether as a possible contributor to higher ozone concentrations in 2011-2012.

The highest ozone in Maricopa County occurs at the North Phoenix monitor, which is located in a suburban area to the north of downtown Phoenix. Discussions with MAG indicate that the neighborhood in which the monitor is located has more irrigated lots and more trees than other neighborhoods in the area. Google Earth satellite imagery shows that the region just southeast of the monitor is greener than surrounding areas. It is possible that a local biogenic hot spot could translate to an ozone hot spot, due to the emission of highly reactive biogenic VOCs (e.g. isoprene) that are extremely conducive to ozone formation.

The Model of Emissions of Gases and Aerosols from Nature (MEGAN) biogenics emission model (Guenther et al., 2012) is used by MAG to develop biogenic emission inventories for Maricopa. MEGAN uses the satellite-derived leaf area index (LAI) in its calculation of biogenic emissions for a given location. LAI data are derived from radiances measured by NASA's Moderate Resolution Imaging Spectroradiometer (MODIS), but LAI data are not available over urban areas. The MEGAN model's urban LAI is set to a regional average for the areas where MODIS does not provide LAI. Therefore, analysis of LAI and resulting biogenic emission estimates cannot answer the question of whether there is a biogenic emissions hot spot near the North Phoenix monitor. However, further analysis of this question may help address the question of why the North Phoenix ozone monitor has the highest readings of any monitor in Maricopa County i.e. is the area's design value monitor.

3.0 VOC-LIMITED OZONE REACTIONS IN THE URBAN CORE AND THE ROLE OF NOX EMISSIONS

We reviewed ozone trends at urban and suburban Maricopa monitors separately to determine whether these two groups of monitors experienced different ozone trends during 2008-2012. We developed diurnal profiles of ozone and NOx emissions at individual monitors to determine whether there were changes in weekday/weekend patterns of high and low ozone during 2008-2012, and used this information to determine whether ozone formation was NOx-limited or VOC-limited at urban and suburban monitors.

3.1 Ozone Trends at Urban and Suburban Monitors

The locations of ozone monitors within Maricopa County are shown in Figure 3-1.

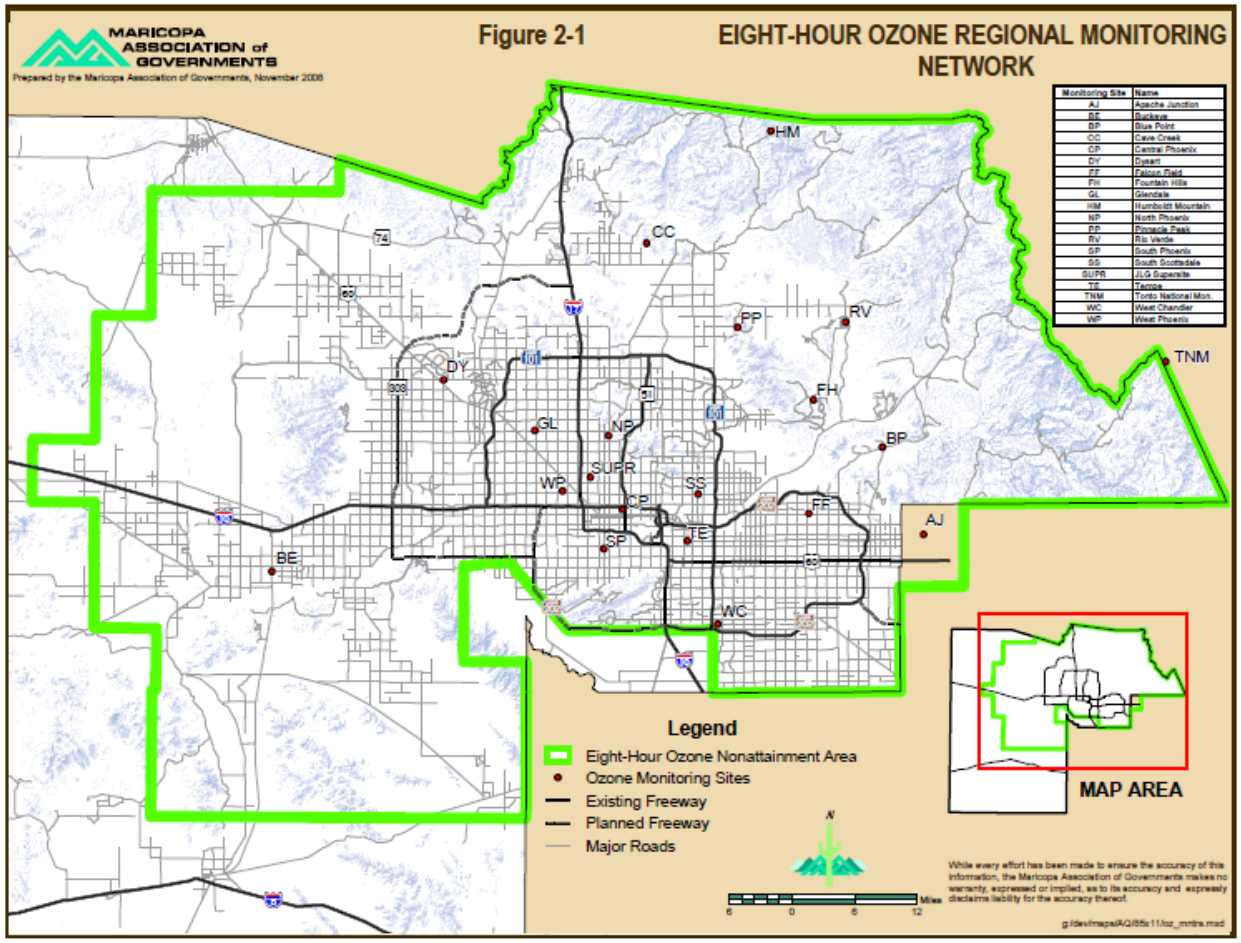

Figure 3-1. Maricopa County ozone monitors. Figure from the MAG Eight-Hour Ozone Redesignation Request and Maintenance Plan for the Maricopa Nonattainment Area. http://www.azmag.gov/Documents/pdf/cms.resource/ES_2009_8Hour-Ozone-Final_MAINTENANCE-PLAN.pdf.

Figure 3-2 shows the ozone monitors used in this study, and classifies each monitor as either urban or suburban. The ARCGIS urban outline layer was used to define the extent of the urban core area.

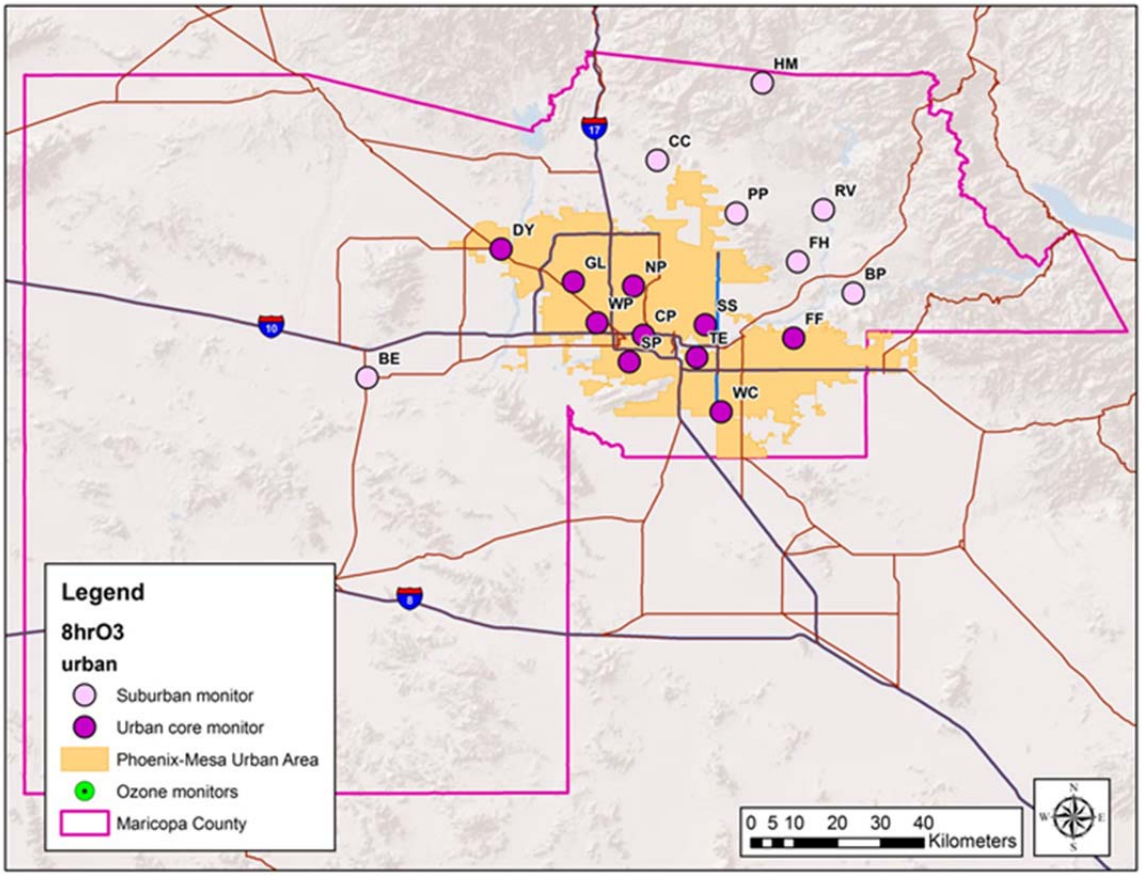

Figure 3-2. Urban core and suburban ozone monitors in Maricopa County.

Figure 3-3 shows trends in maximum 8-hour average ozone at urban core and suburban monitors in Maricopa County. While there is considerable interannual variation in both the urban and suburban ozone time series, the trend for maximum ozone at suburban monitors is downward (slope -1.1 ppb/yr), while the trend for urban core monitors is flat (slope of 0.0 ppb/yr). The time series for the 4th highest 8-hour average ozone concentrations (Figure 3-4) show a downward trend with slopes of -1.1 ppb/year and -0. 3 ppb/year for the suburban and urban core monitors, respectively.

Figure 3-3 and Figure 3-4 indicate that, despite the increase in Maricopa ozone since 2009, there has been an overall decline in ozone from 2000 to 2012. Trends differ at suburban and urban core monitors, with ozone declining faster at suburban sites than at urban core sites.

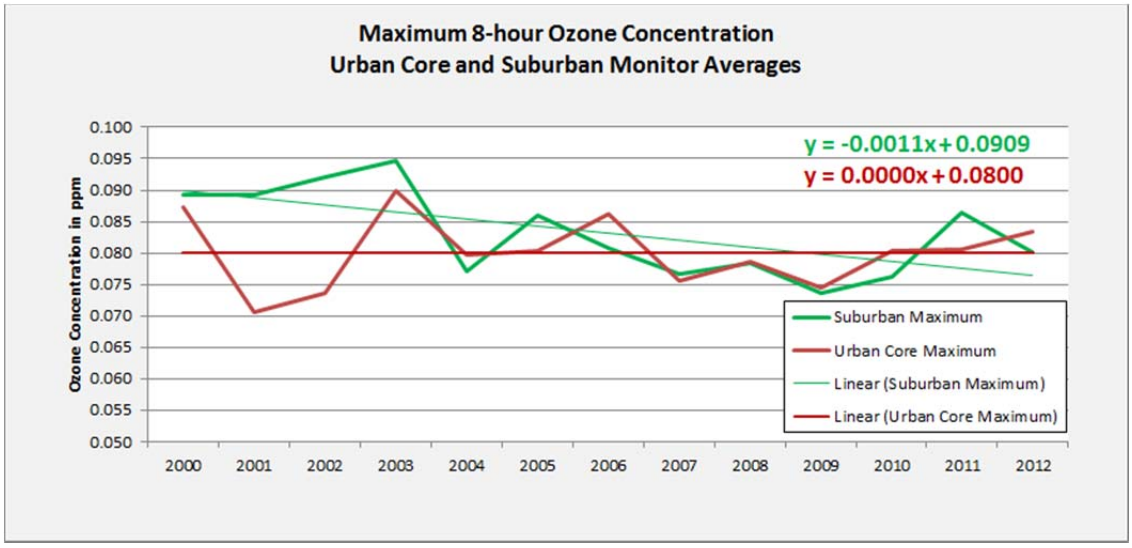

Figure 3-3. 2000-2012 trends in maximum 8-hour average ozone concentrations among Maricopa urban core and suburban monitors.

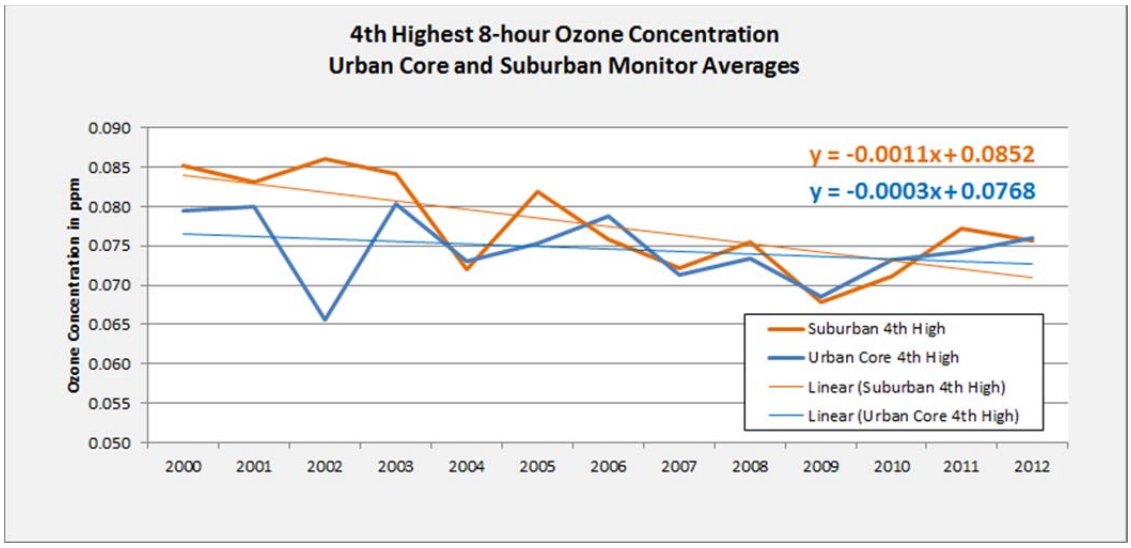

Figure 3-4. 2000-2012 trends in 4th highest 8-hour average ozone concentrations among Maricopa urban core and suburban monitors.

We reviewed the spatial patterns of the 4th high and maximum values of the MDA8 (Figure 3-5 and Figure 3-6, respectively). From these plots, it is apparent that ozone was low across all sites in 2009 and that the suburban monitors to the northeast of the Phoenix urban core saw high ozone in 2011. Aside from these conclusions, the data are not easy to interpret when displayed in this format. Therefore, we show for each monitor the departure from the network mean for each year (Figure 3-7 and Figure 3-8). The network mean is shown in the upper left corner of each plot. The number next to each monitor in these two Figures represents the amount in ppb the monitor is either below or above the network mean. The Buckeye monitor, to the southwest of the urban core, is always below the network mean for both the 4th highest MDA8 and the maximum value of the MDA8. During 2009, 2011 and 2012, the Cave Creek, Pinnacle Peak, Fountain Hills, and Blue Point all exceed the network average. For all years, the North Phoenix monitor exceeds the network average for both the 4th highest MDA8 and the maximum value of the MDA8. No other monitor in the urban core has a pattern that is so consistent; the other urban core monitors are higher than the network average in some years and lower in others.

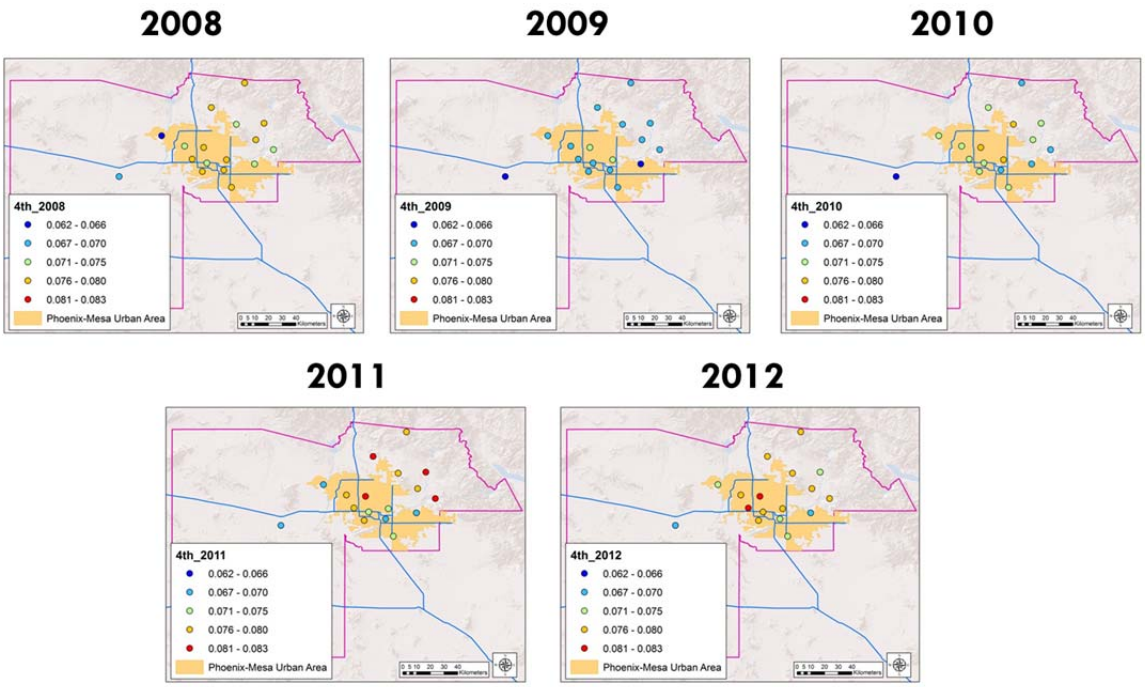

Figure 3-5. 4th highest daily maximum 8-hr average ozone for each year from 2008-2012. Orange shading indicates the extent of the Maricopa urban core.

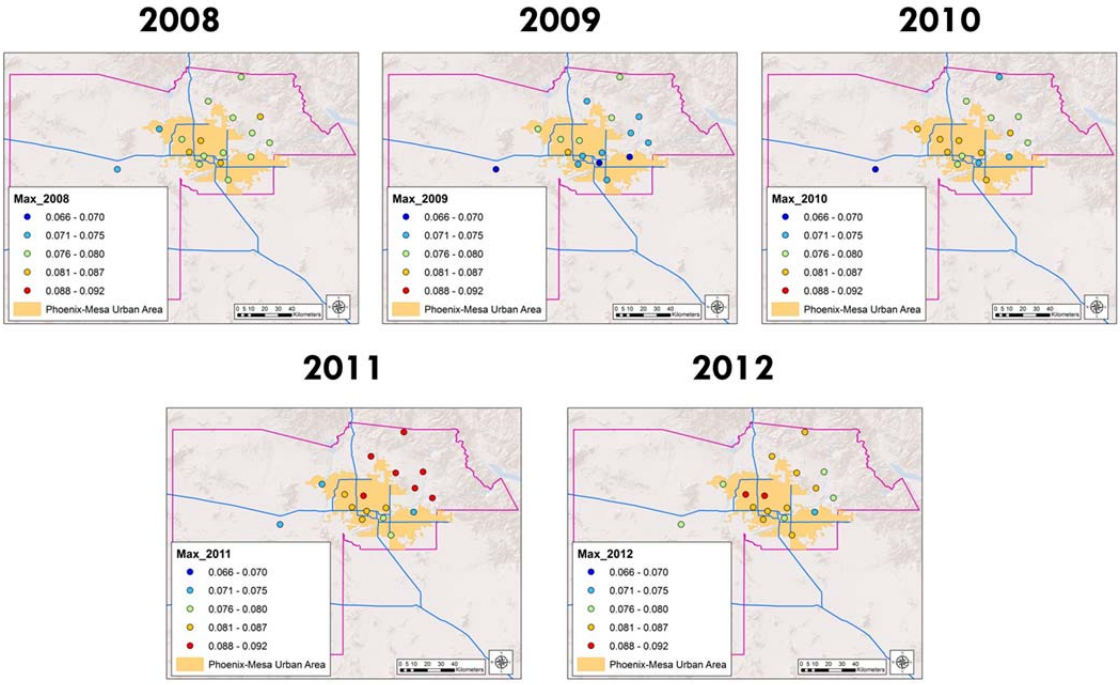

Figure 3-6. Highest daily maximum 8-hr average ozone value for each year from 2008-2012. Orange shading indicates the extent of the Maricopa urban core.

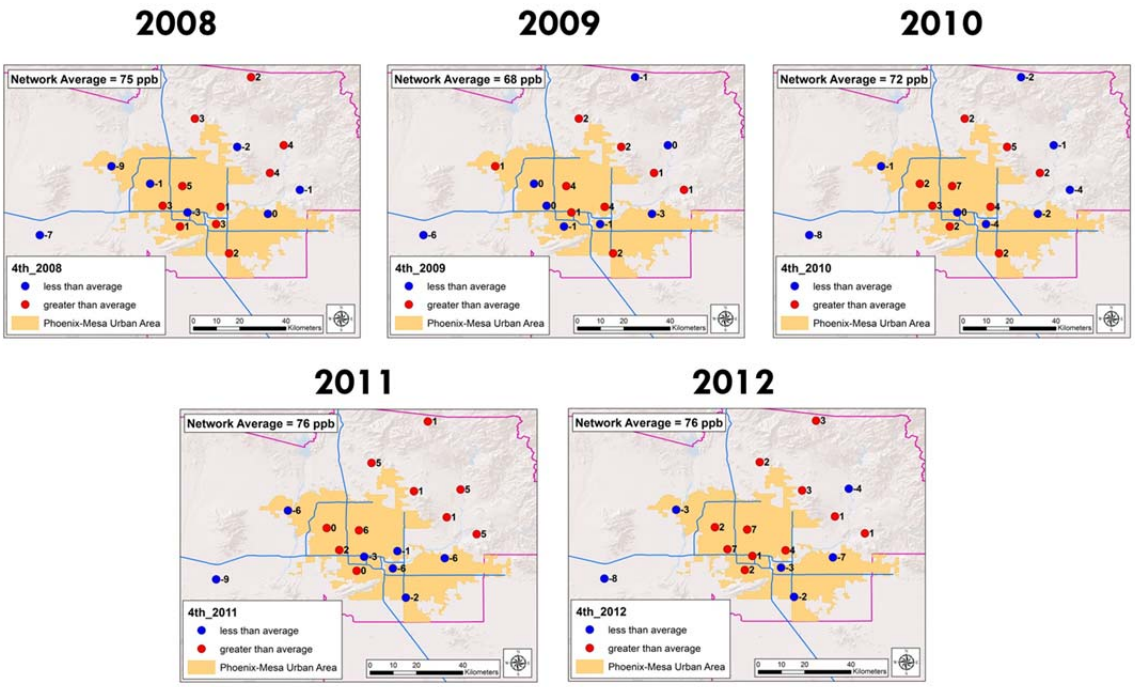

Figure 3-7. Departure from network mean (ppb) for 4th highest daily maximum 8-hr average ozone for each year from 2008-2012. Orange shading indicates the extent of the Maricopa urban core.

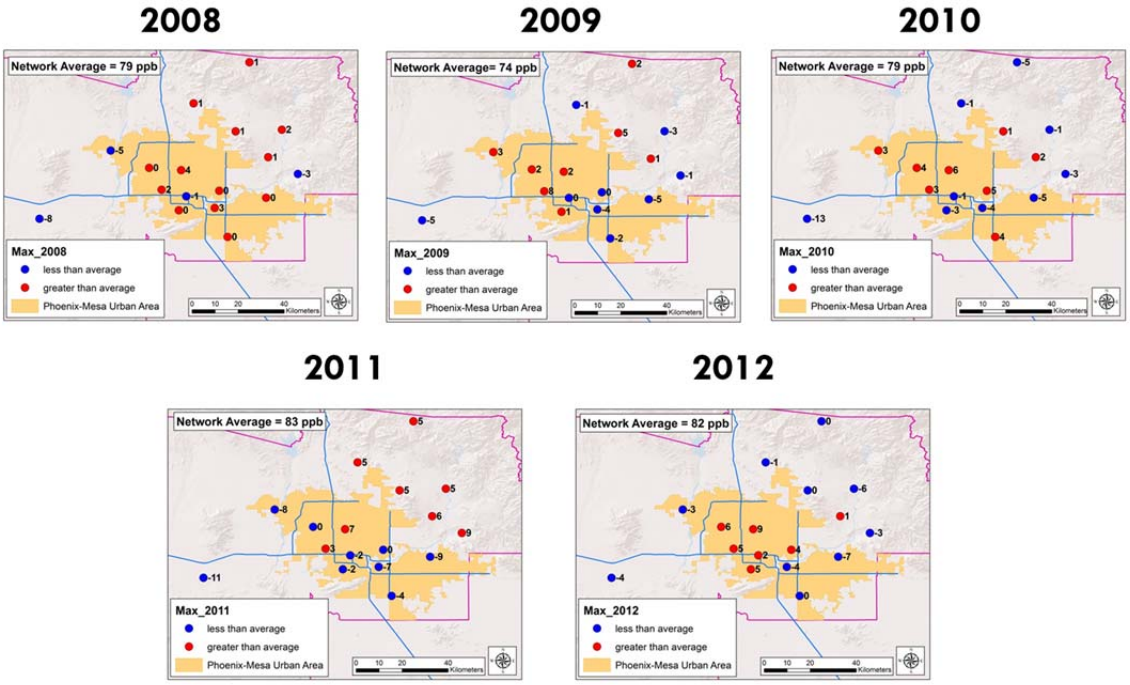

Figure 3-8. As in Figure 3-7 for maximum 8-hr Ozone.

3.2 Weekday/Weekend Effect Analysis

In this section, we carry out an analysis of ambient ozone and NOx monitoring data in order to determine whether ozone formation in Maricopa is NOx-limited or VOC-limited and whether the limiting pollutant in ozone formation has changed during 2008-2012. In designing ozone control strategies for an area, it is important to understand the role played by on-road mobile sources. In areas where on-road vehicles play a key role in determining ozone levels, the typical diurnal cycle of ozone and precursors for weekend days may be different from that of weekdays due to differences in driving activity. The main differences are the absence of morning and evening commute periods on weekends and less heavy-duty truck traffic on weekends. NOx differences between weekday and weekend are most pronounced during morning and afternoon commute hours. We might expect that since weekday NOx and VOC emissions from traffic are higher than weekend emissions, ozone would be consistently higher on weekdays than on weekends. However, in some urban areas, the daily maximum ozone concentrations are higher on weekends than on weekdays; this is known as the weekday/weekend effect.

Ozone formation depends on the amount of NOx and VOC present as well as on the ratio of VOC to NOx, where the ratio is taken in terms of ppbC/ppb. When the VOC/NOx ratio is higher than about 10, ozone formation is limited by the amount of available NOx and reducing NOx tends to decrease peak ozone concentrations. However, if the VOC/NOx ratio is less than about 7, reducing NOx tends to increase ozone levels, and the area is said to be VOC-limited. In this situation, ozone is suppressed in the urban area due to titration by large amounts of fresh NO emissions. When NOx emissions are reduced, the suppression of ozone by NO is lessened and ozone increases.

Here, we examine diurnal profiles of ozone and NOx for a monitor in Central Phoenix in order to determine whether a weekday/weekend ozone effect is evident. Inspection of average diurnal profiles of NOx and ozone allow us to evaluate whether the area exhibits a weekday/weekend effect and to diagnose whether the area is NOx-limited or VOC-limited. If the weekday morning NOx is higher than the weekend NOx, then looking at the weekday-weekend difference is approximately equivalent to testing the effect on ozone of reducing NOx emissions. In a NOx-limited area, the peak ozone will be smaller on the weekend day, because the NOx emissions are smaller on the weekend and the total amount of ozone formed each day is limited by the amount of available NOx. Conversely, if the area is VOC-limited, the peak ozone value will be higher on the weekend than on the weekday.

MAG provided NOx and ozone measurements from the JLG Supersite located in the Phoenix urban core (Figure 3-9) for April-September 2008-2012. We take Sunday to be representative of weekend days, and Wednesday to be typical of weekdays. In Figure 2-10 through Figure 2-12, we show average diurnal profiles (in local time) for NOx and ozone for the JLG Supersite. The averages are taken over all Wednesdays and Sundays during April-September of each year from 2008 through 2012. For each diurnal NOx and ozone profile, we list the number of data points used to form the ozone season average to the right of the legend entry for that profile.

For all years from 2008-2012, the weekday NOx profile shows a peak during the morning commute hours, lower values during the middle of the day, and a second peak during the evening hours. There is a large reduction in the morning NOx peak on Sunday relative to the higher Wednesday values for all years. The morning NOx peak is higher in 2008 than in any other year, with a large reduction in the NOx peak going from 2008 to 2009; this is likely due to reductions in vehicle traffic resulting from the economic recession.

The Wednesday to Sunday ozone difference at the JLG Supersite is inconsistent over the 2008-2012 years. In 2009 and 2012, ozone formation at the JLG Supersite appears to be VOC-limited, while in 2010 and 2011, it is NOx-limited. 2008 shows similar values for the Wednesday and Sunday peaks, so is not clearly NO-limited or VOC-limited.

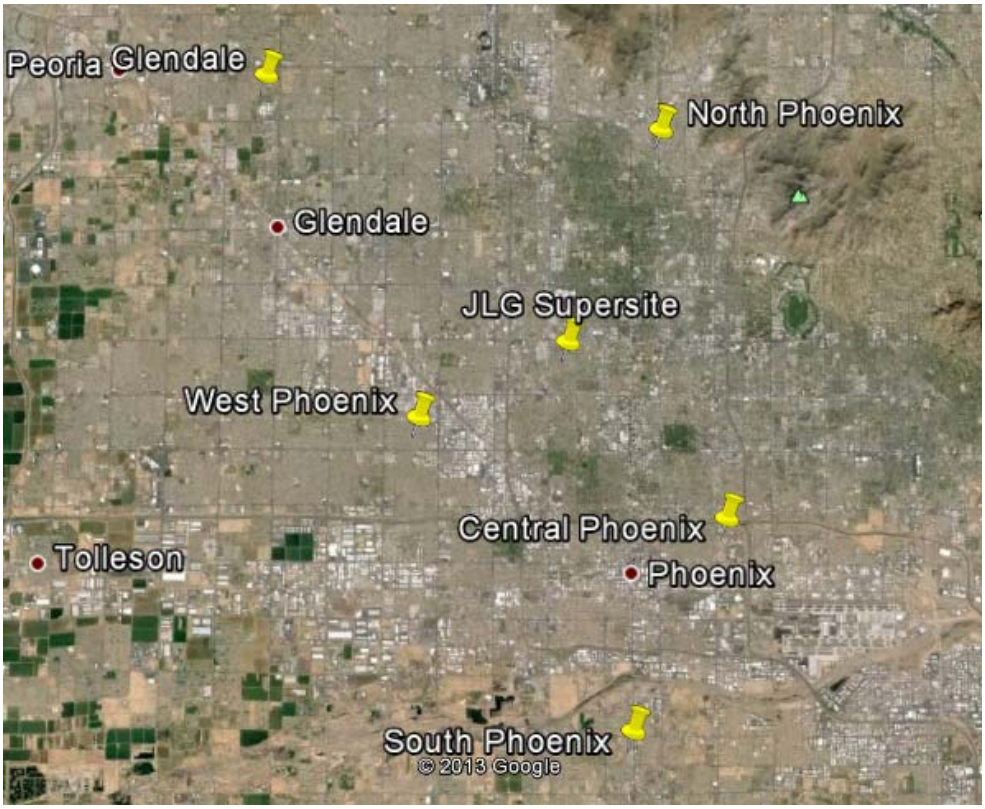

Figure 3-9. Location of the JLG Supersite among the downtown Phoenix monitors. Figure from Google Earth.

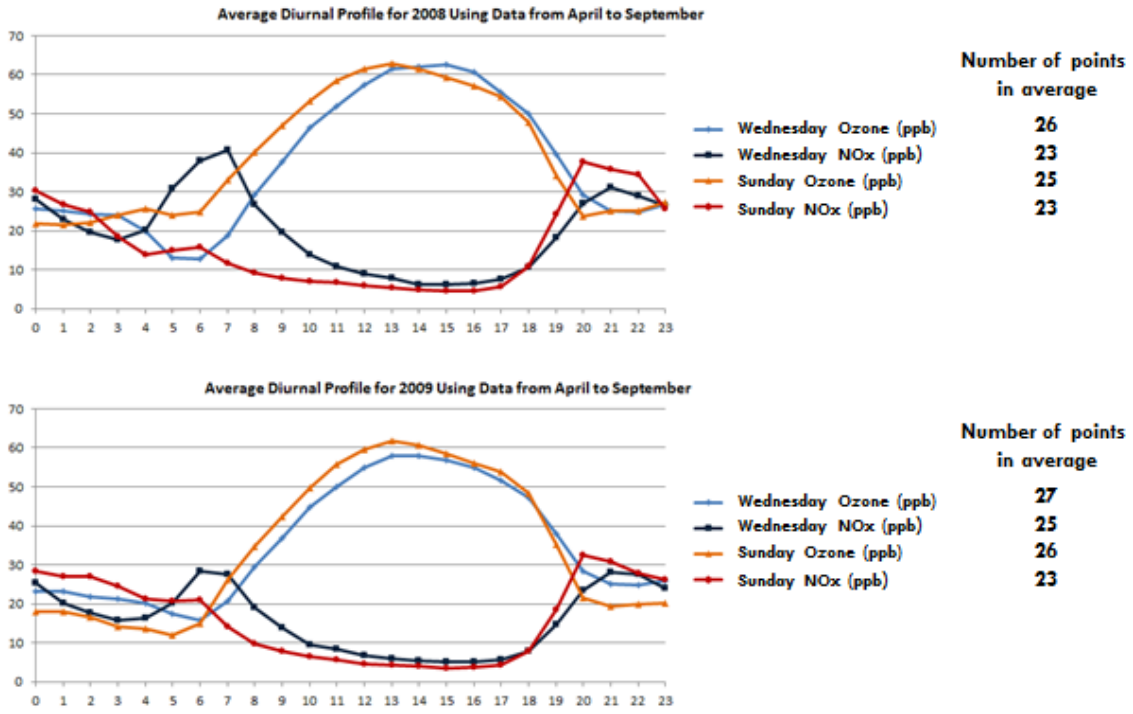

Figure 3-10. JLG Supersite weekday/weekend analysis for 2008 and 2009.

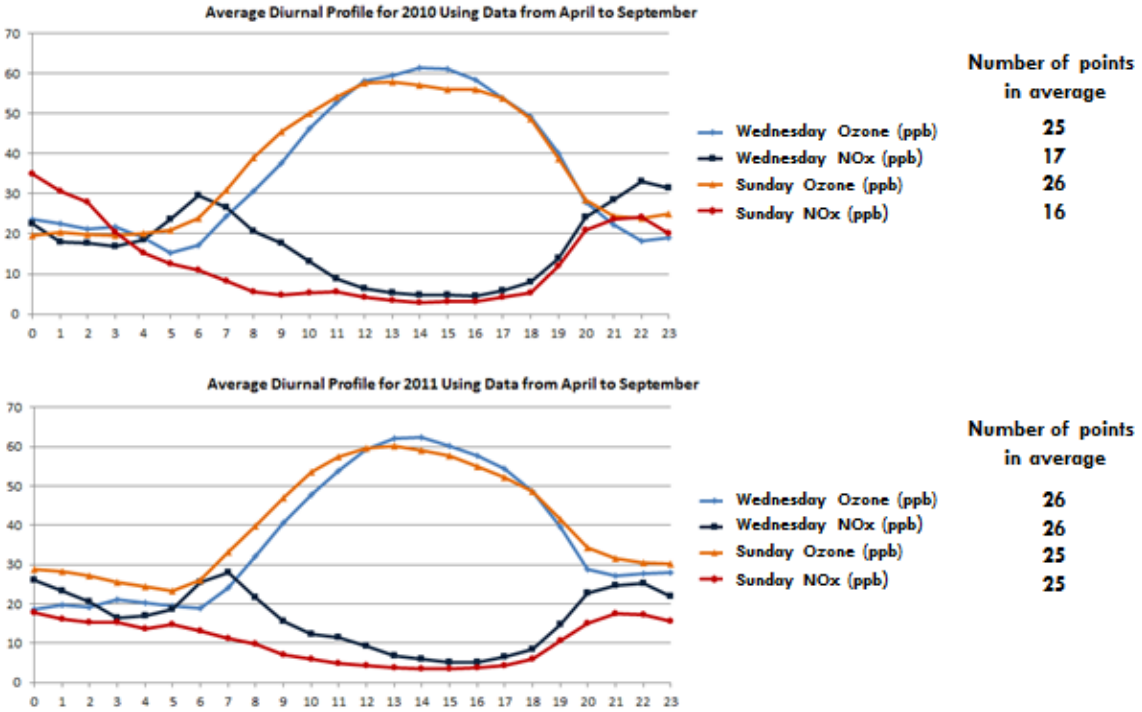

Figure 3-11. JLG Supersite weekday/weekend analysis for 2010 and 2011.

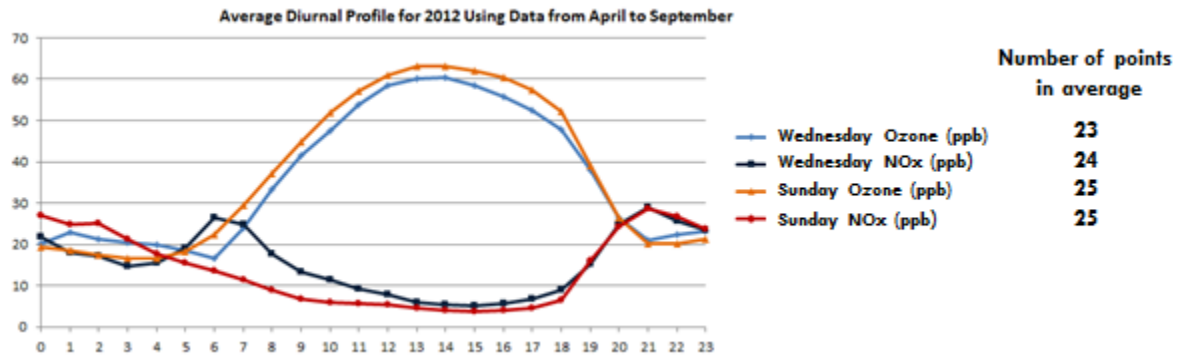

Figure 3-12. 2012. JLG Supersite weekday/weekend analysis for 2012.

We carried out a similar analysis for the Buckeye monitor located southwest of the urban core (Figure 3-13). As at the JLG Supersite, the morning NOx peak is highest in 2008 and is significantly smaller in 2009 and 2010, as the recession takes hold. For all years from 2008-2012, there is a weekday/weekend effect and Buckeye is VOC-limited for all years; it is the only Maricopa monitor with this behavior.

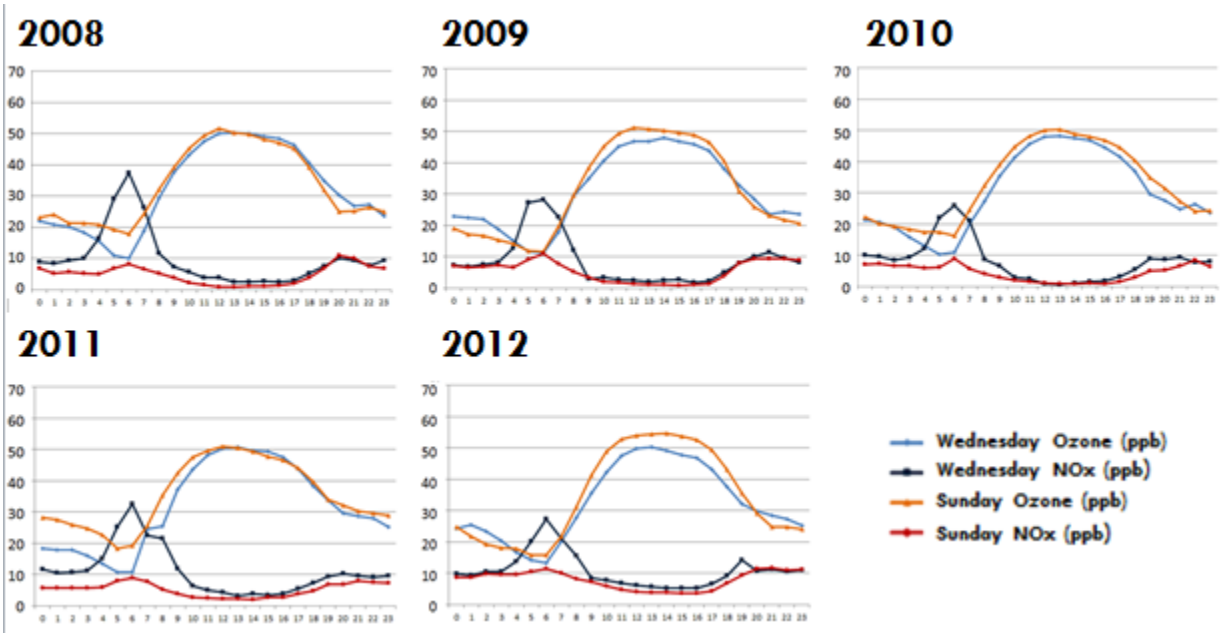

Figure 3-13. Buckeye weekday/weekend analysis for 2008-2012.

Both West Phoenix (Figure 3-14) and Central Phoenix (Figure 3-15) have very high values of the morning NOx peak in 2008, and show the NOx peak decreasing sharply in magnitude in 2009 and rebounding in 2010. Both of these monitors are NOx-limited in some years and VOC-

limited in other years. Years with high ambient weekday NOx and a large weekday/weekend difference (2008, 2010, 2012) can be either NOx- or VOC-limited. For the North Phoenix monitor (Figure 3-16), no NOx data were available, but the ozone profile patterns are similar to the North and West Phoenix monitors in that the monitor is VOC-limited in some years and NOx-limited in others. None of these monitors shows a consistent trend that would indicate that the Phoenix urban area as a whole is trending toward being more NOx- or VOC-limited overall.

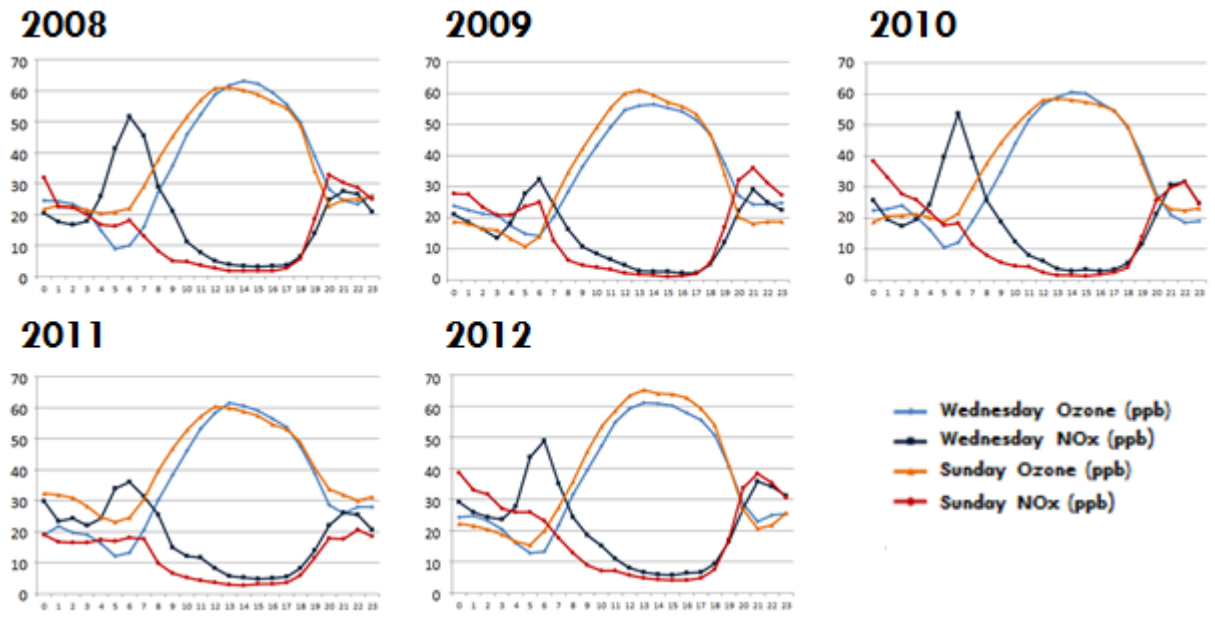

Figure 3-14. West Phoenix weekday/weekend analysis for 2008-2012.

Next, we analyzed downwind monitors that lie to the northeast of the Phoenix urban core. Figure 3-17, Figure 3-18, and Figure 3-19 show weekday/weekend analyses for the Rio Verde, Cave Creek, and Humboldt Mountain monitors, respectively. NOx data were not available for these monitors; however, their ozone profiles show year-to-year similarities and indicate that these downwind sites are NOx-limited. Continued reductions in on-road NOx should cause their ozone to decline.

The Humboldt Mountain monitor (Figure 3-19) is located well outside the Phoenix urban core and has a strikingly different diurnal ozone profile than the North Phoenix monitor, which is located within the urban core. The Humboldt monitor has a relatively small diurnal range, showing variations of ~10-15 ppb from daily minimum to daily maximum. Peak values of ozone range from 50-65 ppb. North Phoenix, on the other hand, has a diurnal range as large as 50 ppb. While the daily ozone minimum never gets below 40 ppb at Humboldt Mountain, the North Phoenix minima range as low as 12 ppb. The small values of the ozone profile minima indicate that ozone is being titrated overnight by fresh NO emissions at North Phoenix.

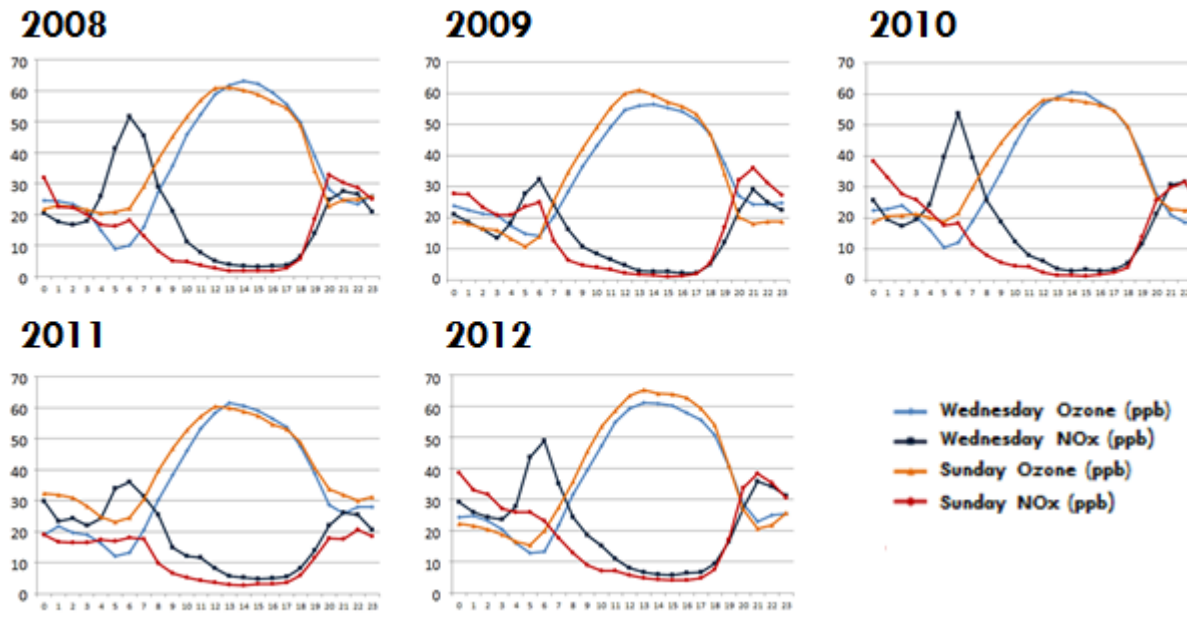

Figure 3-15. Central Phoenix weekday/weekend analysis for 2008-2012.

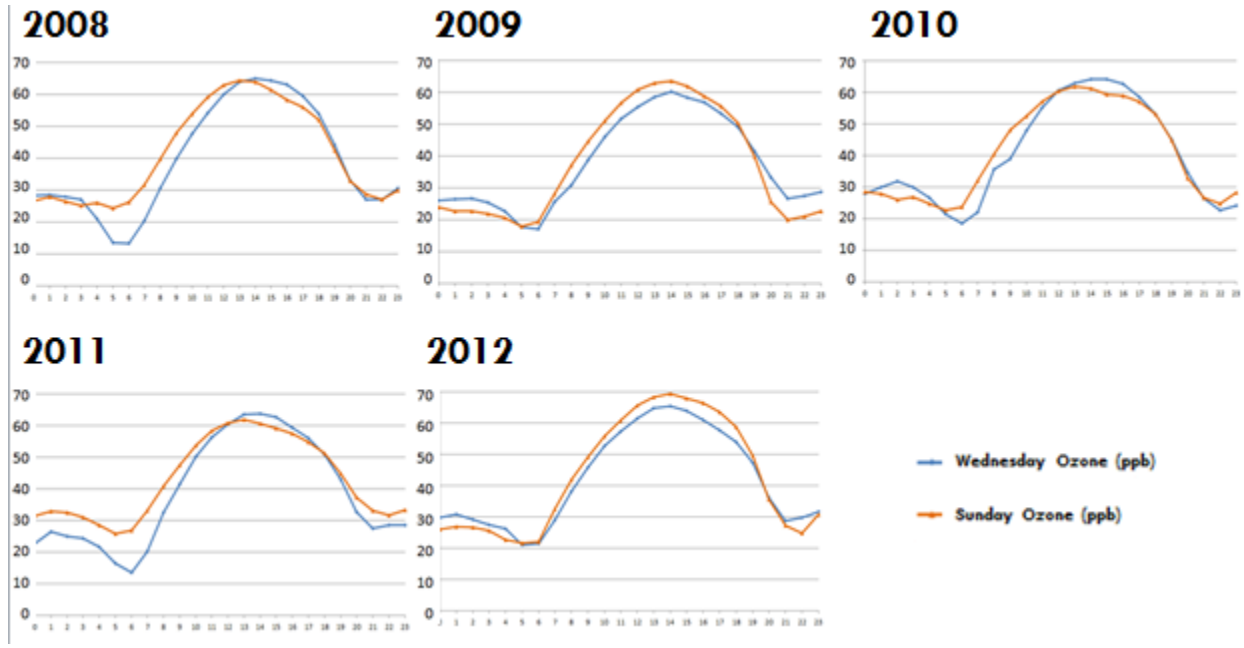

Figure 3-16. North Phoenix weekday/weekend analysis for 2008-2012. No NOx data were available for this monitor.

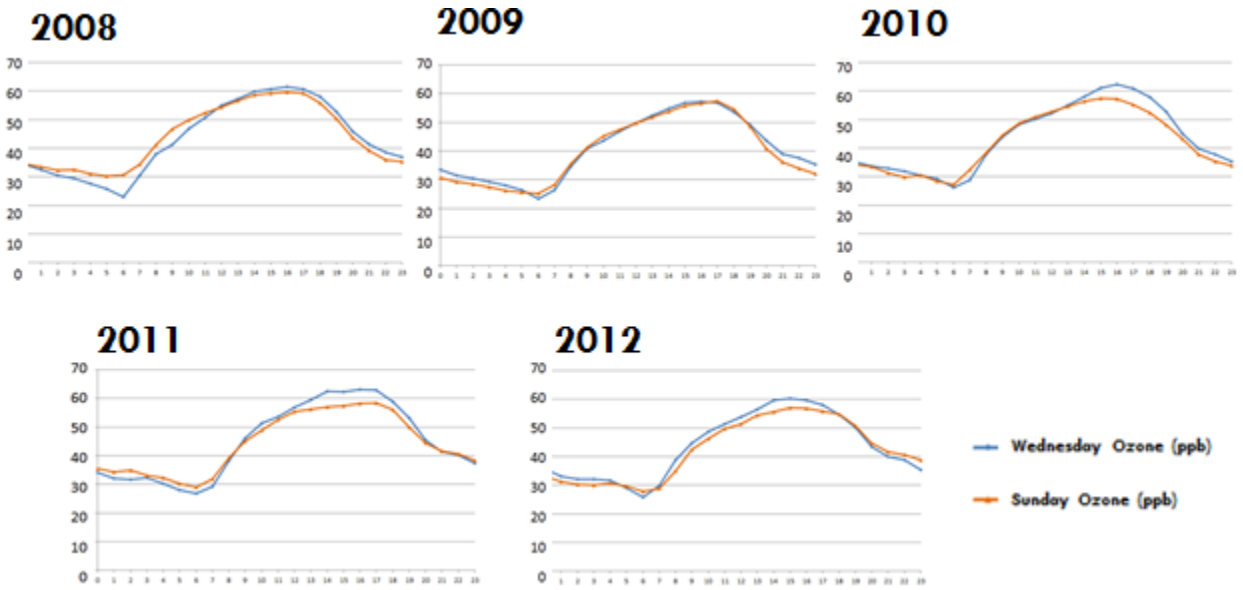

Figure 3-17. Rio Verde weekday/weekend analysis for 2008-2012.

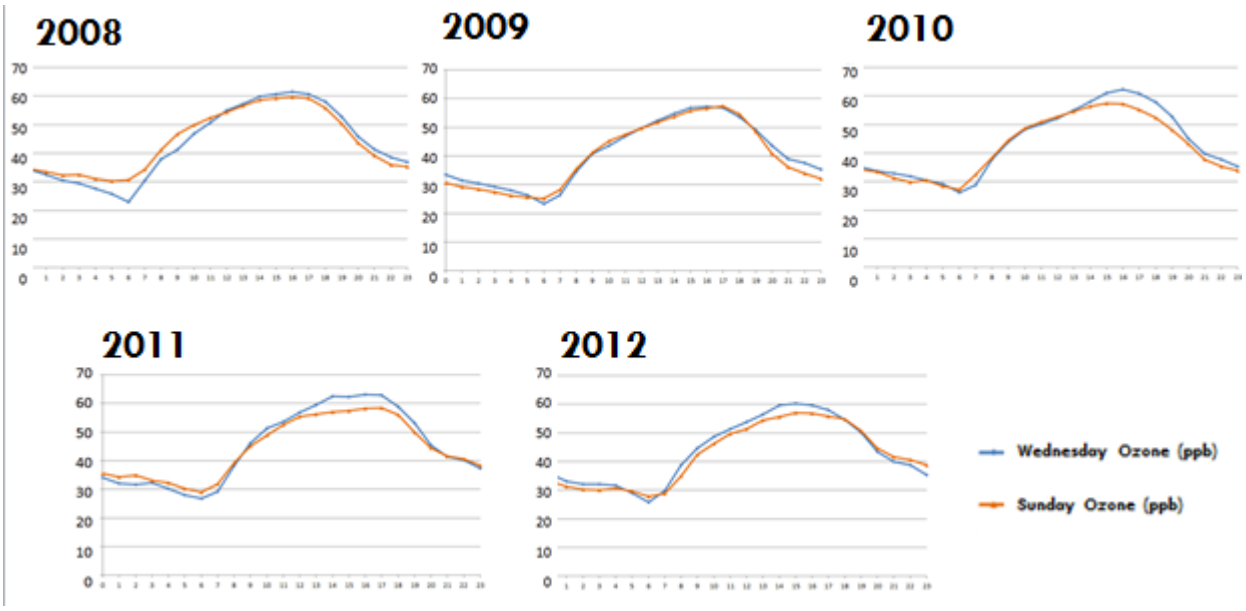

Figure 3-18. Cave Creek weekday/weekend analysis for 2008-2012.

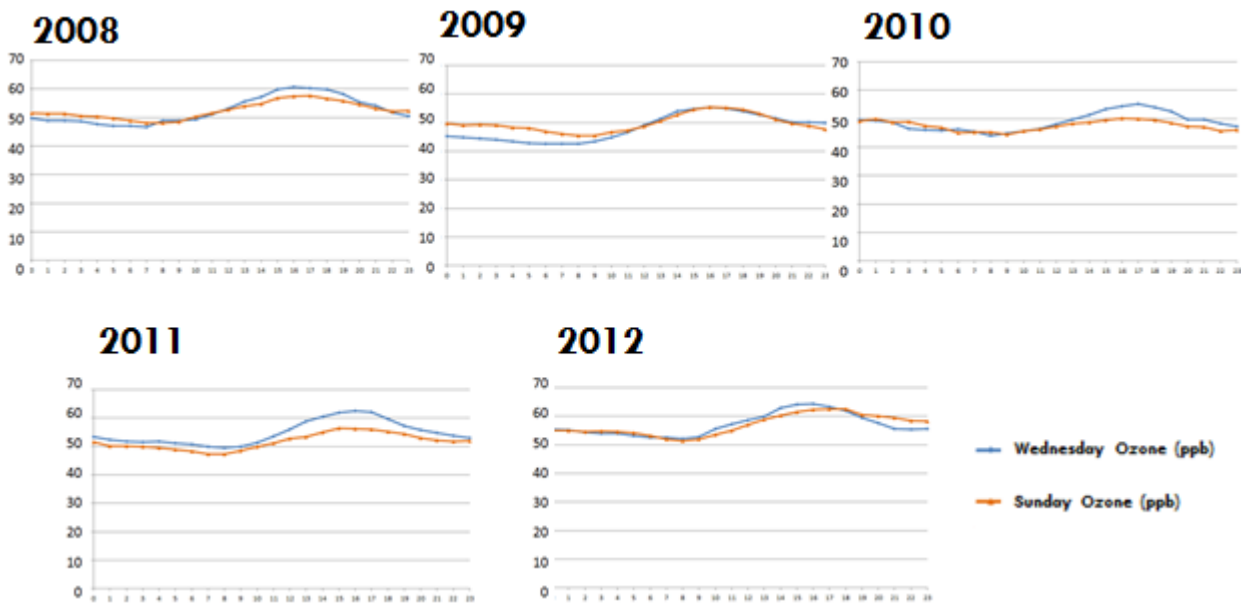

Figure 3-19. Humboldt Mountain weekday/weekend analysis for 2008-2012.

We summarize the weekday/weekend analysis in Figure 3-20, which shows the difference in peak weekend-weekday (WE-WD) ozone for each year's diurnal profile. A WE-WD difference that is less than zero (blue/green colors) indicates that ozone formation is NOx-limited, while a weekend-weekday difference that is positive (yellow/red colors) indicates that ozone formation is VOC-limited. The differences are displayed on a map to make clear spatial patterns in whether the monitors are NOx- or VOC-limited. The suburban sites located northeast of the Phoenix urban core are NOx-limited except in 2009 when some sites have WE-WD differences that are negative, some are positive, and some that are very close to zero. The Buckeye monitor is always VOC-limited.

The urban core sites behave as a bloc except in 2008, when the eastern sites are VOC-limited and most of the western sites are NOx-limited. During 2009-2012, the urban core sites vary together between being VOC- and NOx-limited; they are NOx-limited in 2010 and 2011 and VOC-limited in 2009 and 2012.

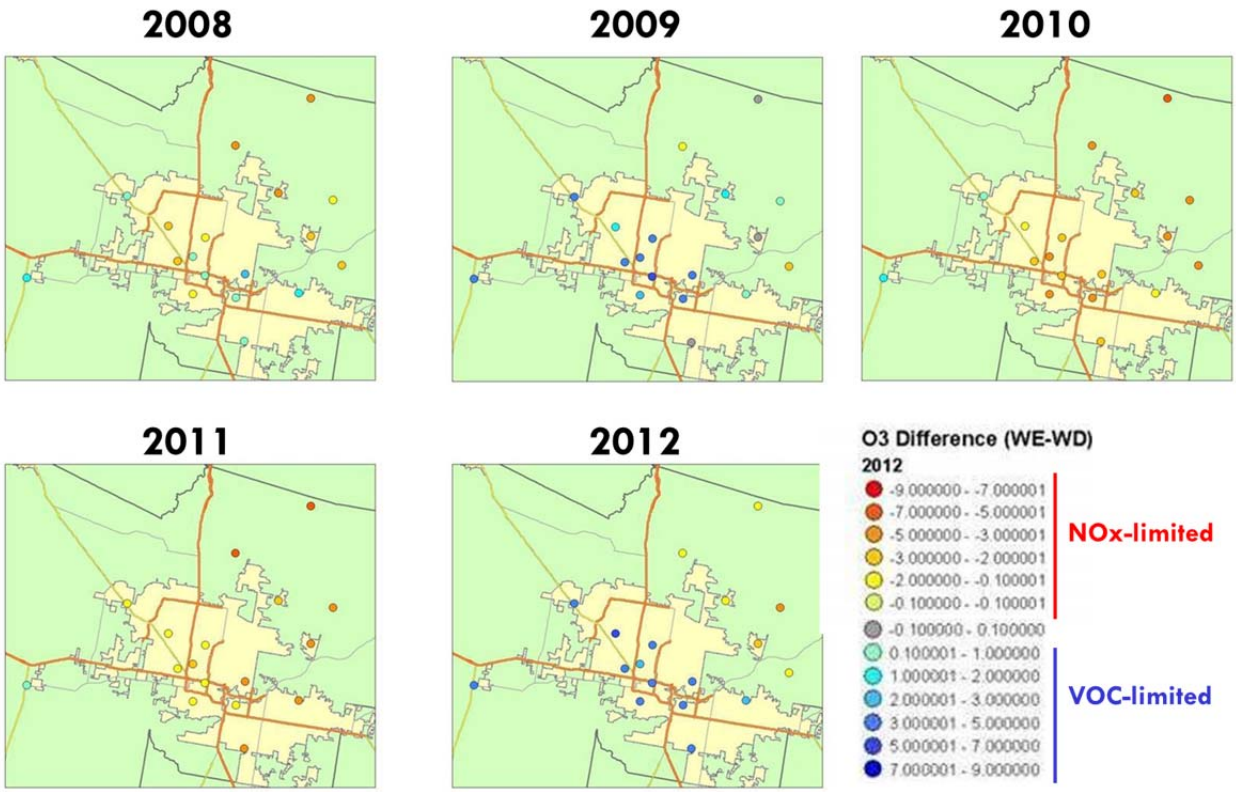

Figure 3-20. Peak weekday/weekend ozone differences.

3.3 VOC/NOx Emissions Ratio

Another indicator of whether ozone formation in a region is NOx-limited or VOC-limited is the VOC/NOx ratio of the emission inventory. We calculated the VOC/NOx ratio for the 2011 Maricopa Non-Attainment Area emission inventory that was supplied by MAG. This inventory used updated biogenic emissions developed by MAG in the spring of 2013. The only change made to the MAG emission inventory was the substitution of the on-road mobile emission inventory developed by ENVIRON using MOVES as described in Section 2.

For the Maricopa Non-Attainment Area, the 2011 VOC/NOx ratio was 6.2, which is within the VOC-limited regime. However, the weekday/weekend analysis shows all monitors except Buckeye to be NOx-limited in 2011. The fact that the urban core sites alternate together by year between being NOx- and VOC-limited suggests that the area is on the cusp of the NOx-limited and VOC-limited regimes. The inconsistency between the weekday/weekend analysis and the emission inventory suggests that the emission inventory VOC/NOx ratio may be biased low.

4.0 EFFECT OF METEOROLOGICAL AND CLIMATIC CONDITIONS

Meteorological conditions are an important factor in determining whether ozone formation is favored on a given day. Conditions that are conducive to ozone formation include high temperatures, clear skies, and light winds. High temperatures speed up the photochemical reactions that produce ozone and enhance evaporative emissions. Clear skies mean there is abundant solar radiation available to drive the ozone photochemistry. Light winds allow the buildup of local ozone precursor emissions, while high winds disperse emitted pollutants and are typically associated with lower ozone. An exception to this is when winds transport ozone into an area from distant regions. In Section 4, we present analyses of Phoenix meteorological data and assess whether meteorological factors can explain increasing ozone in Maricopa County in 2011-2012.

4.1 Analysis of Local Meteorological Data

We tested many hypotheses for meteorological influences on ozone in Maricopa County from 2002-2012. We examined the role of temperature, cloud cover, precipitation, wind speed, wind direction, sea level pressure, stagnant winds, wind reversals, El Nino phase, and North American Monsoon strength among others. In this section, we present a subset of these analyses, including only those that had some correlation with the ozone for at least part of the 2002-2012 period. We used data for the Phoenix Sky Harbor Airport (KPHX; Figure 4-1) from the National Climatic Data Center's ds3505 dataset of hourly surface meteorological observations available at ftp://ftp.ncdc.noaa.gov/pub/data/noaa/isd-lite/. The variables used are temperature wind speed, wind direction, precipitation and cloud cover.

Figure 4-1. Location of the Phoenix Sky Harbor Airport (red circle) in downtown Phoenix.

Figure 4-2 shows the interannual variation in the number of ozone season days with a daily maximum temperature >90°F. Also plotted is the trend in median 4th high MDA8 among all Maricopa County ozone monitors. 2012 was unusual in that it had the highest number of days >90°F during the last decade. This shows that 2012 had an unusually high number of days that were conducive for ozone formation in terms of temperature. 2011, on the other hand, was not an outlier in terms of number of days>90°F. The 2002-2012 correlation coefficient of the number of days with maximum temperature >90°F with daily with Maricopa median 4th high ozone is 0.2. Although 2012 did have an unusually large number of very hot days, the lack of correlation between these time series during 2002-2012 indicates that other factors besides temperature are at work in determining Phoenix ozone levels.

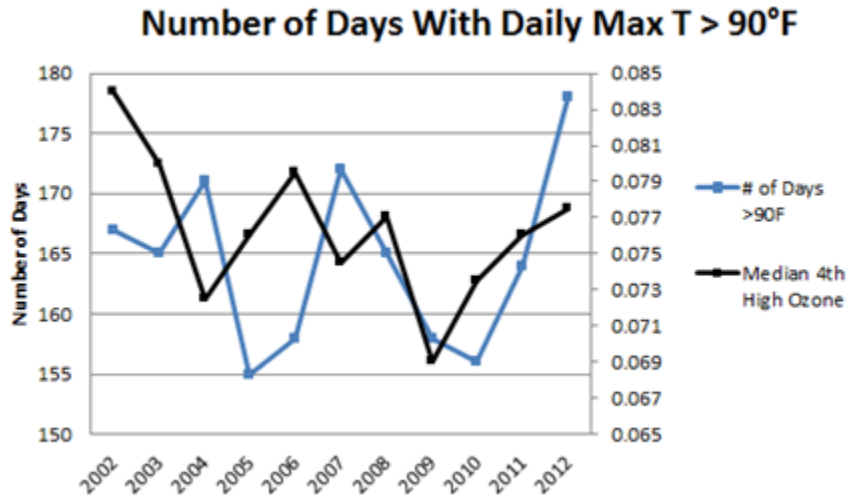

Figure 4-2. Number of days with daily maximum temperature >90°F for each year from 2002-2012 for the Phoenix Sky Harbor Airport, KPHX, and median value of the 4th high MDA8 among all Maricopa County ozone monitors.

Figure 4-3 examines whether there is a correlation between the number of hot days with stagnant winds and high ozone in Maricopa County. The chart shows the number of days in each year that had afternoon average (12 pm-6 pm) wind speeds less than 5 mph and a daily maximum temperature >90°F. If we look only at the period between 2008 and 2012, the correlation coefficient between the number of hot stagnant days and Maricopa ozone is 0.8, indicating a strong correlation. However, the correlation coefficient over the period 2002-2007 is -0.5 and for the entire 2002-2012 period, the correlation coefficient is -0.4. This suggests that this combination of variables does not explain trends in Maricopa ozone during the entire 2002-2012 period, but that high temperatures and stagnant winds may have played a role in high Maricopa ozone values from 2008-2012.

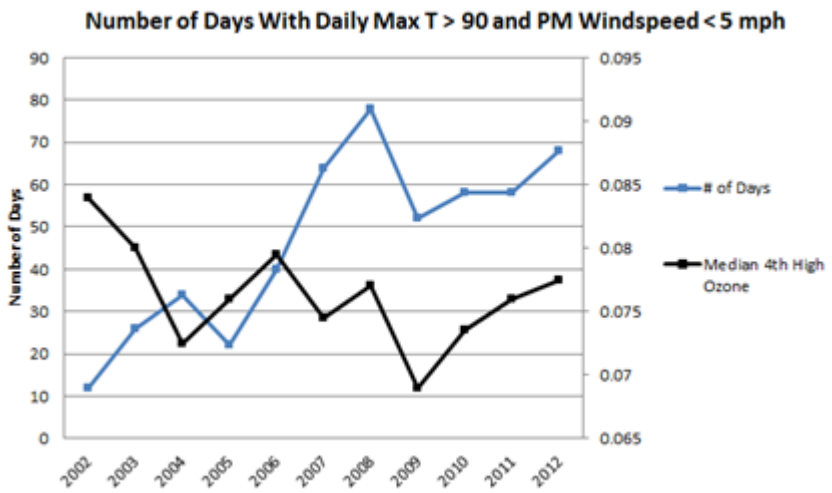

Figure 4-3. Number of days with afternoon average wind speed less than 5 mph and daily maximum temperature >90°F for each year from 2002-2012 for the Phoenix Sky Harbor Airport, KPHX, and median value of the 4th high MDA8 among all Maricopa County ozone monitors.

ENVIRON carried out a wind rose analysis of KPHX winds that showed that the winds during ozone season are frequently from the east during the morning and from the west in the afternoon. Wind roses were used to characterize station near-surface wind speed and direction. In a wind rose diagram, the orientation and length of spokes indicates the frequency with which that wind direction occurs. The spokes show the direction from which wind blows toward the monitor, and the colored bands indicate the percentage of time the winds fall in a given speed range. Figure 4-4 shows the wind rose analysis for May average winds for 2008-2012. This wind pattern would tend to advect ozone precursors to the west of Phoenix during the morning hours, and then move the precursors back over the urban area during the afternoon. Meanwhile, the precursors are undergoing photochemical processing and are being transformed into ozone. A similar pattern was seen in other months for KPHX (not shown).

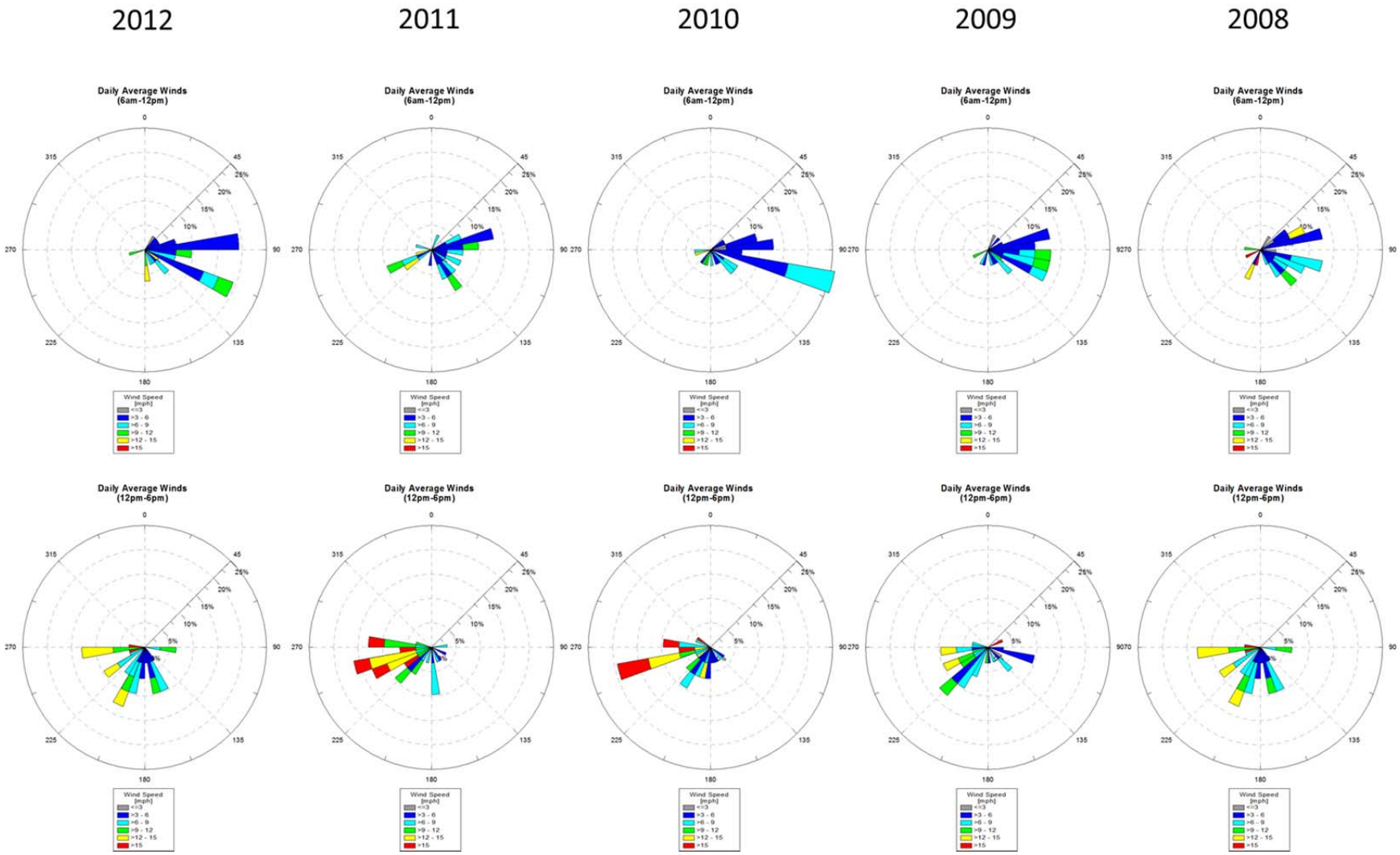

Figure 4-4. Monthly average wind roses for May 2008-2012. Upper panels are morning averages 6 am-11 am and lower panels are afternoon averages for 12-6 pm.

We investigated whether there is a correlation between hot days with east/west wind shifts and high ozone (Figure 4-5). The correlation coefficient between the number of days that fit this profile and the Maricopa 4th high MDA8 ozone trend is 0.3. Therefore, the frequency of days with wind shifts and high temperatures is not a key factor in explaining interannual variations in Maricopa ozone.

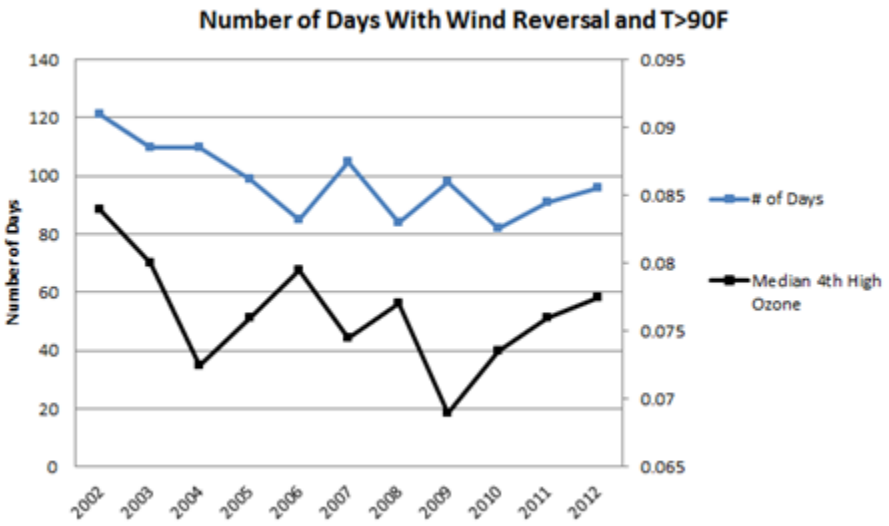

Figure 4-5. Number of days with a wind reversal and daily maximum temperature >90°F for each year from 2002-2012 for the Phoenix Sky Harbor Airport, KPHX, and median value of the MDA8 among all Maricopa County ozone monitors.

Figure 4-6 shows the number of high ozone days (MDA>75 ppb at one or more Maricopa County ozone monitors) in each month for 2008-2012. May, June and August had the most high ozone days during 2008-2012. July has a lower number of high ozone days, as this is the month of the monsoon onset, and is characterized by increased cloud cover and rainfall (see Figure 4-7 and Figure 4-8); these conditions are not conducive to high ozone. October had no high ozone days.

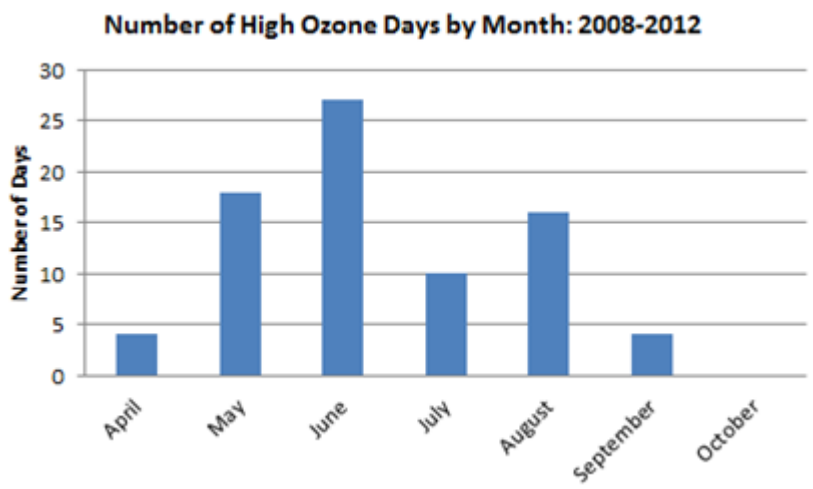

Figure 4-6. High ozone days by month for Maricopa County. High ozone days are defined to be any day for which one or more Maricopa County ozone monitors has MDA8>75 ppb.

Figure 4-8 shows the variation in monthly precipitation totals for the Phoenix Sky Harbor Airport for each year from 2002-2012. In March and April, the Phoenix area can be affected by the passage of mid-latitude storm systems. By May, the storm track has moved well to the north and precipitation totals fall relative to the earlier months. By June, precipitation has reached a minimum value, and is down to a trace for all years. July brings the onset of the North American monsoon in the Phoenix area, and precipitation totals increase to their maximum values in July and August. By September, the monsoon subsides, and in October, precipitation begins to increase again in some years as the mid-latitude storm track begins to move southward again as winter approaches Overall, May and June are the two months with the least precipitation and July and August are the two ozone season months with the most precipitation.

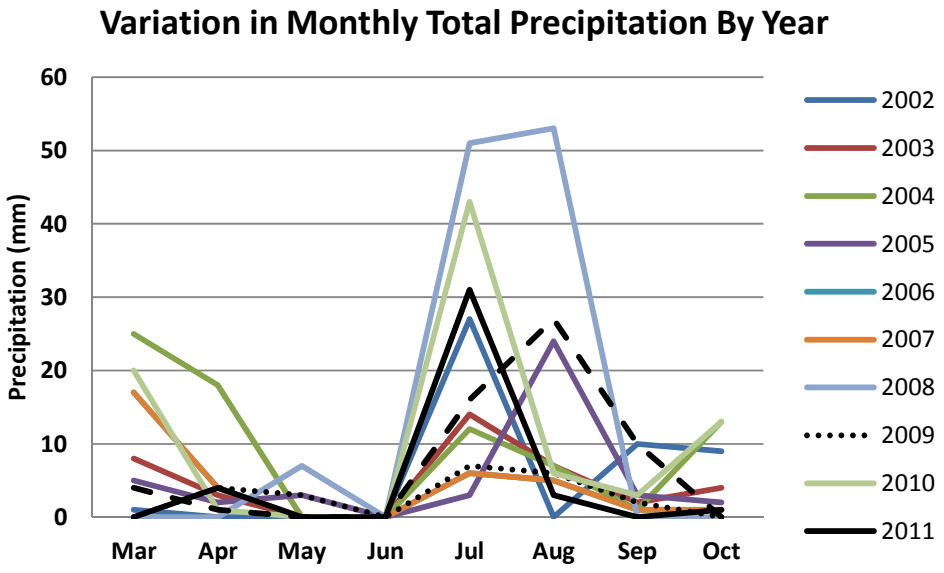

Figure 4-7. Monthly precipitation totals for each year from 2002-2012 for the Phoenix Sky Harbor Airport, KPHX.

The precipitation data show that 2011 and 2012 were very dry in May-June. 2008 and 2009 have the wettest May-June period of all years from 2002-2012. For July-August, it was not especially dry in 2011-2012; 2011 and 2012 are among the wetter years. 2008 has the largest amount of precipitation during the July-August monsoon season, followed by 2010. Overall, there is no clear relationship between interannual variations in precipitation at Phoenix Sky Harbor Airport and ozone trends in Maricopa County.

In Figure 4-8, monthly cloud coverage for each year from 2002-2012 is plotted for the Phoenix Sky Harbor Airport. The cloud coverage is measured in oktas, or eighths of the sky that are obscured. 0 oktas corresponds to a completely clear sky while a measurement of 8 oktas indicates that the sky is completely overcast. The measurement only describes whether the sky is clear or obscured and does not measure cloud amount or thickness. The overall trend in cloud coverage during the ozone season is that there is a minimum in cloudiness in June, and enhanced cloud cover during the July-August monsoon season.

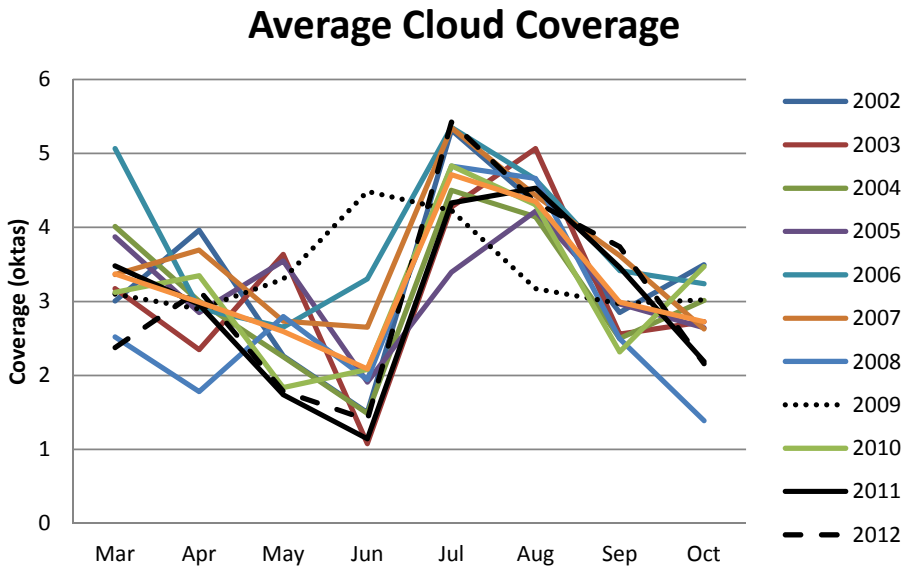

Figure 4-8. Monthly average cloud coverage for each year from 2002-2012 for the Phoenix Sky Harbor Airport, KPHX.

2011 and 2012 have lower than average cloud cover during May and June. They are the two years with the least amount of May cloud cover during the 2002-2012 period. During June, 2011 and 2012 are two of the four years with the least amount of cloud cover; the other two years with the least amount of cloud cover are 2003 and 2004. 2009, on the other hand, has the largest amount of cloud cover in June of any year, and is among the years with the largest amount of cloud cover in May. In July and August, 2009 has a relatively small amount of cloud cover; 2009 was a year with relatively weak monsoon rainfall (Figure 4-7). Figure 4-9 shows the departure from the 2002-2012 average cloud cover for each year across all months of the ozone season. 2009 stands out among all years as having enhanced cloudiness in June, a month that typically sees a large number of ozone days. Having an unusually large amount of cloudiness would tend to suppress ozone formation, as sunlight is needed to drive the photochemical reactions that produce ozone. 2011 and 2012, on the other hand, have lower than average cloud cover during May-June, which would favor ozone formation during those years.

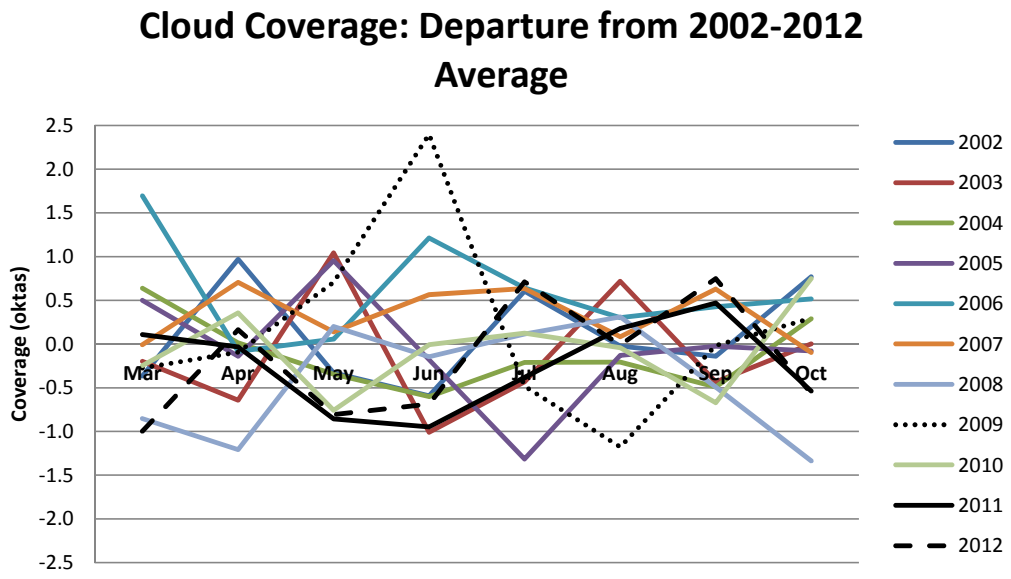

Figure 4-9. Departure from monthly average cloud coverage for each year from 2002-2012 for the Phoenix Sky Harbor Airport, KPHX.

Plots of additional meteorological variables that were analyzed but did not show evidence of a relationship with Maricopa County ozone trends are shown in Appendix B.

5.0 OZONE TRANSPORT

We analyzed back trajectories on high ozone days at Maricopa County monitors in order to determine whether 2011-2012 transport patterns were different from previous years such that they might have contributed to ozone being higher during 2011-2012 than during 2008-2010. For example, if back trajectories went more frequently over the Los Angeles area during 2011-2012 or showed a higher number of stagnant episodes, we might conclude that transport patterns played a role in determining Maricopa ozone trends during those years.

We prepared 72-hour HYSPLIT back trajectories ending at 1,000 m AGL above the Central Phoenix monitor. The Central Phoenix monitor was chosen as the endpoint for the back trajectories because of its central location among the Maricopa monitors. We prepared three sets of HYSPLIT back trajectory plots ending at the central Phoenix monitor. The first set of plots shows all days in each year from 2008-2012 when any Maricopa County monitor had MDA8 > 75 ppb. These are defined to be high ozone days (Figure 5-1). The second set of plots shows all days in each year from 2008-2012 when any Maricopa County monitor had MDA8 between 65 ppb and 75 ppb (moderately high ozone; Figure 5-2). Finally, the third set of plots shows all days in each year from 2008-2012 when any Maricopa County monitor had MDA8< 60 ppb (low ozone;

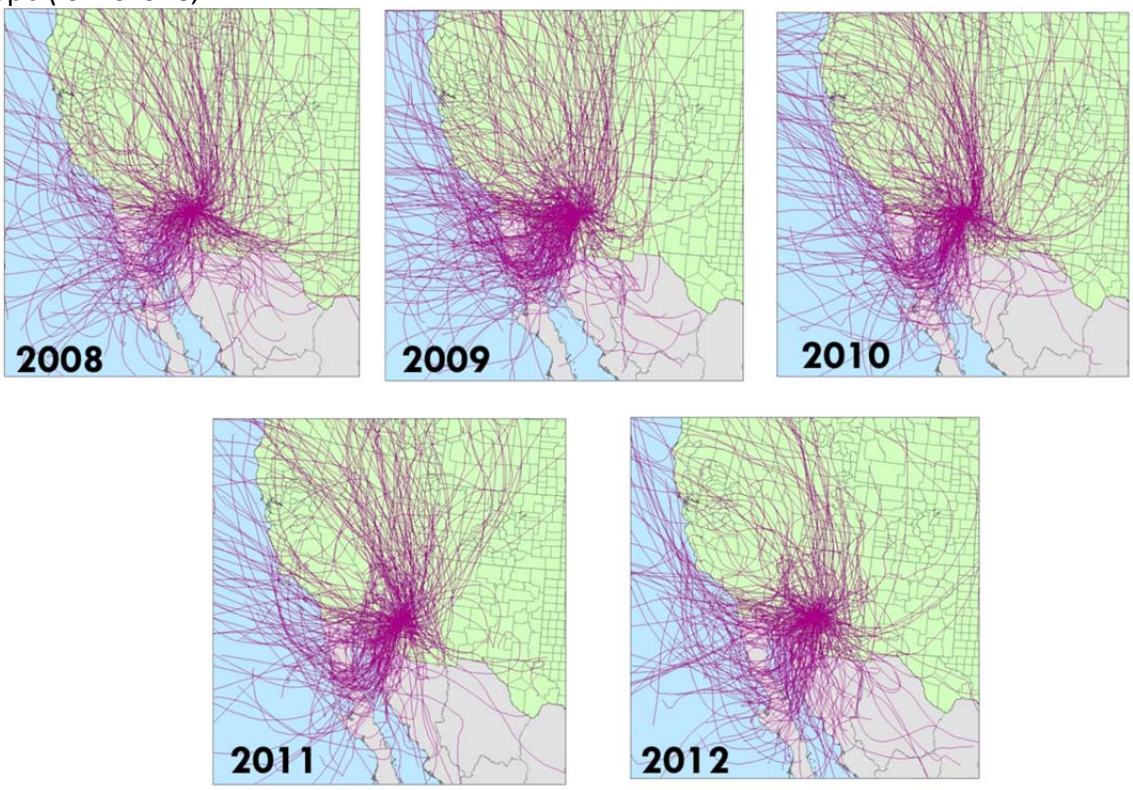

Figure 5-3). We examine these plots to evaluate whether transport patterns were different in 2011 and 2012 than during 2008-2010.

Comparison of Figure 5-1 and

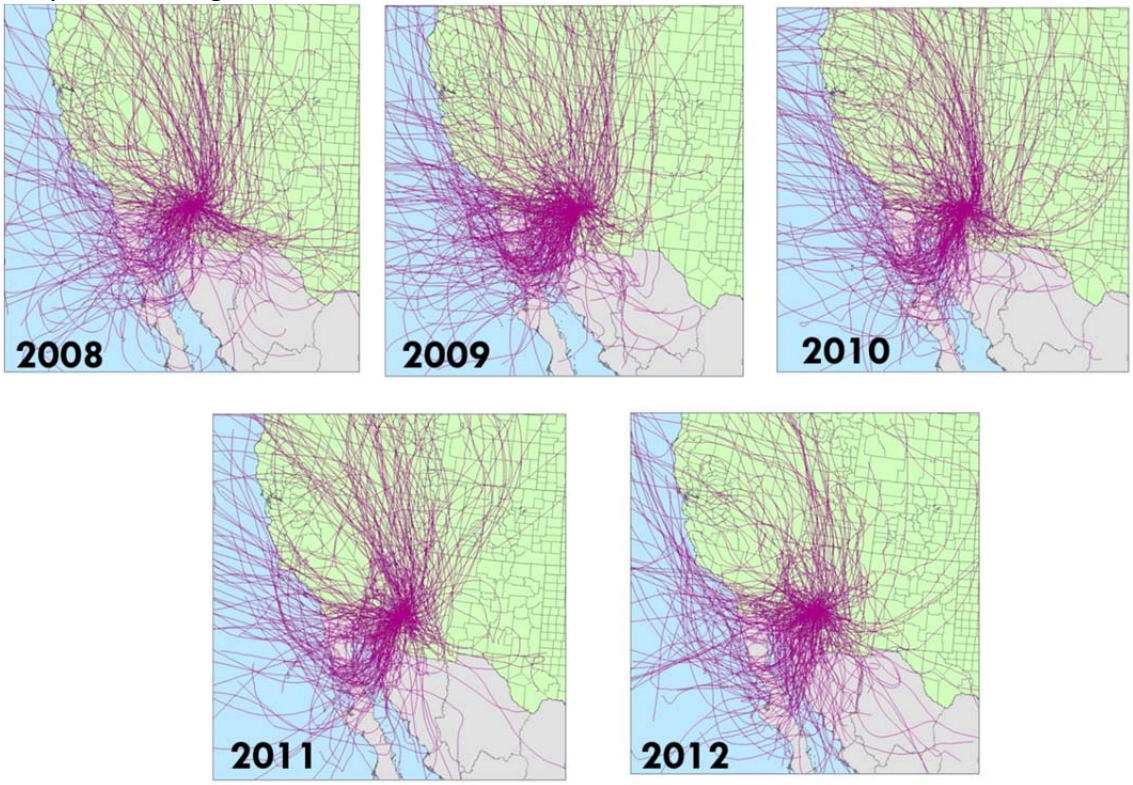

Figure 5-3 shows that the 72-hour back trajectories are longer on the low ozone days than on the high ozone days. Longer back trajectories correspond to higher wind speeds. Higher wind speeds are associated with low ozone days because the increased ventilation prevents the buildup of emissions of ozone precursors. Stagnant air, on the other hand, allows precursors to remain in the area, and is conducive to ozone formation. The trajectory directions are similar on high and low ozone days. Although the high ozone days have fewer trajectories than the low ozone days, their trajectory orientations fall into one of several groups:

- Northerly trajectories
- Trajectories that bring air southward along the coast, then eastward across Baja California before turning northeastward and heading to the Maricopa area
- Westerly/northwesterly trajectories
- Southeasterly trajectories

One difference among the years is the variation in the number of northerly back trajectories on high ozone days. On the days with MDA8>75 ppb, 2008, 2010 and 2012 all have trajectories extending to the north/northwest. Neither 2009 nor 2010 has back trajectories extending to the north. However, on moderate and low ozone days, these two years do have northerly back trajectories, which suggests that it is not variation in the transport paths that contributes to lower ozone in 2009 and 2010.

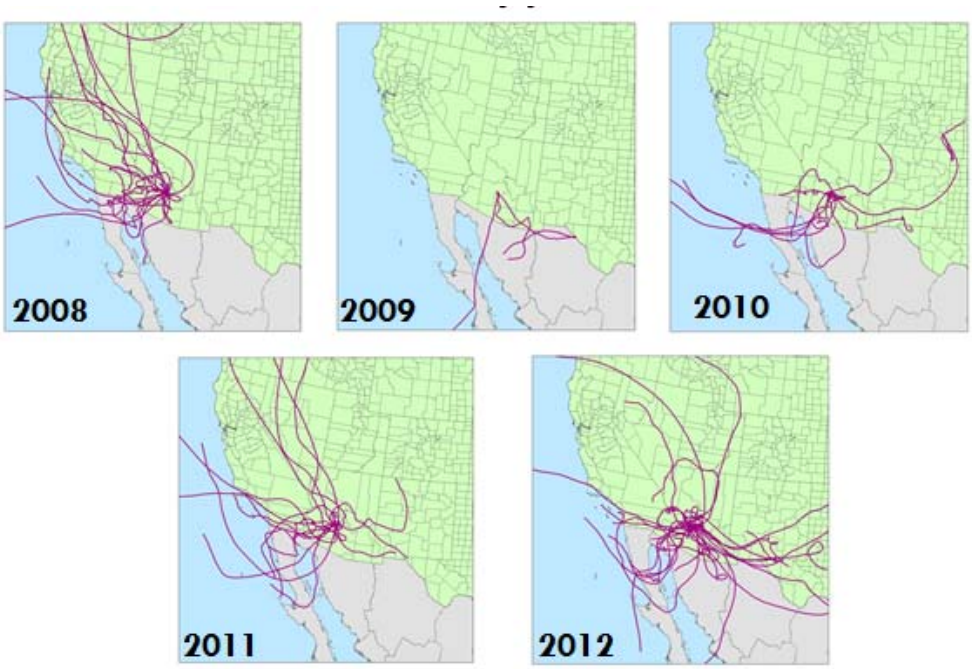

Figure 5-1. 72-hour HYSPLIT back trajectories for the Central Phoenix monitor for 2008-2012. Back trajectories ending at 1,000 m AGL at the monitor at 3 pm local time on days when the MDA8>75 ppb; high ozone days.

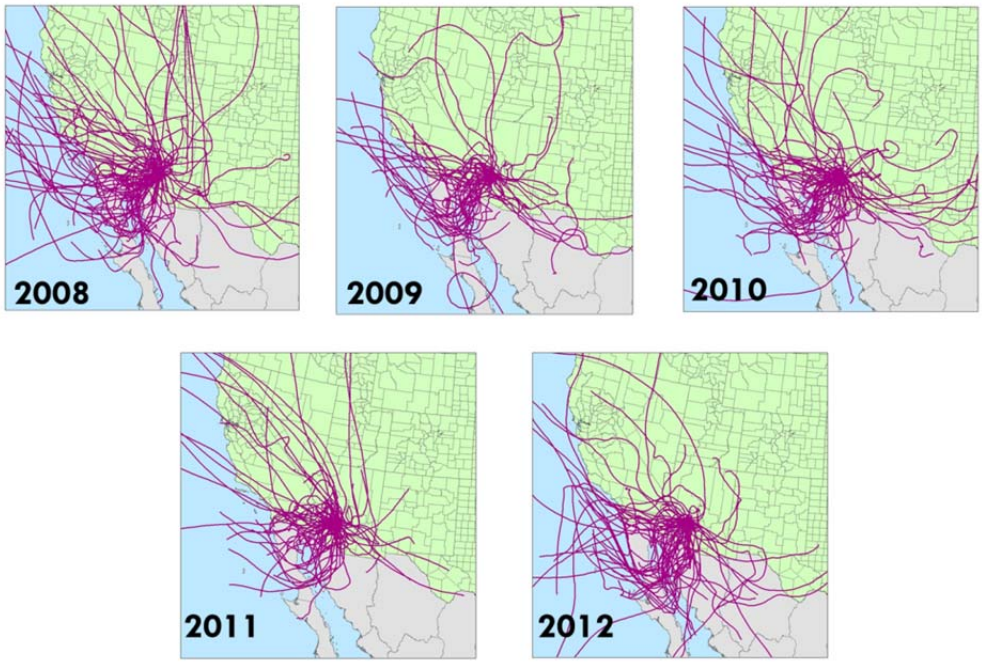

Figure 5-2. 72-hour HYSPLIT back trajectories for the Central Phoenix monitor for 2008-2012. Back trajectories ending at 1,000 m AGL at the monitor at 3 pm local time on days when the 65<MDA8≤75 ppb; moderate ozone days.

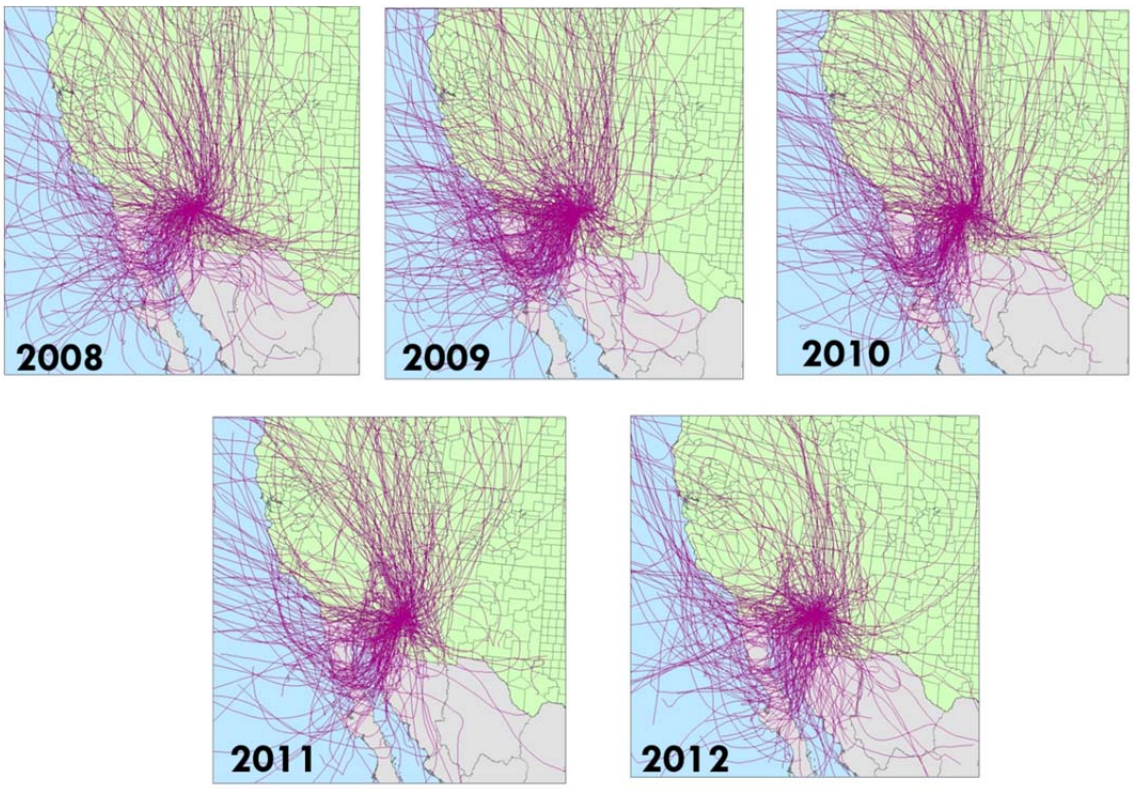

Figure 5-3. 72-hour HYSPLIT back trajectories for the Central Phoenix monitor for 2008-2012. Back trajectories ending at 1,000 m AGL at the monitor at 3 pm local time on days when the MDA8<60 ppb; low ozone days.

The fact that the trajectory paths are similar on high and low ozone days and that these paths are similar across the years suggests that it is not transport path changes that cause higher ozone in 2011-2012. Figures 5-1 through Figure 5-3, taken together do not show distinct trends in back trajectories in 2008-2012, suggesting that there were no unique transport patterns in 2011 and 2012; however, it is important to note that transport can play a role in the ozone exceedances in Maricopa County, as past evaluations of specific exceedance days clearly identify days when either ozone concentrations or precursors have been transported into the valley and were primarily responsible for specific exceedances.

6.0 BACKGROUND OZONE AND REGIONAL TRENDS

6.1 Background Ozone

The U.S. EPA defines 3 different types of background ozone for its regulatory assessments:

- Natural background
  - No global anthropogenic sources of ozone precursors
  - Includes biogenic, wildfire, lightning, pre-industrial carbon monoxide and methane emissions and stratospheric ozone
- North American Background (NAB – formerly Policy Relevant Background, or PRB)
  - Adds global anthropogenic sources outside North America
  - Current levels of carbon monoxide and methane
- US Background
  - Adds Canadian and Mexican anthropogenic sources

NAB ozone is the metric that the EPA has historically used in its standard setting process to define "uncontrollable" background concentrations (EPA, 2006; 2007).

Background ozone can vary significantly over daily, seasonal, and inter-annual time scales, and over a wide range of spatial scales. Over the long term, background is influenced by global industrialization and climate change trends. Natural sources contribute significantly to the daily-to-seasonal variability (e.g., fires, biogenics, stratosphere). Intercontinental transport can contribute significantly to U.S. background levels over seasonal to inter-annual time scales, and their contributions appear to be increasing. Parrish et al. (2009) present evidence that ozone entering the US west coast between 1980 and 2008 is increasing at 3-5 ppb per decade, while 2004-2012 measurements from Mt. Bachelor in Oregon (Jaffe, 2012) suggest increases of nearly 1 ppb/year (Figure 6-1). Based on aircraft and ozonesonde measurements made during 1995-2008, Cooper et al. (2011) report that background ozone is increasing by 0.6 ppb/year

Historical estimates of background ozone relied upon observations at remote sites on "clean" days or from ozone soundings. Observations generally range between 30-40 ppb with short term variability often exceeding 50 ppb, but they usually include some unknowable influence from North American sources (Lefohn et al., 2001; Cooper et al., 2005; Hocking et al., 2007; Oltmans et al., 2008; Langford et al., 2009). Instruments at elevated (mountain peak) sites record higher ozone concentrations in the mid-troposphere, and thus more readily sense Asian transport plumes and stratospheric influences that tend to peak in intensity during the late winter and spring seasons. However, discrete observational data are few and scattered, and thus are difficult to extrapolate to lower altitudes and across the entire U.S.

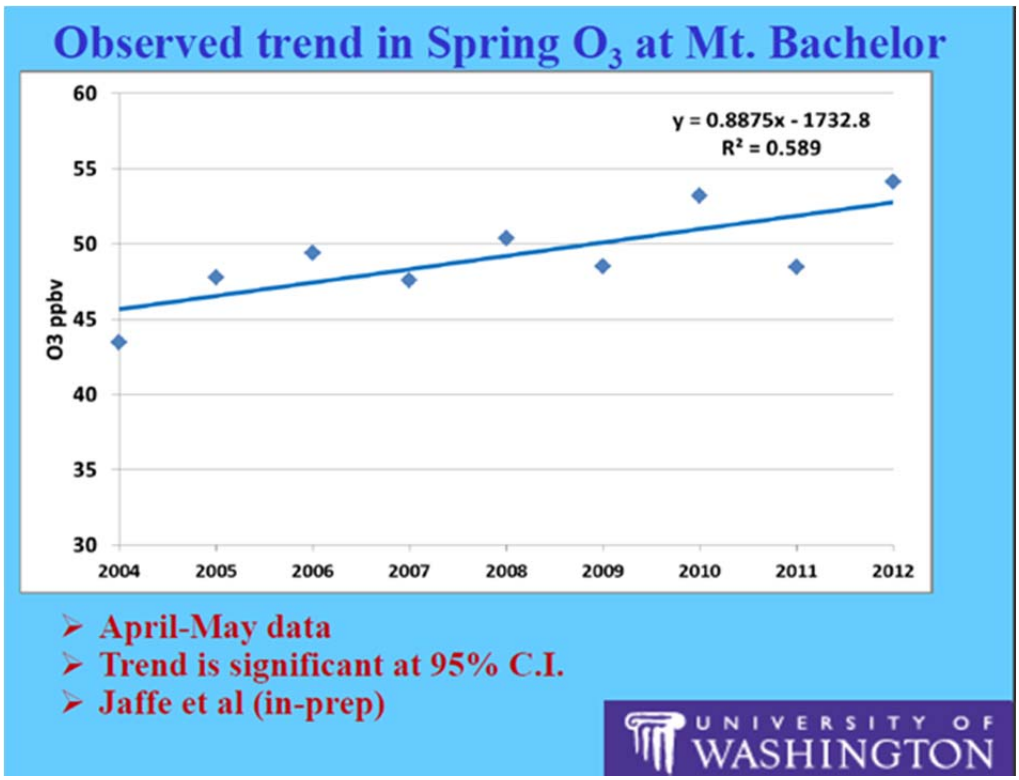

Figure 6-1. Observed ozone trends in spring from Mount Bachelor, OR. Figure from Jaffe (2012).

Background ozone is a policy construct that cannot be absolutely measured everywhere. State-of-the-science global and regional modeling has become widely used to better characterize the spatial and temporal patterns of background ozone simply by turning off all anthropogenic sources of emissions in the U.S. Over the years, improvements in model resolution, chemistry, meteorology, and global and natural emissions have yielded larger ranges of background ozone estimates with higher temporal variability (Fiore et al., 2003; Wang et al., 2009; Meuller and Mallard, 2011; Zhang et al., 2011; Emery et al., 2012). These models suggest that background ozone over the US ranges between 20-50 ppb, with peak levels reaching 50-70 ppb. The highest background levels most typically occur at high altitudes in the western U.S. during the spring (via Asian transport and stratospheric influences) and summer (from heightened fire, biogenic, and lightning activity).

Background ozone patterns in Phoenix are most likely influenced by regional natural sources, such as biogenic, fires, and lightning NOx, all of which have enhanced summertime activity. Occasionally, Phoenix ozone may also be influenced by long range transport mechanisms, including international contributions from Mexico and Asia and stratospheric intrusion events caused by vigorous low pressure systems during the late winter and spring. Recent modeling by Zhang et al. (2011) and Emery et al. (2012) suggest that the strongest stratospheric impacts occur at high altitudes and latitudes, while frequencies and intensity of stratospheric ozone events decrease for lower elevations and latitudes.

There exists no readily available information on stratospheric ozone events over the western U.S. Over the past few years, individual western States have been documenting stratospheric ozone episodes on a case-base-case basis to support their exceptional event filings to the EPA. From the standpoint of natural ozone sources, there is better evidence that summertime fire influences may have more direct impact on recent ozone increases in Phoenix. Furthermore, measurement and modeling studies are spatially/ temporally spotty. There are no routine or consistent data available to assess 2008-2012 background ozone trends in Phoenix.

6.2 Regional Ozone Trends

We examined regional ozone data to determine whether other areas of Arizona and nearby states had ozone trends similar to that of Maricopa County during 2002-2012. 4th high daily maximum 8-hour ozone average data for core-based statistical areas (CBSAs) in the western U.S. were downloaded from the EPA web site at www.epa.gov/airdata/ad_rep_mon.html. Figure 6-2 shows the 4th high MDA8 for large metropolitan areas in the west that are located to the east of the Sierra Nevada Mountains and are beyond the direct influence of the sea breeze circulation induced by the Pacific Ocean.

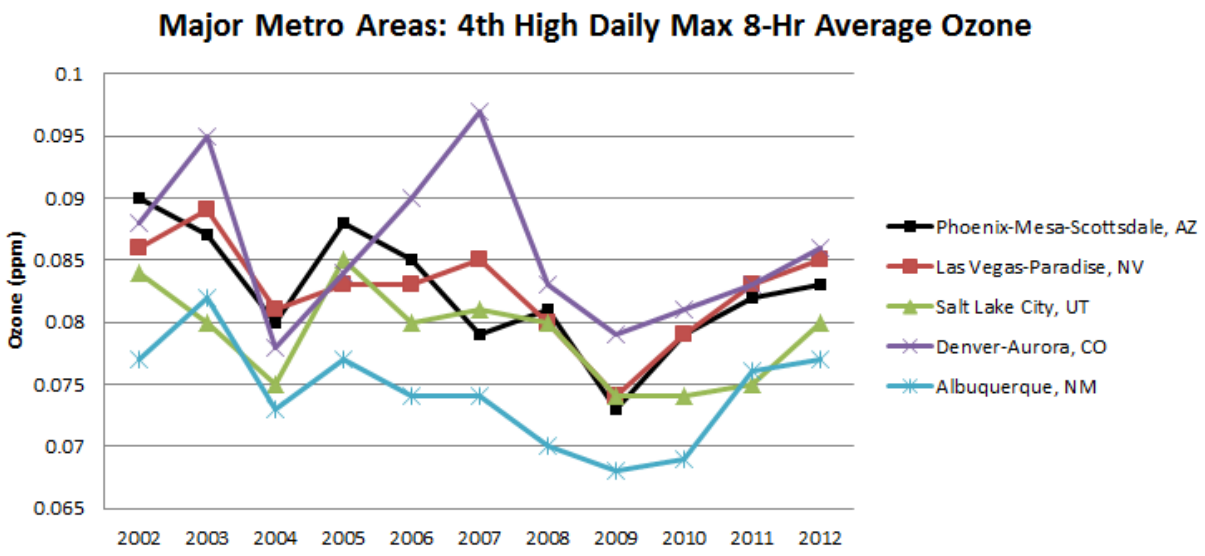

Figure 6-2. 2002-2012 4th high MDA8 ozone trends for major metropolitan areas in the western U.S. located east of the Sierra Nevada Mountains. Data from U.S. EPA www.epa.gov/airdata/ad_rep_mon.html.

During 2008-2012, all of these large metropolitan areas have trends similar to Maricopa, with ozone declining from 2008 to reach a minimum in 2009, and then increasing from 2009 through 2012. The fact that all of these areas show similar patterns from 2008-2012, including increasing ozone in 2011-2012, indicates that the 2011-2012 ozone increase in Maricopa align with a regional trend, and is not solely due to the impact of local emissions.

Figure 6-2 shows that all of the large metropolitan areas have relatively low ozone in both 2004 and 2009. From 2003-2005, ozone trends are similar for all sites. However, trends differ among monitors during 2005-2008. From 2005-2007, Las Vegas has increasing ozone, while Albuquerque has generally decreasing ozone during this period.

Figure 6-3 shows ozone trends for Arizona CBSAs. Areas with a 2008-2012 trend similar to that of Maricopa County are shown in gray. Trends are similar after 2007 for most areas, with ozone decreasing from 2008 to 2009 and reaching a local minimum in 2009. All areas showed an overall increase in ozone from 2009 to 2012; however, some areas experienced a decrease in ozone from 2011 to 2012 (Tucson, Flagstaff, Sierra Vista-Douglas). Trends for Show Low and Prescott diverge from others in 2002-3.

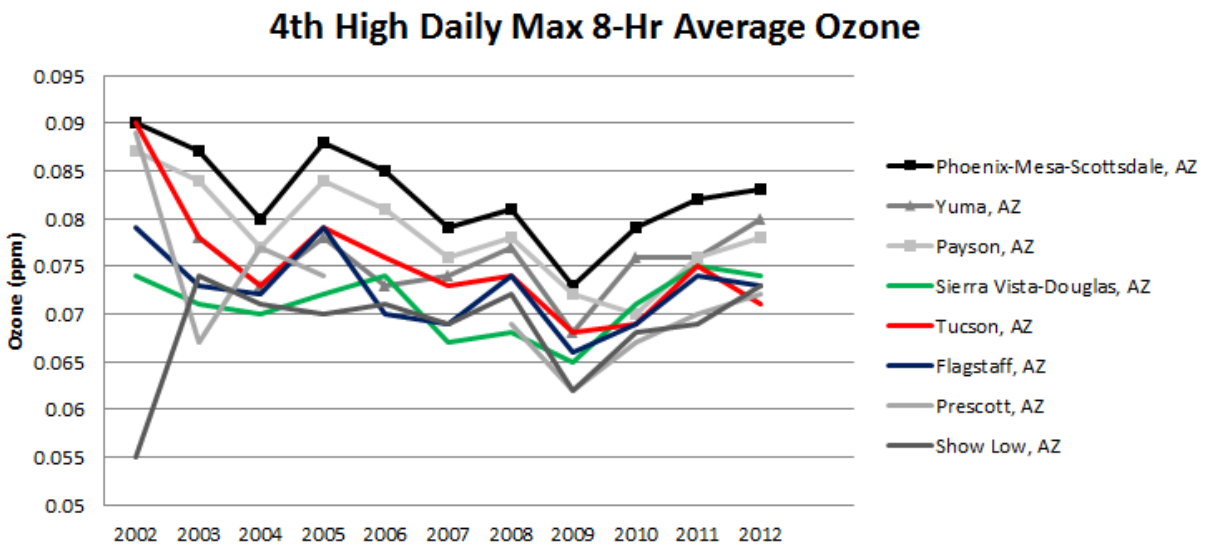

Figure 6-3. 2002-2012 4th high MDA8 ozone trends for Arizona CBSAs.

For New Mexico (Figure 6-4), areas with 2008-2012 ozone trends similar to Maricopa are shown in gray. The Maricopa ozone trend is shown in black on the New Mexico plot for the sake of comparison. All New Mexico areas show a 2008-2009 decrease, and most of the areas show increasing ozone from 2011-2012. Silver City and Hobbs have ozone trends that are different from the rest of the areas.

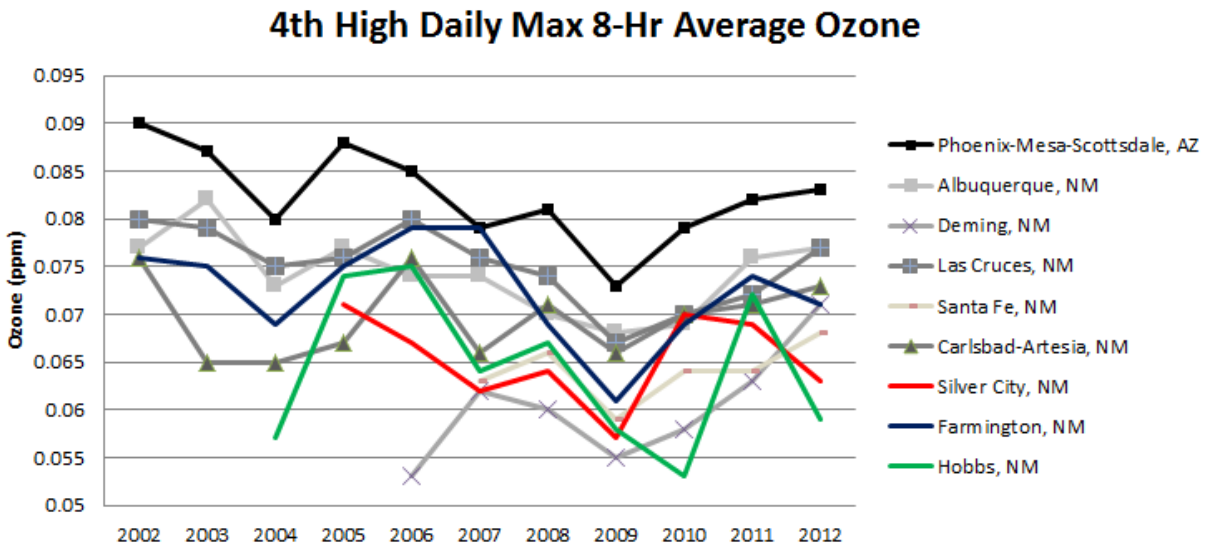

Figure 6-4. 2002-2012 4th high MDA8 ozone trends for New Mexico CBSAs.

In Colorado (Figure 6-5), all areas except Durango show a decrease in ozone in 2004 relative to 2003 and increasing ozone going from 2004 to 2005. Ozone trends vary among the areas from 2005-2008, but all areas except Durango have a relative minimum in 2009 and then show generally increasing ozone from 2009-2012. Some areas (Boulder, Grand Junction) show declines in ozone in 2012 relative to 2011, but others (Denver, Greeley, Fort Collins-Loveland) show monotonic increases in ozone from 2009-2012 similar to Maricopa.

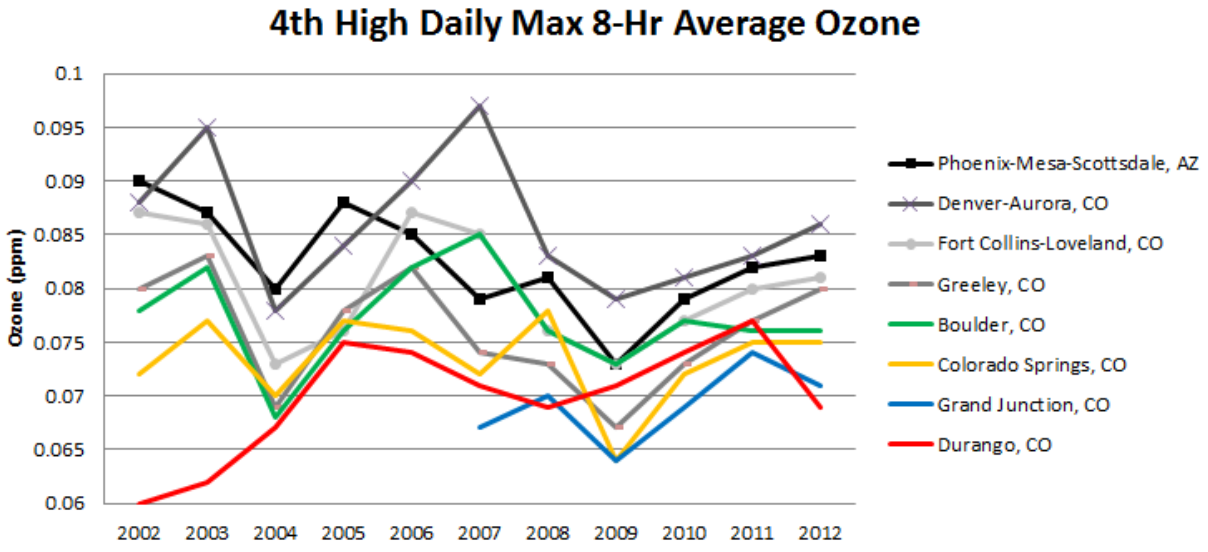

Figure 6-5. 2002-2012 4th high MDA8 ozone trends for Colorado CBSAs.

Ozone trends for all Utah areas except Vernal are shown in Figure 6-6. Vernal was excluded from this analysis because ozone formation in this area occurs under very different circumstances than in Maricopa or other Utah areas. Vernal is a rural area with intensive oil and gas development. During winter when there is snow cover, high ozone occurs. The mechanisms for ozone production under winter conditions in the vicinity of oil and gas development is a subject of current research. However, ozone production in other areas of Utah and in Maricopa occurs during the summer, and is driven by a different mix of emissions; therefore we remove Vernal ozone trends from the analysis because they do not help shed light on the causes of high ozone in Maricopa.

Figure 6-6 shows that Utah areas had similar trends to Maricopa and to one another during 2003-2005. Most areas (except Logan) saw ozone decrease from 2008 to 2009 and an increase in ozone going from 2011 to 2012.

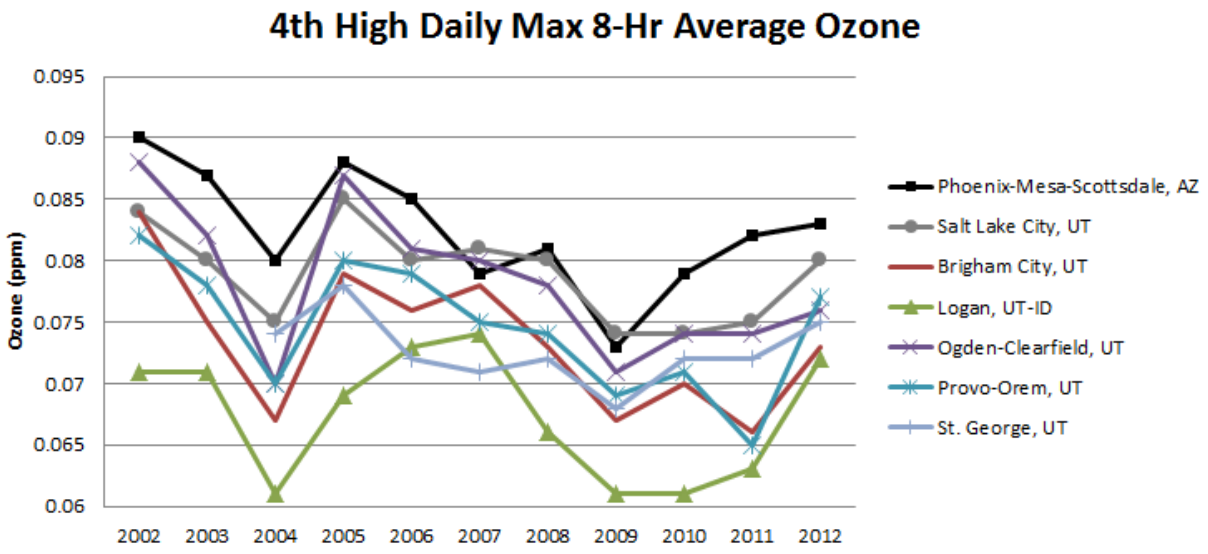

Figure 6-6. 2002-2012 4th high MDA8 ozone trends for Utah CBSAs.

Nevada CBSAs (Figure 6-7) show differences in their ozone trends. While Las Vegas is quite similar in magnitude and trends to Maricopa, Fernley, Fallon and Carson City and Reno-Sparks differ from Las Vegas and from one another. All sites, however, show a decrease in ozone from 2008 to 2009.

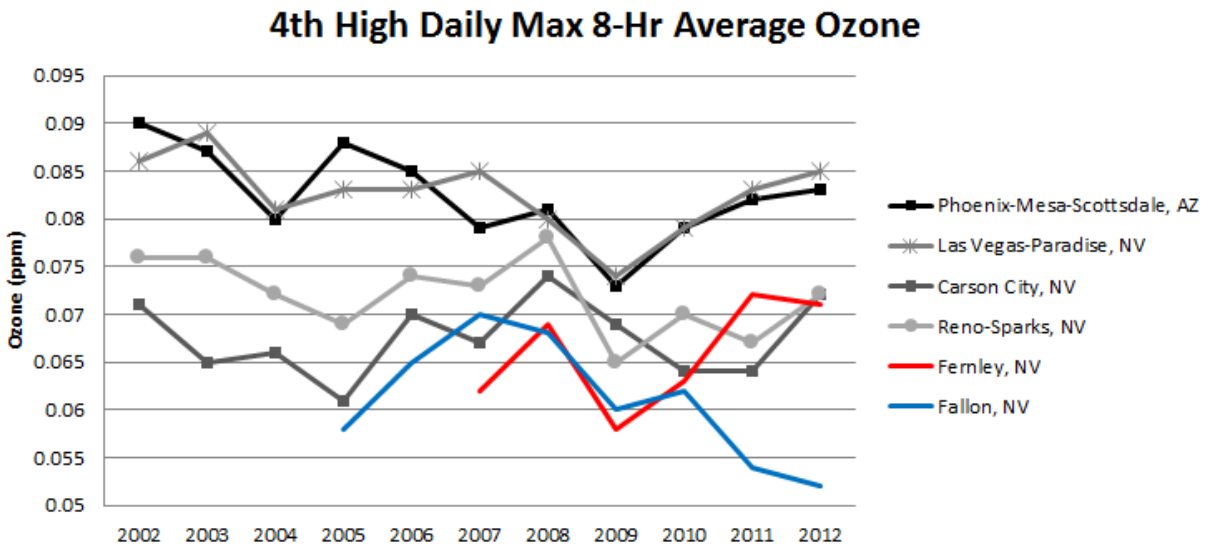

Figure 6-7. 2002-2012 4th high MDA8 ozone trends for Nevada CBSAs.

Figure 6-8 shows ozone trends for large metropolitan areas in California that are near the Pacific Ocean and are strongly influenced by coastal meteorology. All of these areas show a decrease in ozone in 2004 relative to 2003 and in 2009 relative to 2008, similar to Maricopa. An important difference in the trends in these coastal cities and in Maricopa is that ozone in California metropolitan areas shows an overall decrease from 2009-2012 while ozone increases in Maricopa from 2009-2012. For all of these California areas, ozone decreases going from 2011 to 2012. This indicates that rising Maricopa ozone in 2012 is not due to increased ozone levels in California coastal cities.

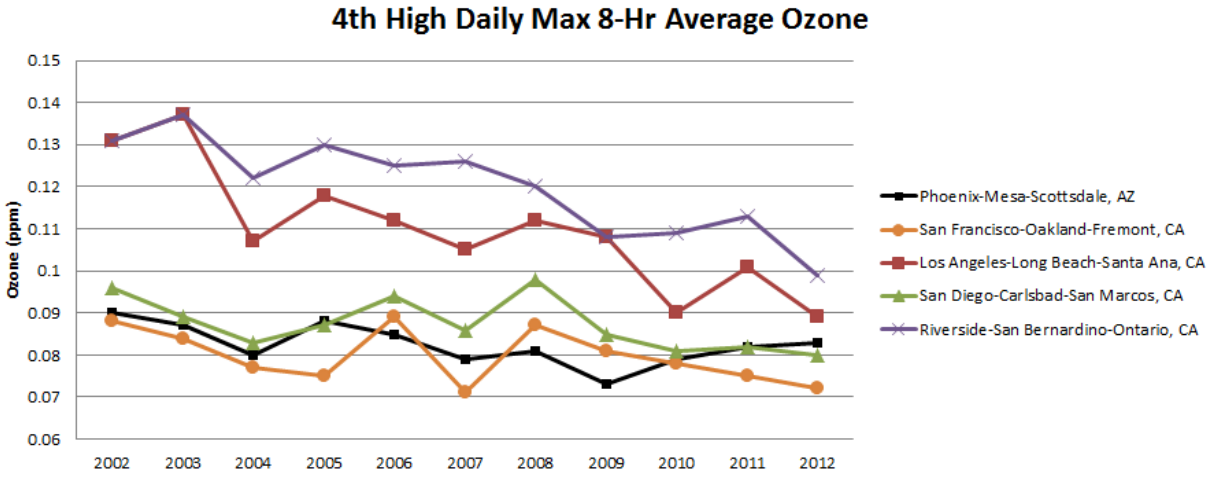

Figure 6-8. 2002-2012 4th high MDA8 ozone trends for large coastal metropolitan areas of California.

In Figure 6-9, we show California sites that are east of the coastal mountains (El Centro) and east of the Sierra Nevada Mountains (Bishop). Also shown on this plot is Yuma, AZ, which is located near El Centro. These sites lie outside the influence of the coastal sea breeze circulation. In contrast to the ozone trends in the coastal California metropolitan areas shown in Figure 6-8, the ozone trends in the eastern California areas are similar to that of Maricopa and to Yuma. There is an overall rising trend during 2009-2012 for all sites shown in Figure 6-9. All sites show relative minima in 2004 and all show decreases in 2009 ozone relative to 2008.

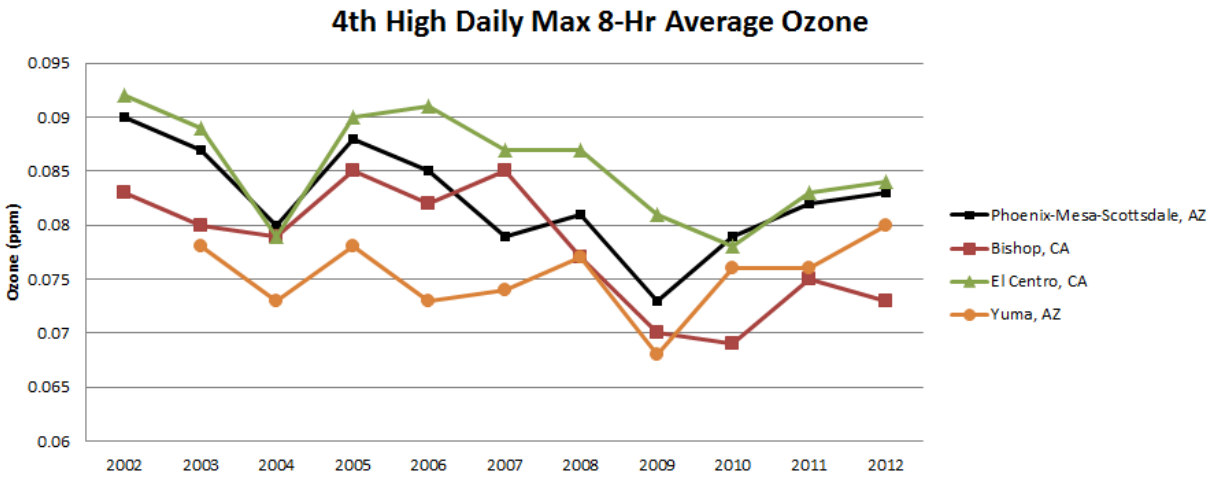

Figure 6-9. 2002-2012 4th high MDA8 ozone trends for eastern California and Yuma, AZ CBSAs.

6.2.1 Summary of Regional Ozone Trends

During 2003-2005 and 2008-2012, many CBSAs in states near Arizona had ozone trends similar to Maricopa. This suggests that the increase in ozone in Maricopa during 2011-2012 is driven at least in part by factors that are regional in spatial scale. It is possible that regional meteorological factors could cause conditions conducive to ozone formation across a broad area of the western U.S. For example, a high pressure anomaly may induce large-scale subsidence that brings clear skies, high temperatures, and light winds to a region that can span several states.

6.3 Regional Meteorological Factors

We reviewed National Climatic Data Center (NCDC) Climate Summaries for each year from 2008 to 2012 to evaluate the potential for regional meteorological factors to affect ozone levels in the western U.S. Figure 6-10 and Figure 6-11 show climate summaries for spring (March-May) and summer (June-August), respectively. Spring and summer of 2012 were unusually hot across large portions of the country. The summer of 2011 was also unusually warm in the southern half of the U.S. The summer of 2009 is notable for its unusually cold temperatures in the northern and central U.S. The North American monsoon precipitation was weak during 2009, with Arizona experiencing its 3rd driest recorded summer.

For other years and seasons, the spatial signature of interannual variations in temperature is less coherent. However, the fact that 2009 (unusually low ozone in the west) and 2011-2012 (unusually high ozone in the west) show large-scale temperature anomalies suggests that investigation of large-scale atmospheric anomalies may shed some light on the variations in ozone throughout the west during 2008-2012. In our analysis, we investigated a number of atmospheric fields to determine whether their variations in 2008-2012 are consistent with variations in ozone levels across broad regions of the western U.S.

Figure 6-12 and Figure 6-13 show monthly maps of 500 mb heights (contours) and 500 mb height anomalies (shading) from the National Center for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) Climate Data Assimilation System (CDAS). The higher ozone years 2008, 2011 and 2012 are shown in Figure 6-12 and the lower ozone years 2004 and 2009 are shown in Figure 6-13. 2012 is notable for the intensity and persistence of positive 500 mb height anomalies throughout the spring and summer seasons. This is consistent with the temperature anomalies shown in Figure 6-10 and Figure 6-11. In no other year is there such a strong signal in the 500 mb height/anomaly plots. In both 2004 and 2009 there are negative 500 mb height anomalies near the Great Lakes region and across the northern tier states. This is consistent with the cool surface temperature anomalies shown in Figure 6-11. The negative 500 mb height anomalies do not persist across the entire season.

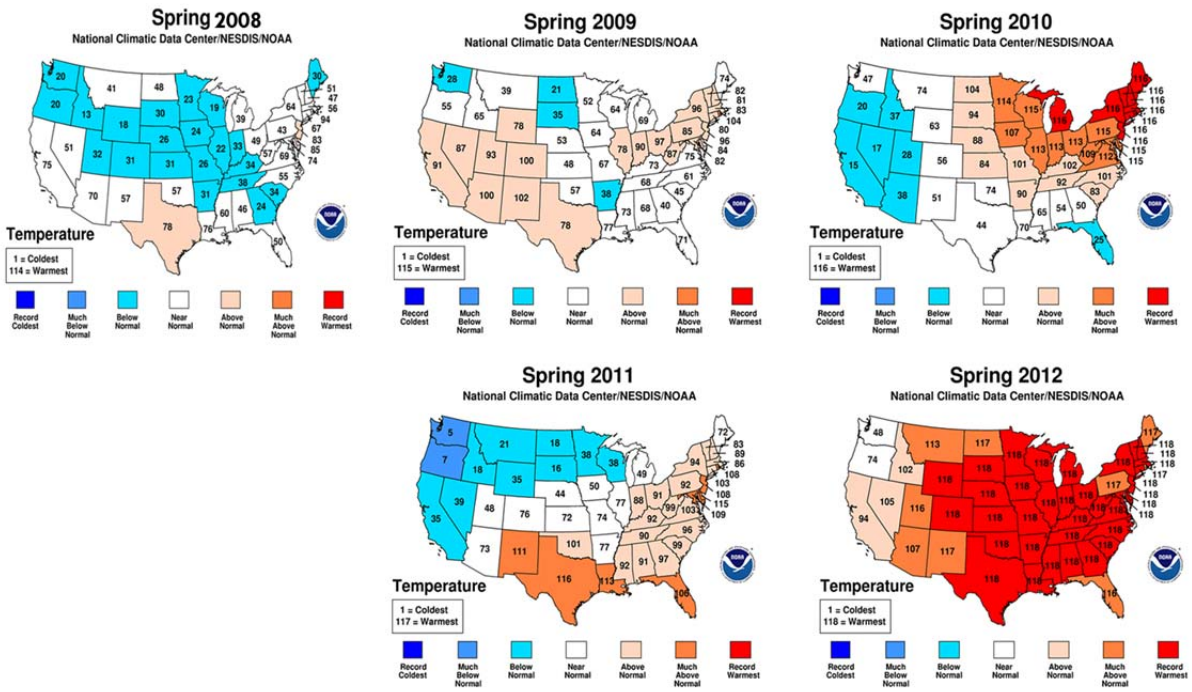

Figure 6-10. NCDC Spring climate summaries.
http://www.ncdc.noaa.gov/sotc/national/2012/13.

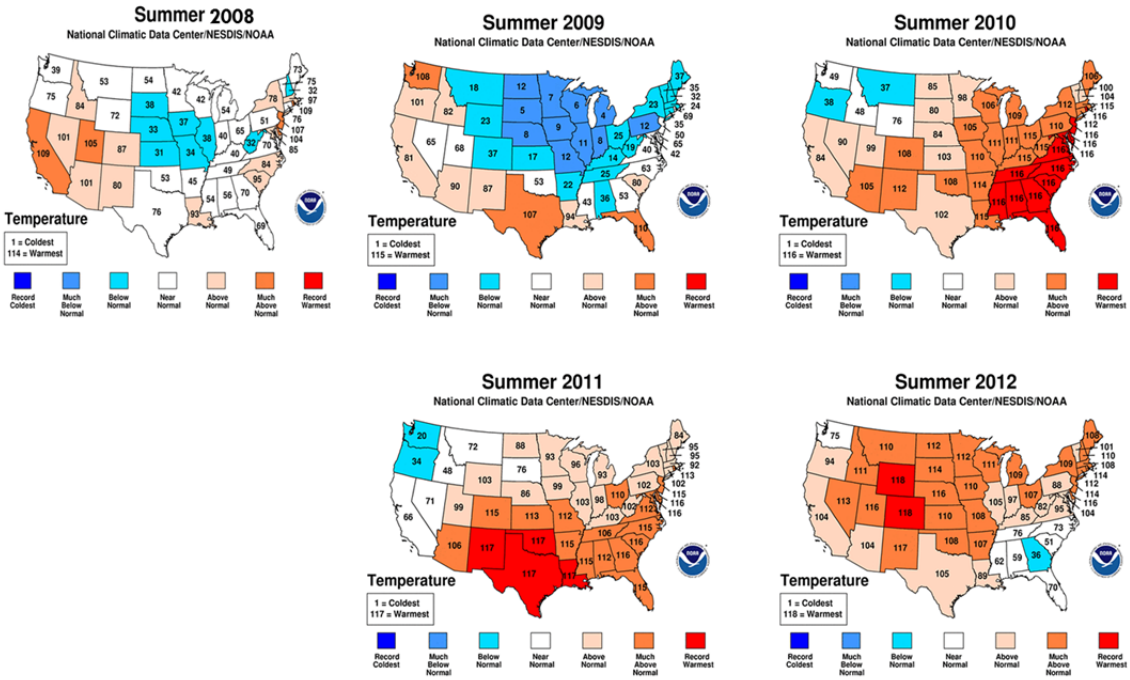

Figure 6-11. NCDC Summer Climate Summaries.
http://www.ncdc.noaa.gov/sotc/national/2012/13.

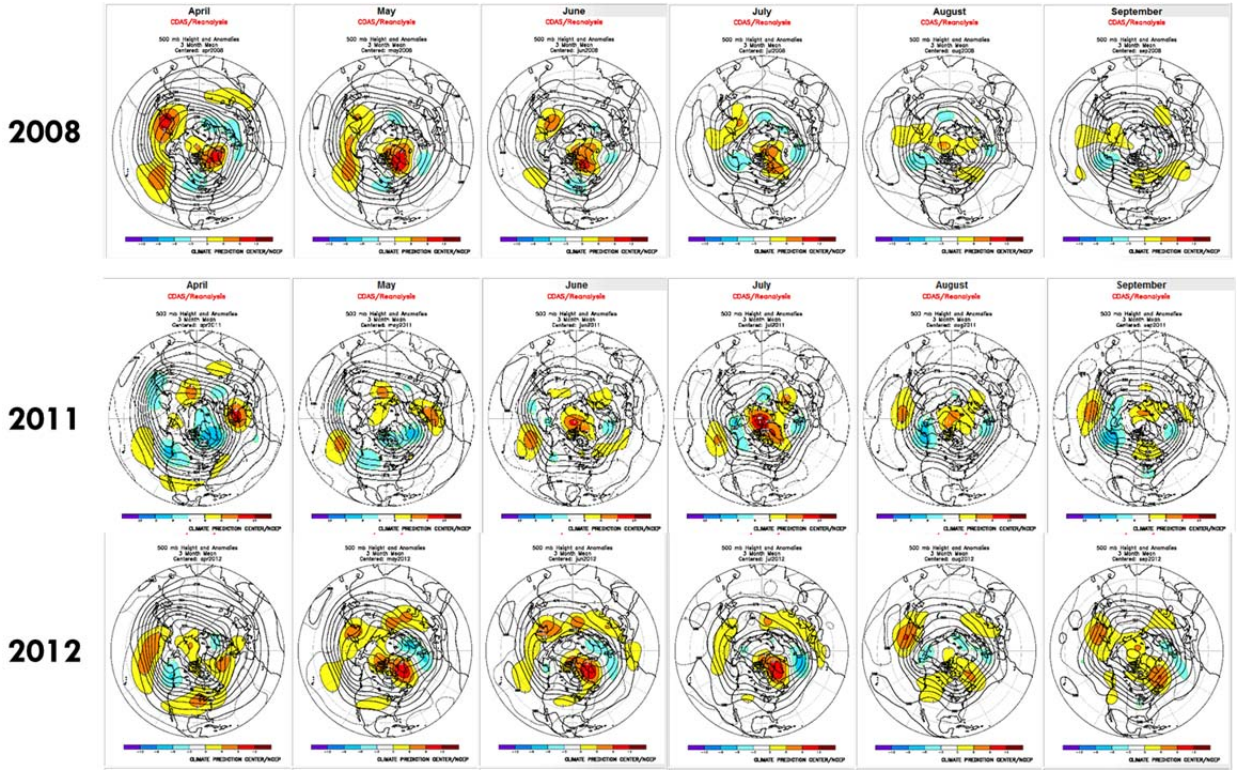

Figure 6-12. CDAS/reanalysis 500 mb height and anomaly for high ozone years 2008-2012. http://www.cpc.ncep.noaa.gov/products/predictions/90day/tools/briefing/500hgtarch.php.

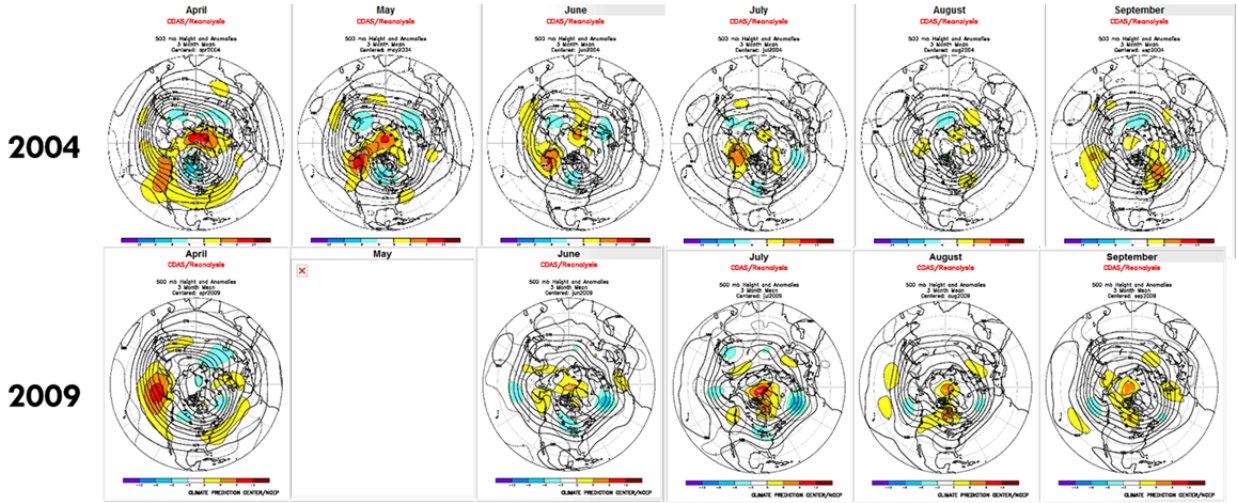

Figure 6-13. CDAS/reanalysis 500 mb height and anomaly for low ozone years 2008-2012. http://www.cpc.ncep.noaa.gov/products/predictions/90day/tools/briefing/500hgtarch.php.

Positive anomalies in the 500 mb heights can be associated with high temperatures, and sinking motions i.e. large-scale subsidence. Under these conditions, cloudiness is suppressed. We examined National Oceanic and Atmospheric Administration (NOAA) interpolated satellite outgoing longwave radiation fields to determine whether interannual changes in large-scale cloud cover are consistent with the ozone trends. Outgoing longwave radiation (OLR) is measured by the Advanced Very High Resolution Radiometer (AVHRR) instrument aboard NOAA polar orbiting spacecraft. OLR is dependent on the skin temperature and surface emissivity of the earth, the distribution of water vapor, ozone and CO_2 in the earth's atmosphere, and on clouds. OLR can be used to diagnose the presence of clouds. Upwelling longwave radiation is absorbed by cloud and is re-radiated at the temperature of the cloud. High clouds, whose temperature is much lower that the surface of the earth, show up as areas of lower OLR compared to clear areas, which have higher OLR because the radiation from the earth's surface (higher temperature) reaches the radiometer unimpeded.

In Figure 6-14 and Figure 6-15, we show the May-June OLR anomaly. We focus on May-June because Phoenix airport data showed enhanced cloudiness in May-June 2009 and little cloud cover in 2011-2012; these are the two months that saw the largest number of high ozone days during 2008-2012 (Figure 6-14). Because of the influence of the North American Monsoon, the July-August OLR fields and anomalies (Figure 6-16 and Figure 6-17) look significantly different from the May-June anomaly. Therefore the signal of the OLR anomaly when averaged over a full season is an average over signals that are not alike.

The May-June OLR anomaly, however, shows coherent spatial variability that is consistent with the regional ozone trends in 2008-2012. During 2011-2012, there is a strong positive OLR anomaly over the southern and western U.S. that is consistent with reduced cloudiness and high temperatures; these conditions are conducive to high ozone. In 2008 and 2010, there are generally positive anomalies over the southwestern U.S. that are not as strong as the 2011-2012 positive anomalies. In 2009, however, there is a negative OLR anomaly over the southwest, which is consistent with enhanced cloudiness and lower atmospheric temperatures. This is consistent with the Phoenix temperature and cloud data as well as the NCDC climate summary plots for spring and summer. Enhanced cloudiness inhibits ozone formation by reducing the amount of radiation available to drive photochemical reactions and low temperatures reduce evaporative emissions and slow the rate of chemical reactions. The fact that the OLR anomaly varies in a manner consistent with both regional ozone trends and local phoenix cloudiness suggests that during May-June from 2008-2012, regional meteorological factors contributed to increasing ozone trends in 2011-2012 in Phoenix and across the western U.S.

The 2002-2007 period (Figure 6-15), however, does not show the same relationship between OLR anomaly and regional ozone trends in the southern and western U.S. In 2004, for example, there is a positive OLR anomaly over the southwestern U.S. but 2004 was a year of relatively low ozone in the southwestern U.S (Figure 6-2 through Figure 6-9).

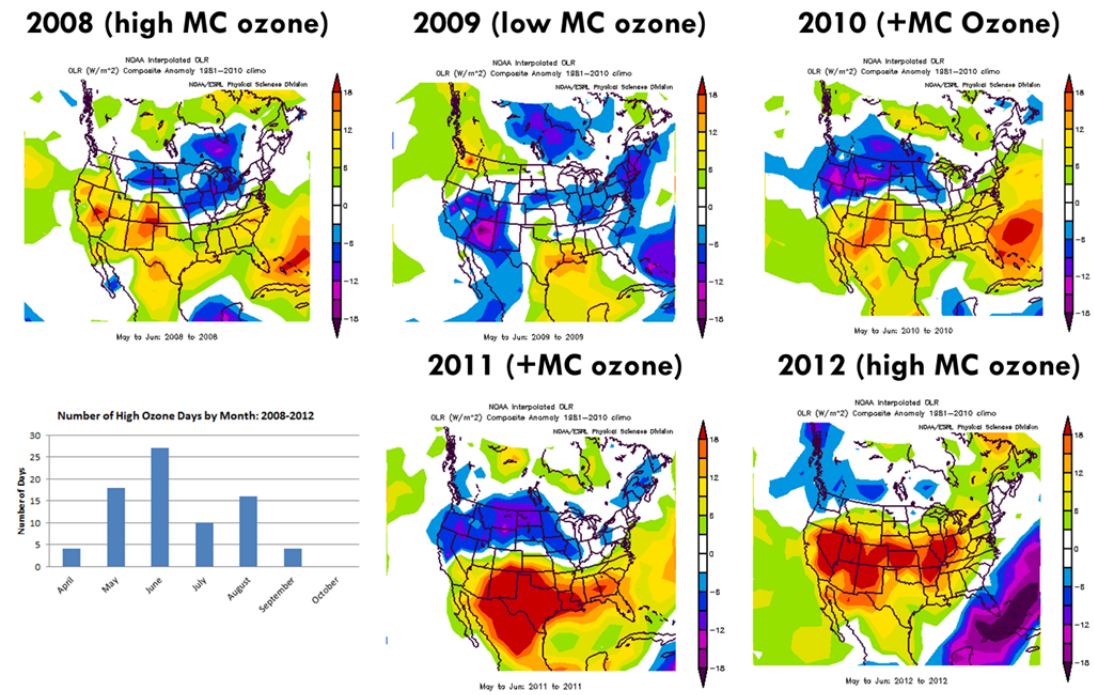

Figure 6-14. May-June NOAA interpolated OLR anomaly and number of days in each month during 2008-2012 when any monitor in Maricopa has MDA8>75 ppb.

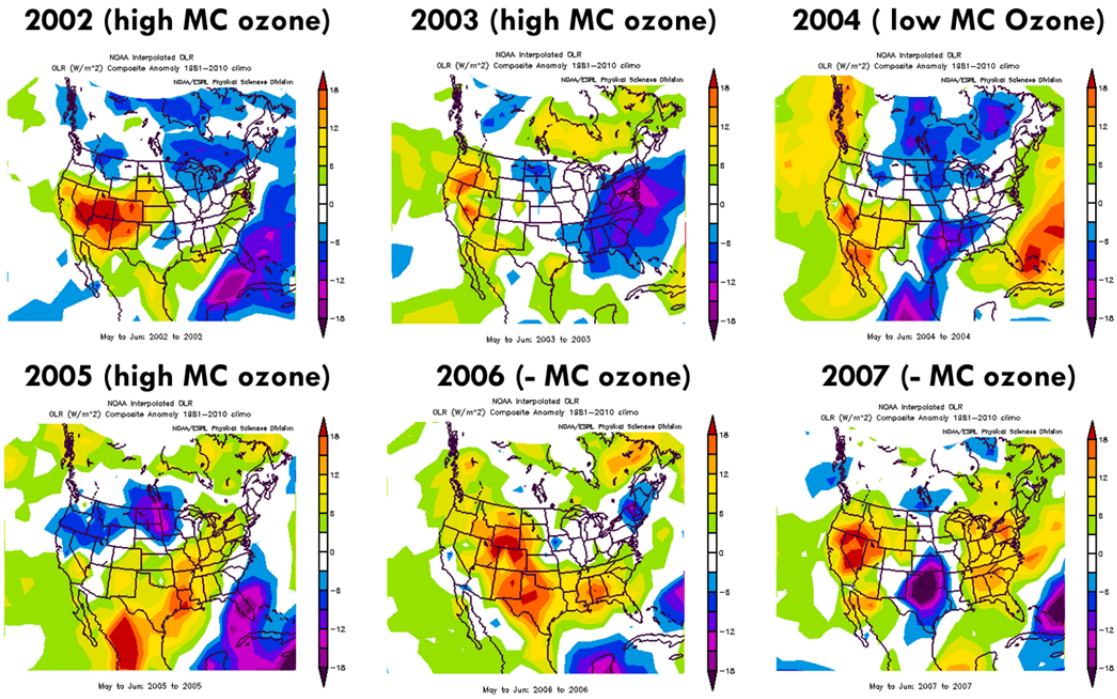

Figure 6-15. May-June NOAA interpolated OLR anomaly.

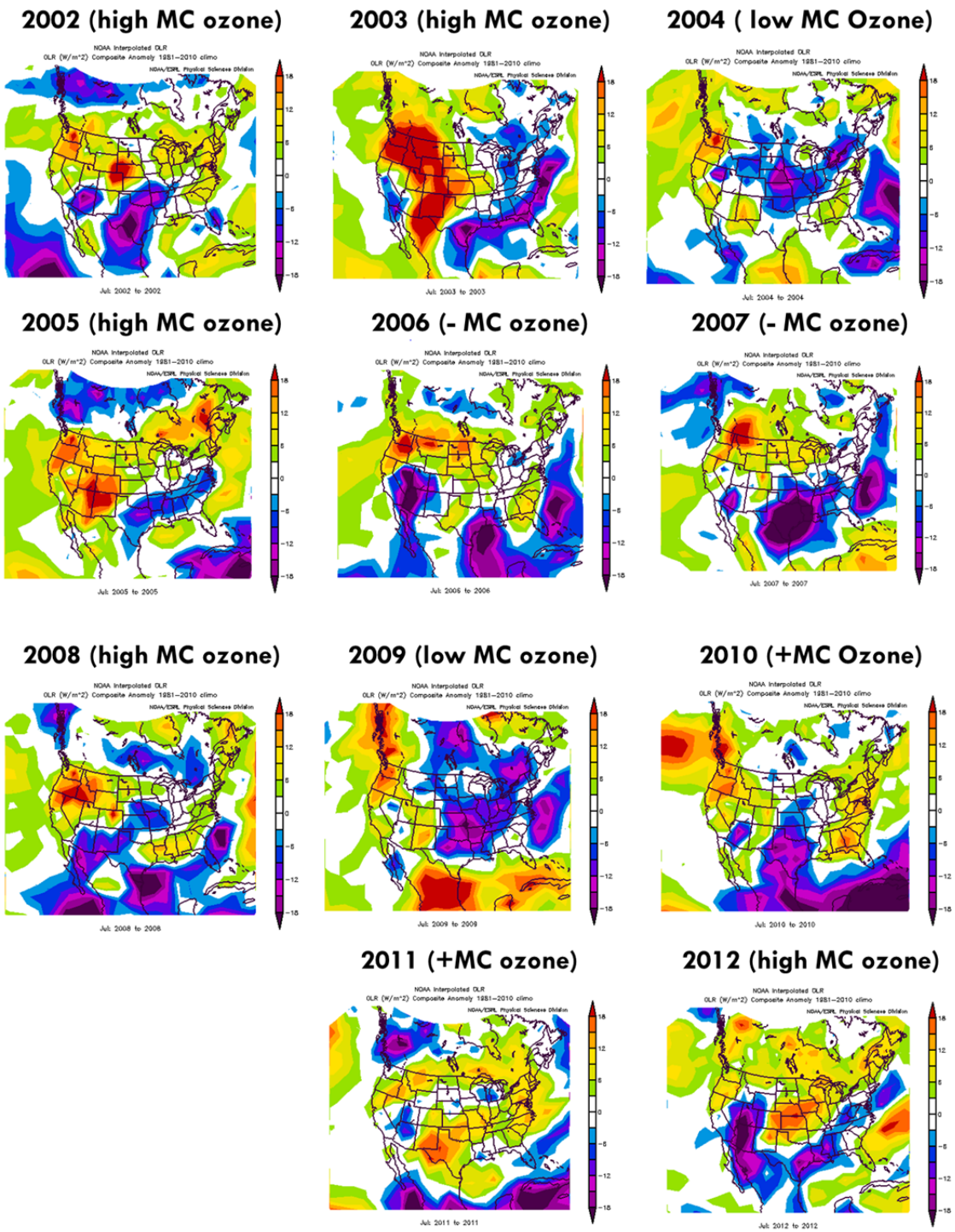

Figure 6-16. July NOAA interpolated OLR Anomaly.

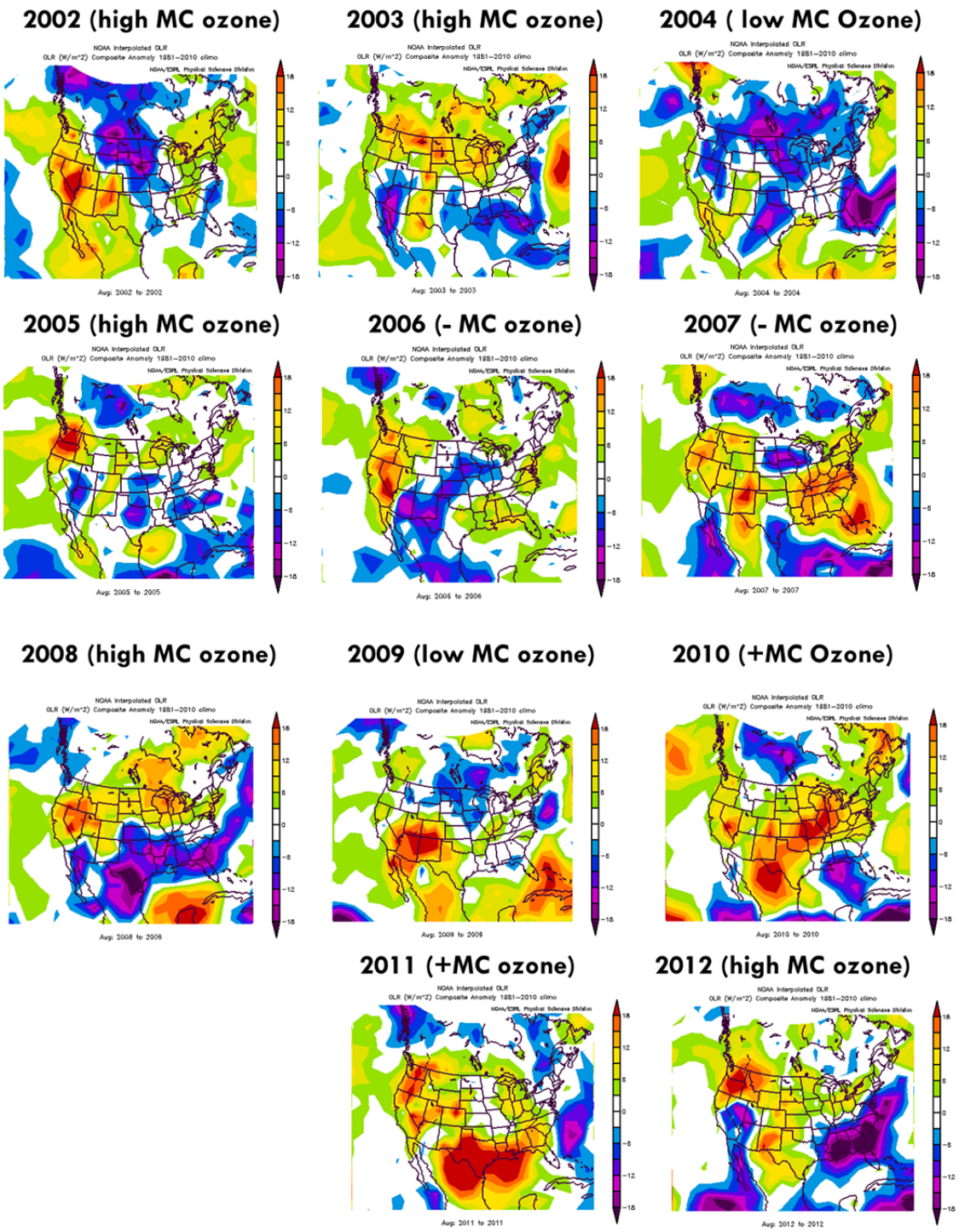

Figure 6-17. August NOAA interpolated OLR Anomaly.

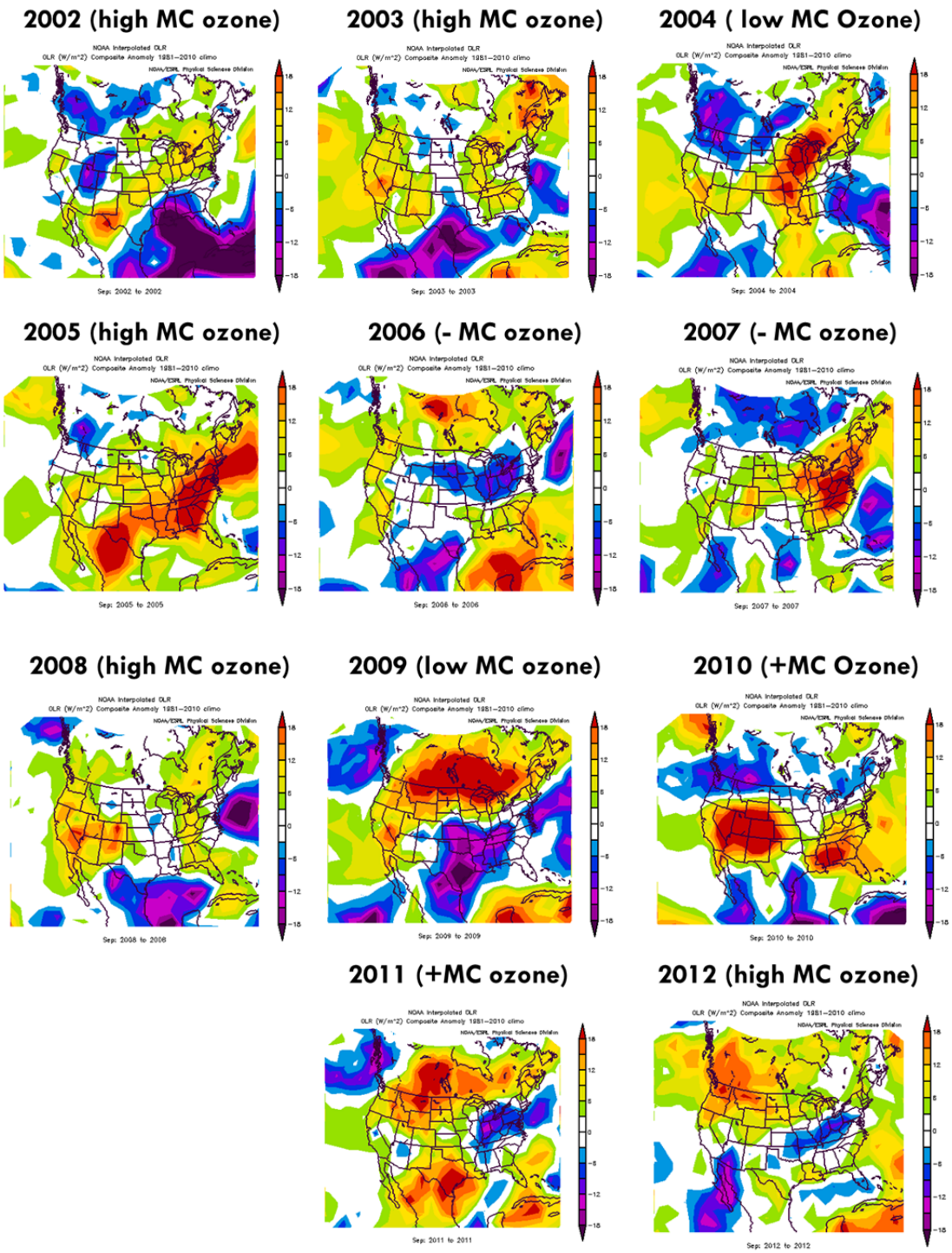

Figure 6-18. September NOAA interpolated OLR Anomaly.

We reviewed a series of NCEP/NCAR reanalysis anomaly fields to determine whether their variability during 2002-2012 is consistent with variability in ozone in Maricopa and nearby states during this period. Fields which did not show patterns consistent with these ozone trends during 2002-2012 were:

- ω(500 mb) anomaly
- 250 mb height anomaly
- 500 mb height anomaly
- 700 mb height anomaly, scalar wind speed anomaly
- 1000-500 mb thickness anomaly
- CPC Soil Moisture anomaly
- NOAA SST anomaly
- Surface air temperature anomaly

Plots of these fields are shown in Appendix B,

6.3.1 Large-Scale Meteorological Analysis Conclusions

Taking averages of large-scale anomaly fields over the ozone season can be problematic because of monsoon effects that appear in July-August. Therefore, we looked at large-scale meteorological anomaly fields for each month over the ozone season. Most fields we examined did not show large-scale variability that correlated well with trends in ozone in Maricopa and Arizona and nearby states. However, the May-June OLR anomaly shows variations consistent with trends in regional ozone from 2008-2012 and these variations were consistent with variations in cloudiness at the Phoenix Sky Harbor Airport. It is possible that for the years 2008-2012, large-scale meteorological factors were important in creating conditions conducive to ozone formation, but in other years (2002-2007), local factors dominated. During 2004, many areas in the southwestern U.S. saw relatively low ozone levels, but the May-June OLR anomaly is not negative over the southwestern U.S. as it was during the low ozone year (2009) during the 2008-2012 period. It is possible that large-scale factors aside from cloudiness caused the widespread decrease in ozone during 2004, or that local factors were more important.

7.0 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The analyses performed in this study found that the 2008-2012 ozone trend observed at Maricopa County monitors is similar to ozone trends measured in other large metropolitan areas in nearby states in the western U.S. This suggests that regional-scale factors were important in determining 2011-2012 ozone levels in Maricopa County.

In Maricopa County, the May-June period preceding the summer monsoon tends to be associated with high ozone and variations in May-June cloudiness during 2008-2012 were consistent with Maricopa ozone trends. Satellite-derived measures of regional cloudiness and local Phoenix cloud cover data showed an unusually large amount of cloud cover in May-June 2009 and an unusually small amount of cloud cover in May-June 2011-2012. May and June were the two months with the largest number of high ozone days in Maricopa during 2008-2012.

Other factors that may have contributed to high ozone levels in 2012 were an unusually large number of high-temperature days in 2012, and more potential impacts from wildfire emissions in 2012 than in 2008-2011. No changes were evident in transport patterns or in the North American background ozone that would indicate that transport played a significant role in rising Maricopa ozone levels in 2011-2012.

Anthropogenic NOx and VOC emissions generally decreased during 2008-2011 in the Maricopa Non-Attainment Area. Modeling of on-road mobile sources using EPA's MOVES model indicated that vehicle emissions declined overall during 2008-2012, but do show an increase in VOC emissions after 2010 due to the use of E10 fuel.

Our evaluation of whether the Maricopa Non-Attainment area is NOx-limited or VOC-limited with respect to ozone formation showed that the suburban monitors to the northeast of the Phoenix urban core are NOx-limited. For these monitors, on-the-books NOx reductions should continue to bring ozone levels down. The Buckeye monitor, located to the southwest of the urban core, is clearly VOC-limited. Analysis of weekday/weekend ozone differences showed that from 2009-2012, monitors in the Phoenix urban core varied together by year between being NOx-limited and VOC-limited. These results indicate that the Phoenix urban area is in a transitional regime between being VOC-limited and NOx-limited with respect to ozone formation. The 2011 VOC/NOx ratio derived from the Maricopa Non-Attainment Area emission inventory indicated that the area was VOC-limited, while the weekday/weekend analysis showed all monitors except Buckeye to be NOx-limited in 2011. The VOC/NOx ratio of the emission inventory may be biased low.

MAG's Maricopa Non-Attainment Area emission inventory data for 2008 and 2011 indicate that NOx reductions have been larger than VOC reductions during 2008-2011. Recent Federal emissions control programs (e.g. reductions in highway and off-road vehicle emissions limits) have been primarily aimed at reducing NOx emissions. Wolff et al. (2013) note that,

nationwide, a larger decline in NOx emissions than VOC emissions has pushed many areas from being VOC-limited to being NOx-limited. We conclude that the Maricopa area is in transition from being VOC-limited to becoming NOx-limited. This means the area may benefit from both NOx and VOC emission controls to reduce ozone in the short term, but that in the long term, NOx emissions controls are the best mechanism for decreasing Maricopa ozone levels.

7.2 Avenues for Further Investigation

On May 9, 2013, MAG and ENVIRON participated in a conference call with Joseph Paul, who carries out ozone air quality forecasts for the ADEQ. ADEQ's analysis of Phoenix high ozone days shows that the following phenomena contribute to high ozone:

- In spring, surface high pressure over the Four Corners region causes easterly flow over the Phoenix area that "locks" ozone in the Valley.
- High ozone at urban core monitors occurs when easterly morning winds persist until afternoon, delaying onset of westerly upslope winds
- Phoenix ozone often increases following convective storms or ahead of 500 mb troughs that migrate westward from Southern California
- Stratosphere-troposphere exchange may play a role in early season ozone events

An approach for further investigation of causes of increased ozone in 2011-2012 would be to analyze 2008-2012 high ozone days by using archived meteorological data to form a composite picture of each type of event listed above. Individual high ozone days could be classified according to which phenomena occurred on that day, if any. The intensity and annual frequency of each type of event would be determined as well as the year-to-year variability of the frequency of each type of event. The correlation of the frequency and intensity of each type of event with Maricopa high ozone would be assessed.

A second avenue for further inquiry is investigation of the possible biogenic emissions "hot spot" near the North Phoenix monitor. This may help address the question of why the North Phoenix monitor has the highest ozone readings of any monitor in Maricopa County. Discussions with MAG indicate that the neighborhood in which the monitor is located is older, and has irrigated lots and more trees than other neighborhoods in the area. Google Earth satellite imagery shows that the region just southeast of the monitor is greener than surrounding areas. It is possible that a local biogenic hot spot could translate to an ozone hot spot.

7.3 Recommendation

We recommend short duration canister sampling at the JLG Supersite during the 6-9 am period to determine the ambient VOC/NOx ratio in the morning when ambient measurements best reflect emissions. The VOC composition should be analyzed to investigate the contributions of

on-road mobile evaporative emissions and other sources. The canister VOC samples should be analyzed for ethanol, if possible, to quantify the contribution of ethanol in gasoline.

8.0 REFERENCES

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APPENDIX A

Analysis of Wildfires: 2008-2012

Appendix A. Analysis of Wildfires: 2008-2012

We evaluated wildfire activity during 2008-2012 to determine whether Interannual changes in wildfire activity could have contributed to 2008-2012 ozone trends at Maricopa monitors. On all days during 2008-2012 when a Maricopa monitor had MDA8>75 ppb, we plotted the FINN fire locations in Arizona and surrounding states. For some days, we include plots of the Hazard Mapping System (HMS) Fire and Smoke Analysis Product. These plots show satellite fire and smoke plume detections. The HMS product blends data from the GOES Imager, the AVHRR instrument, and MODIS. Smoke plumes that are detected by the satellites are outlined by an analyst. Current HMS images are available from http://www.ospo.noaa.gov/Products/land/fire.html. Archived images for the time period of interest were not available, so images were taken from the University of Maryland's U.S. Air Quality Smog Blog at http://alg.umbc.edu/usaq/.

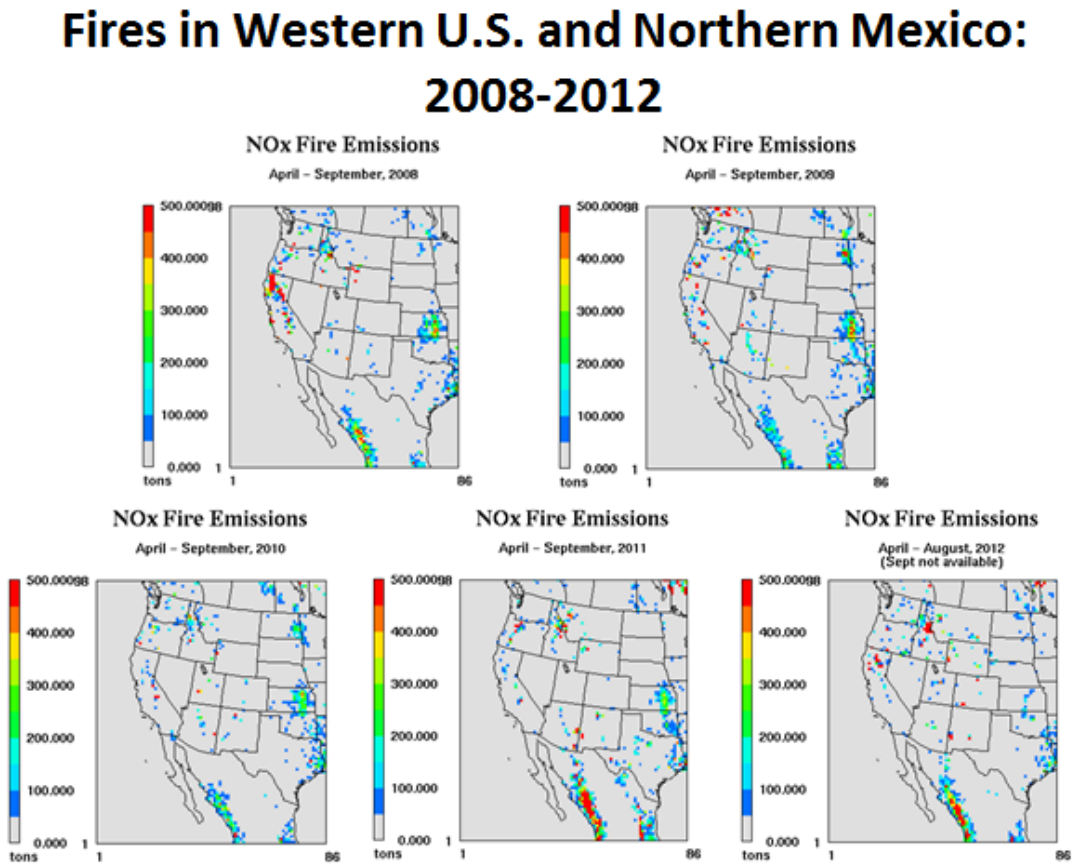
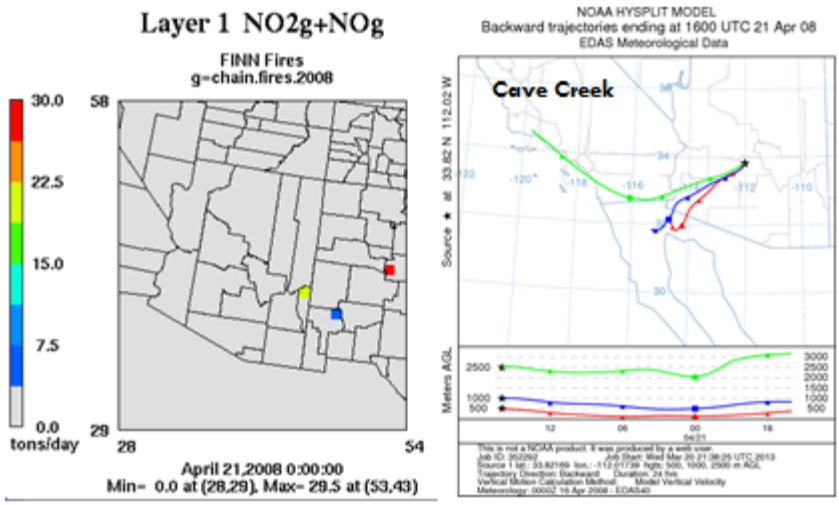
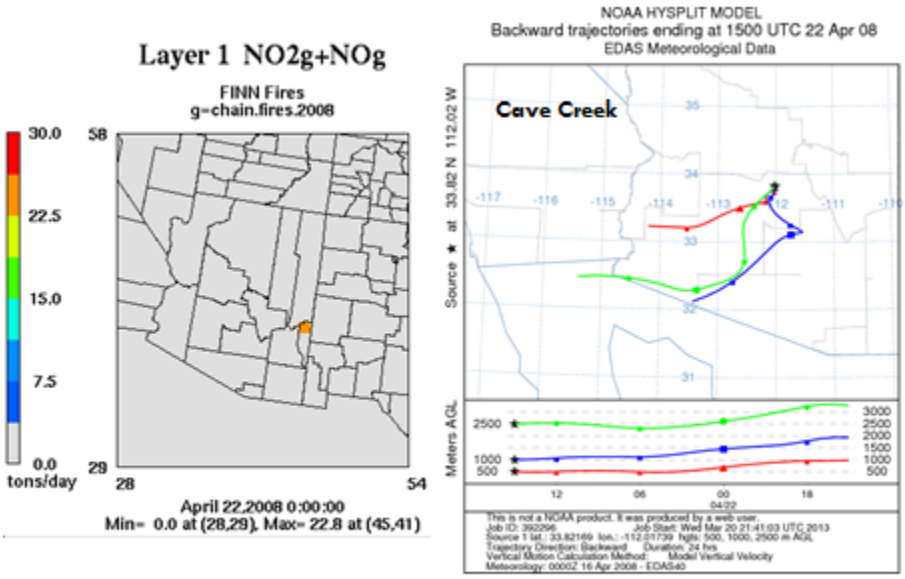


Figure A-1. Overview of fire activity in the western U.S. 2008-2012.



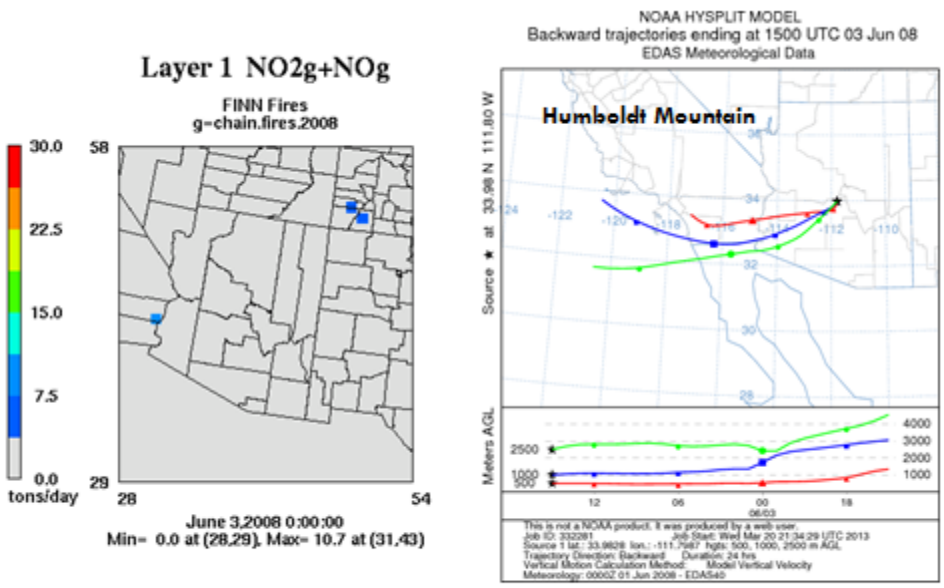
- Back trajectory indicates not a fire impact

Figure A-2. April 21, 2008.



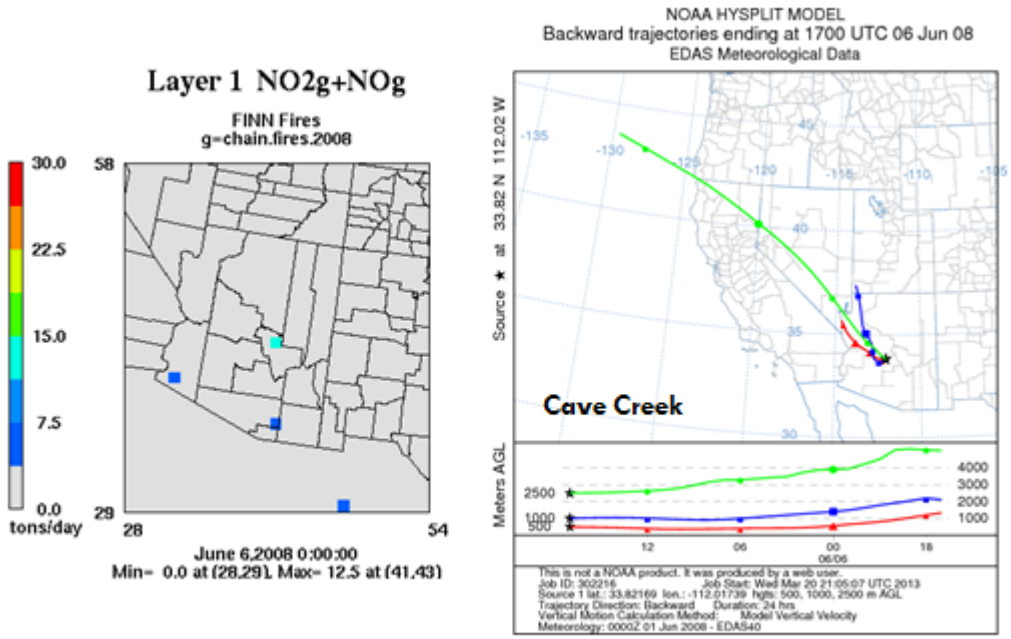
- Back trajectory indicates not a fire impact

Figure A-3. April 22, 2008.



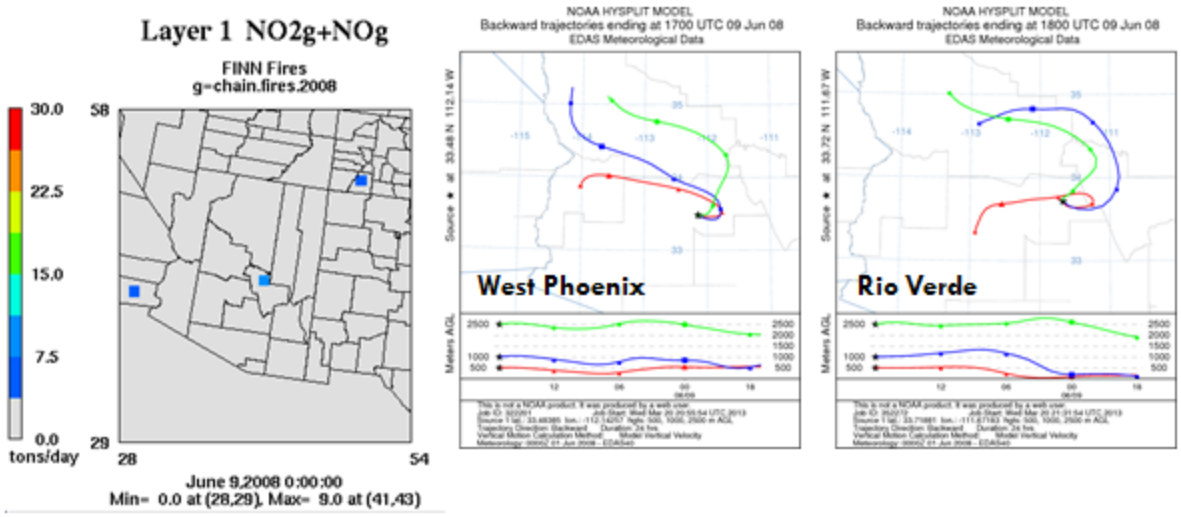
- Possible fire impact, but Phoenix urban plume likely a larger contributor

Figure A-4. June 3, 2008.



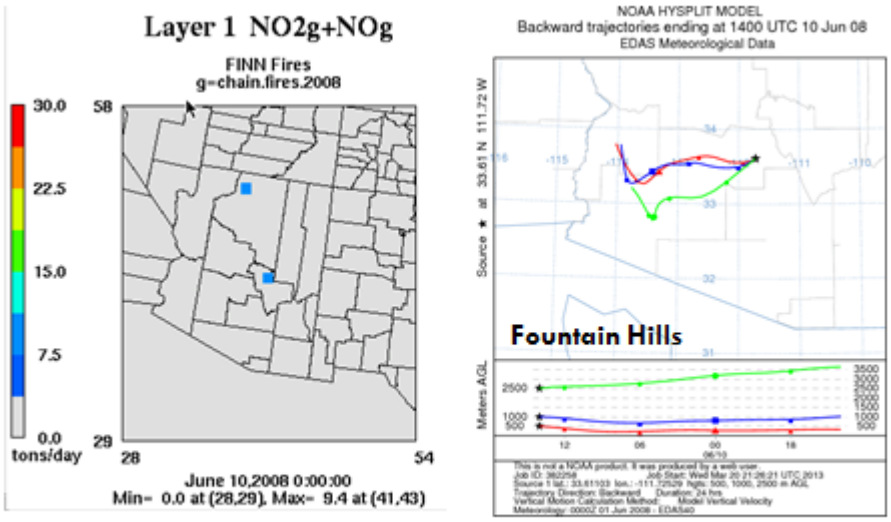
- Back trajectory indicates not a fire impact

Figure A-5. June 6, 2008.



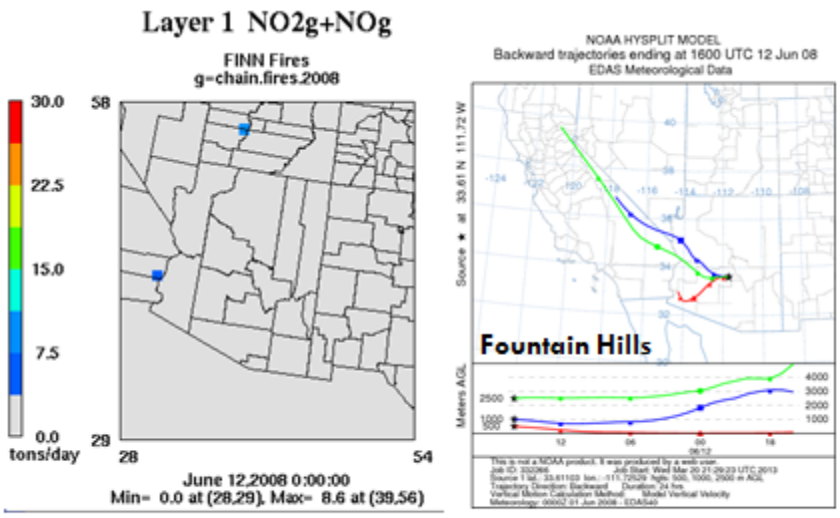
- Possible fire impact at Rio Verde

Figure A-6. June 9, 2008.



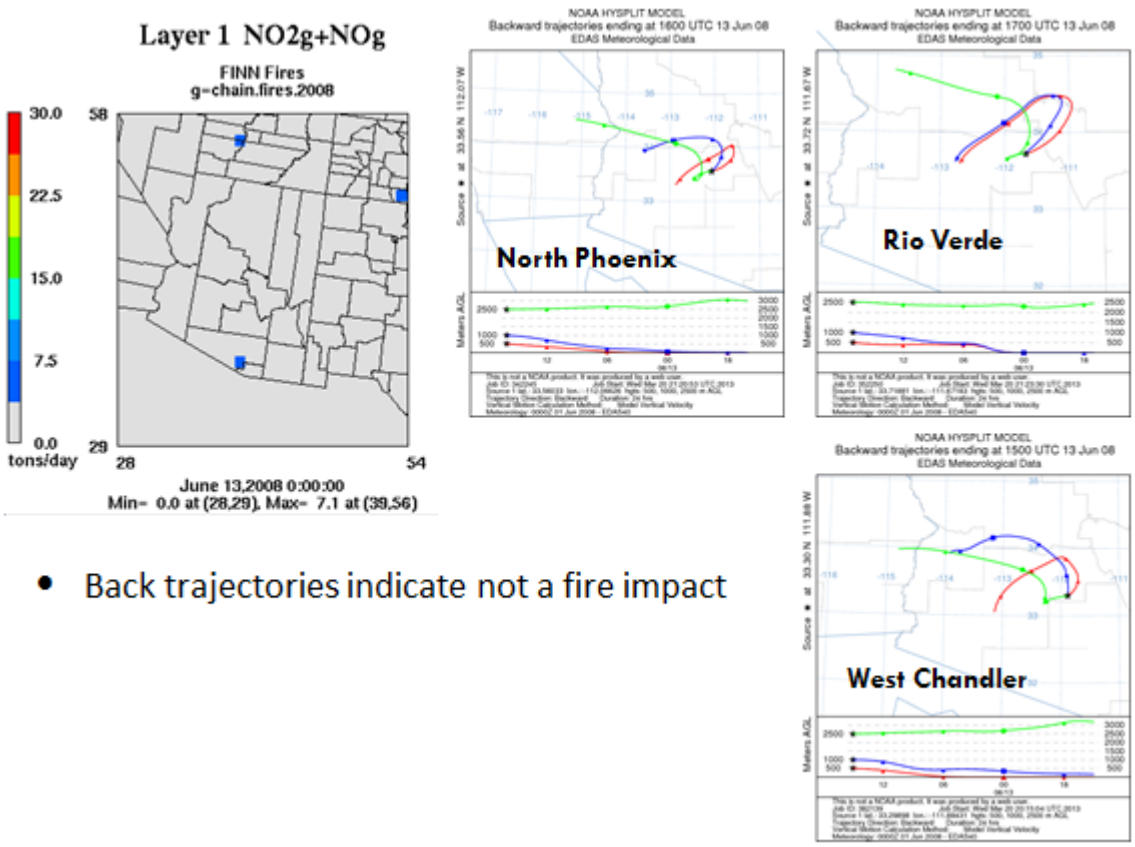
- Back trajectories indicate not a fire impact

Figure A-7. June 10, 2008.



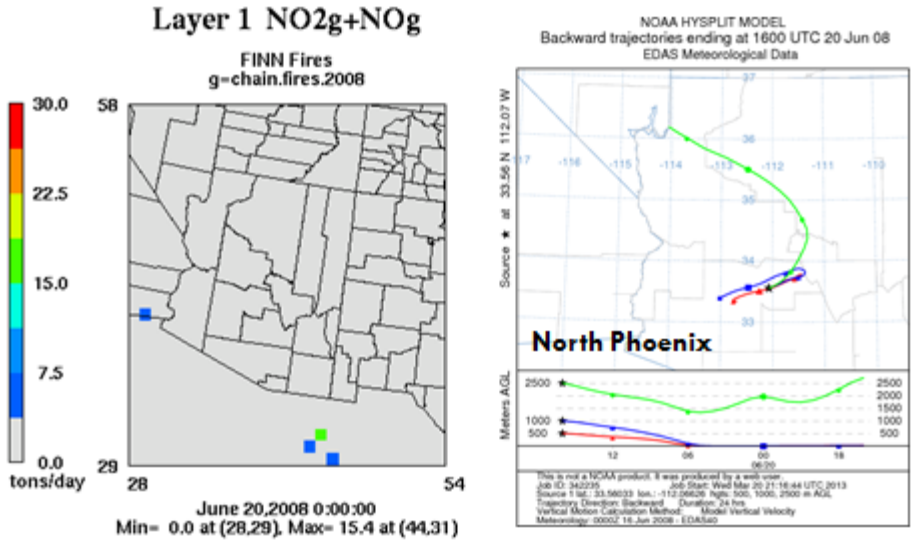
- Back trajectories indicate not a fire impact

Figure A-8. June 12, 2008.



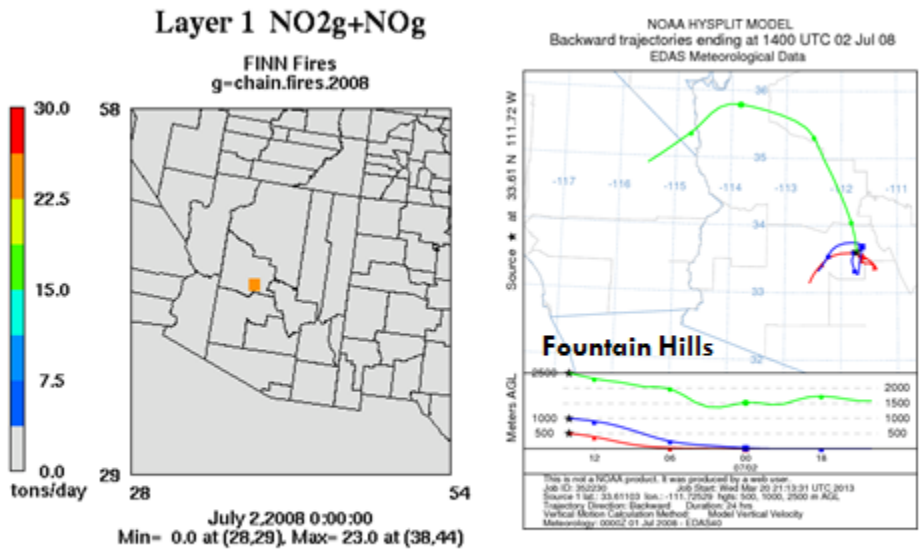
- Back trajectories indicate not a fire impact

Figure A-9. June 13, 2008.



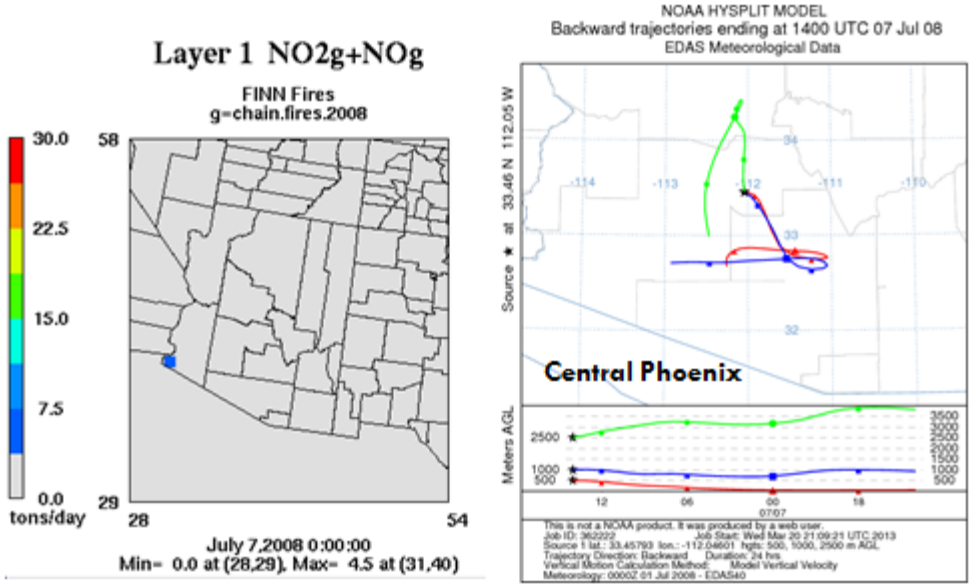
- Back trajectories indicate not a fire impact

Figure A-10. June 20, 2008.



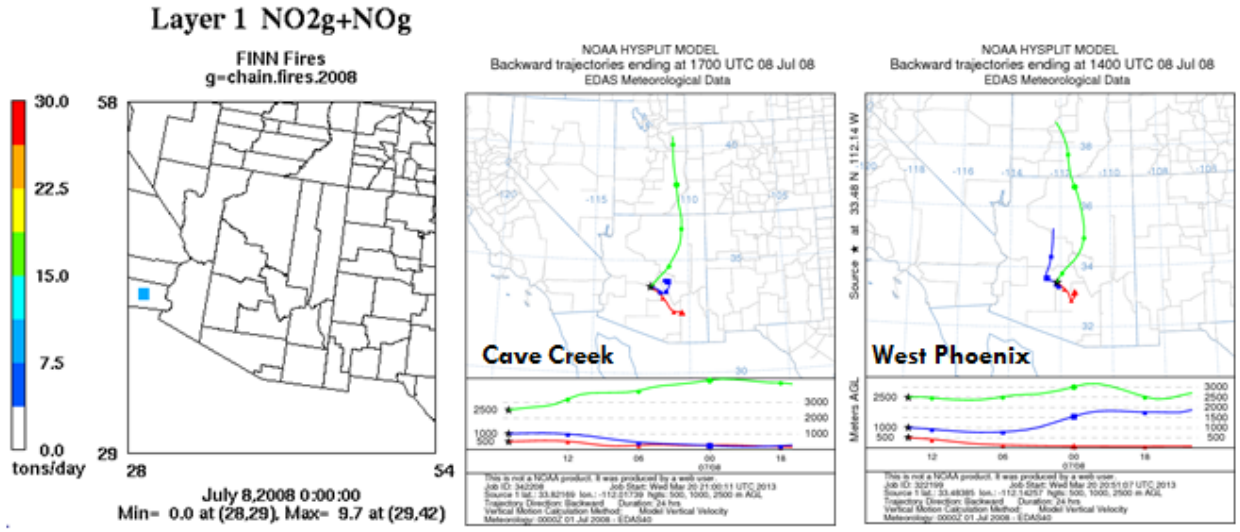
- Back trajectories indicate possible fires impact

Figure A-11. July 2, 2008.



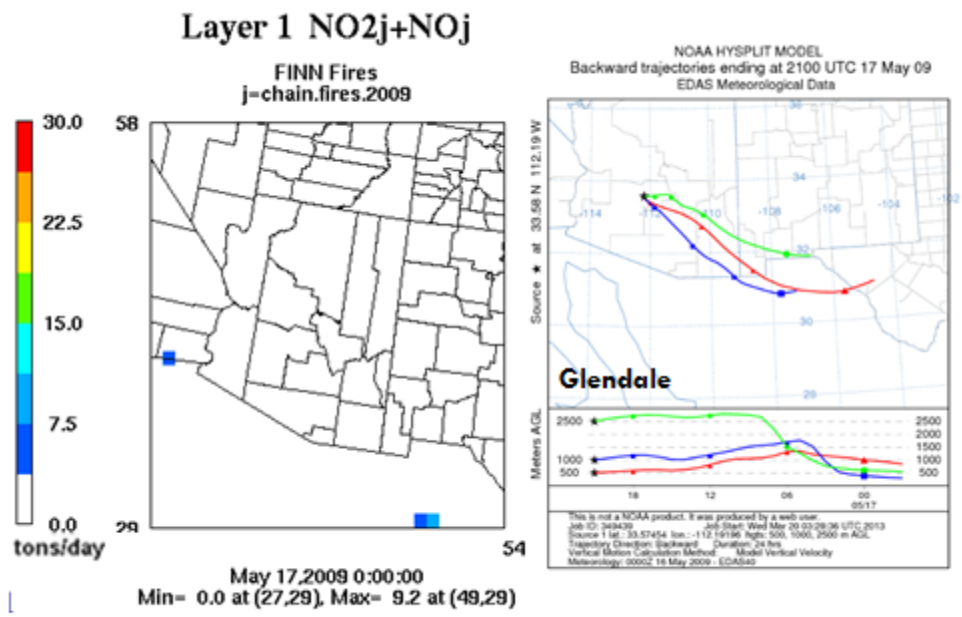
- Back trajectories indicate not a fire impact

Figure A-12. July 7, 2008.



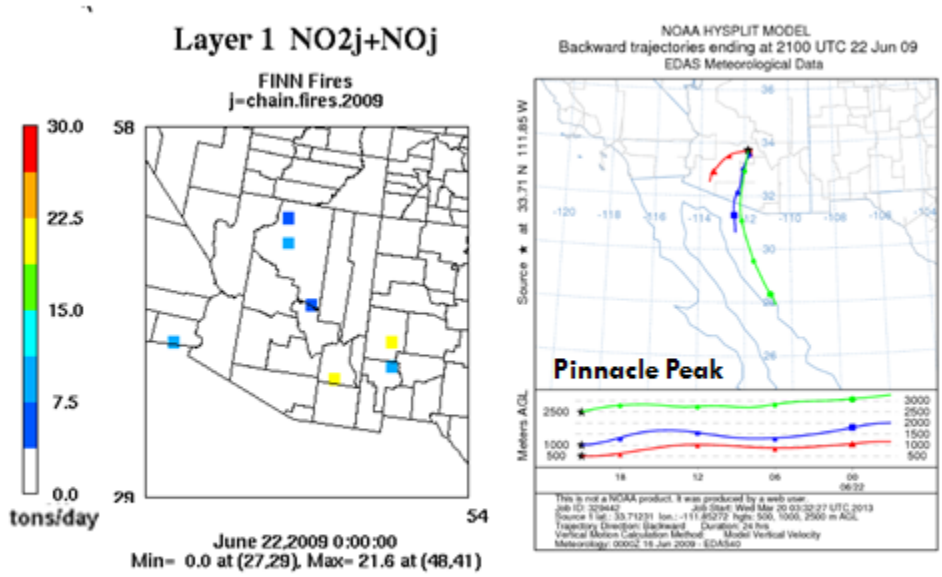
- Back trajectories indicate not a fire impact

Figure A-13. July 8, 2008.



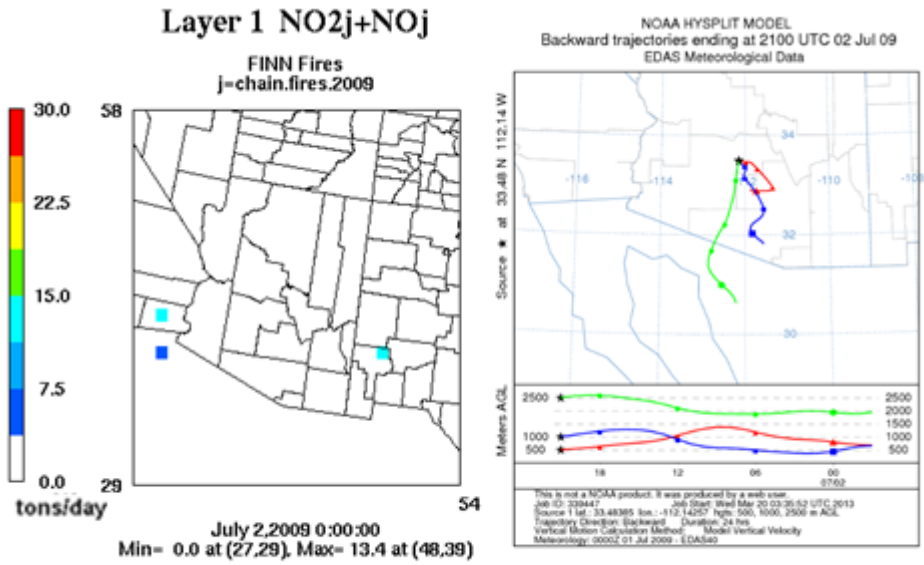
- Back trajectories indicate not a fire impact

Figure A-14. May 17, 2009.



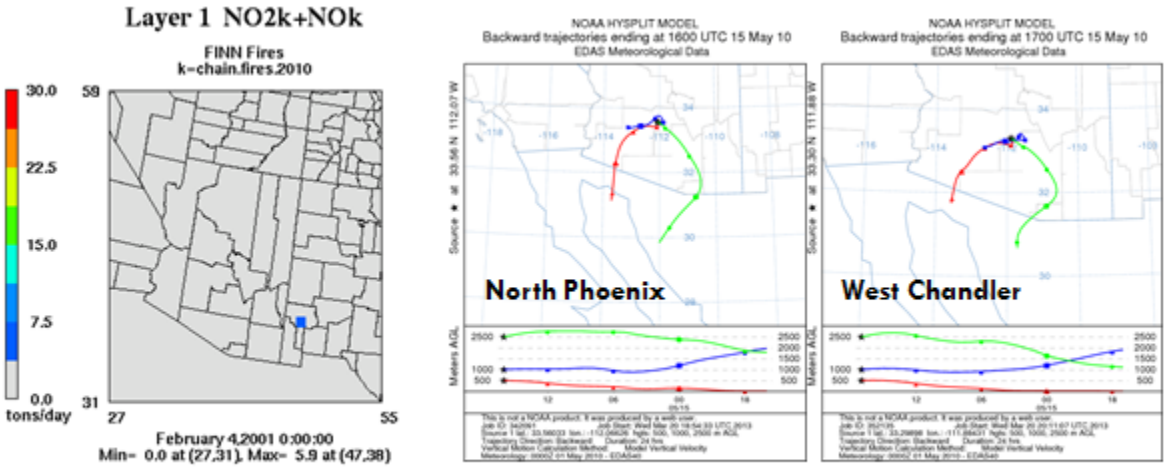
- Back trajectories indicate not a fire impact

Figure A-15. June 22, 2009.



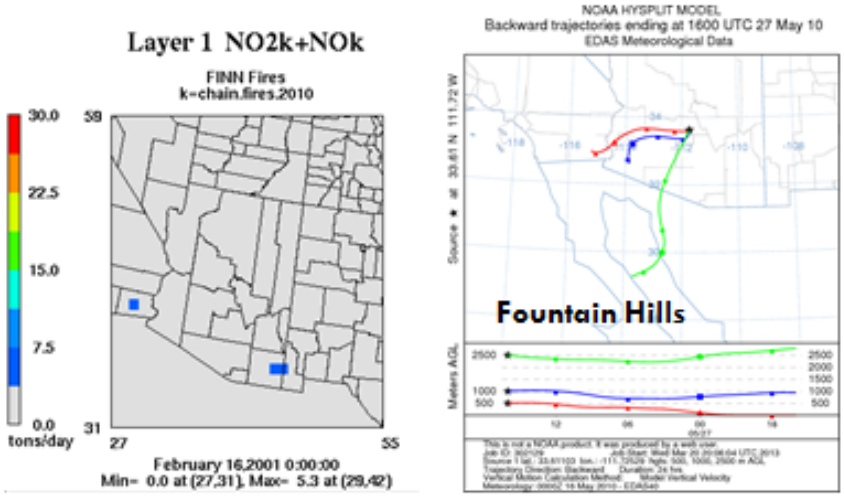
- Back trajectories indicate not a fire impact

Figure A-16. July 2, 2009.



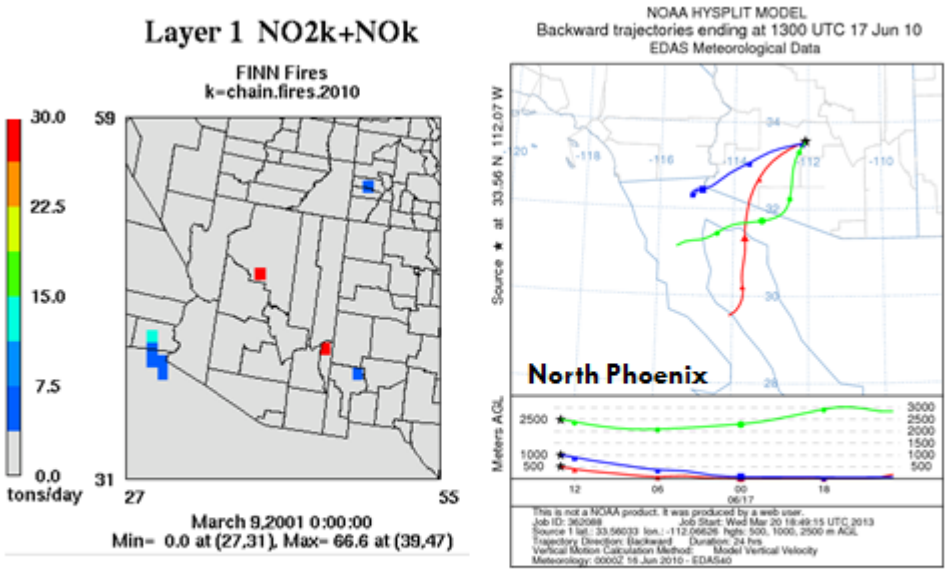
- Back trajectories indicate not a fire impact

Figure A-17. May 15, 2010.



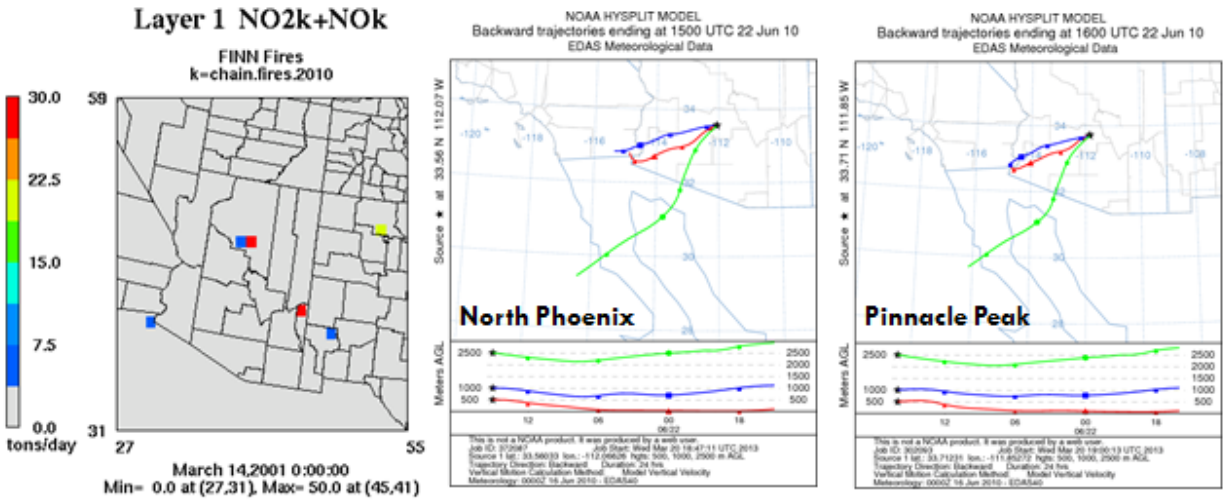
- Possible fire impact, but fire is likely a far smaller contributor than the Phoenix urban plume

Figure A-18. May 27, 2010.



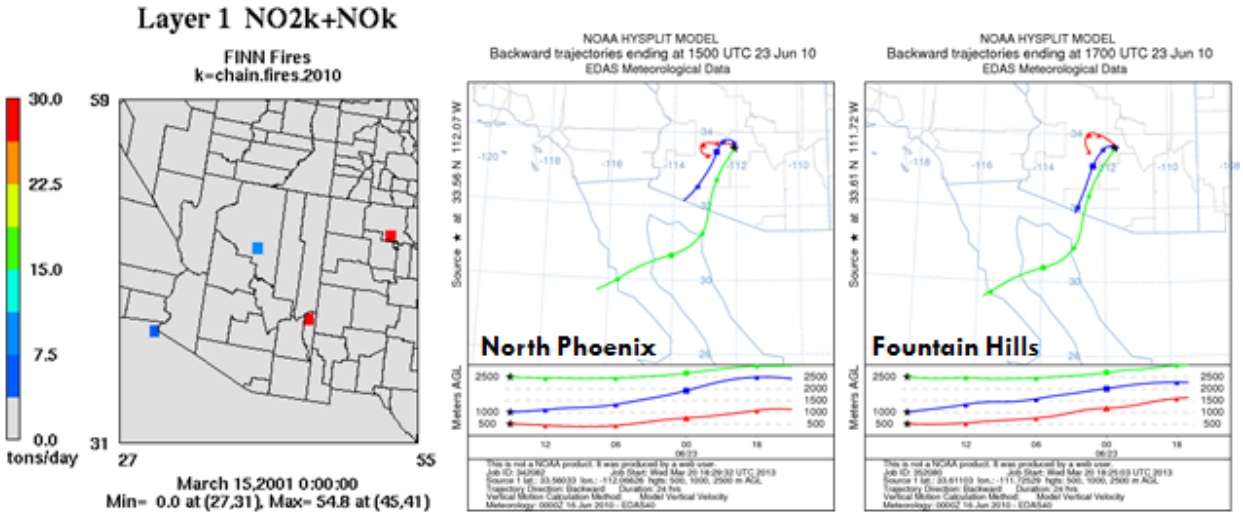
- Possible Mexican fires impact, but Phoenix urban plume likely contributes more to North Phoenix ozone

Figure A-19. June 17, 2010.



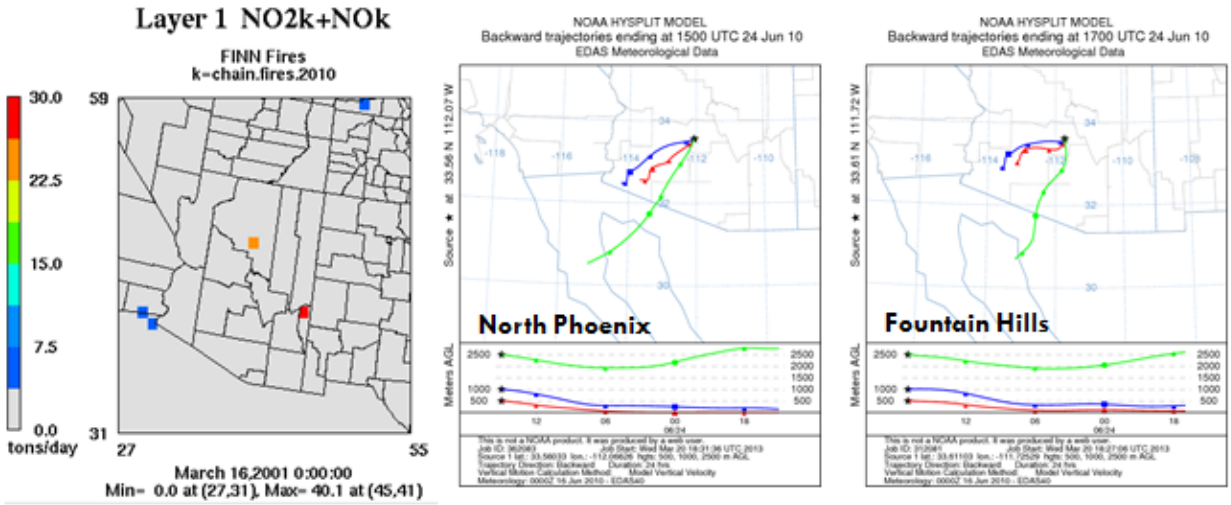
- Back trajectories indicate not a fire impact

Figure A-20. June 22, 2010.



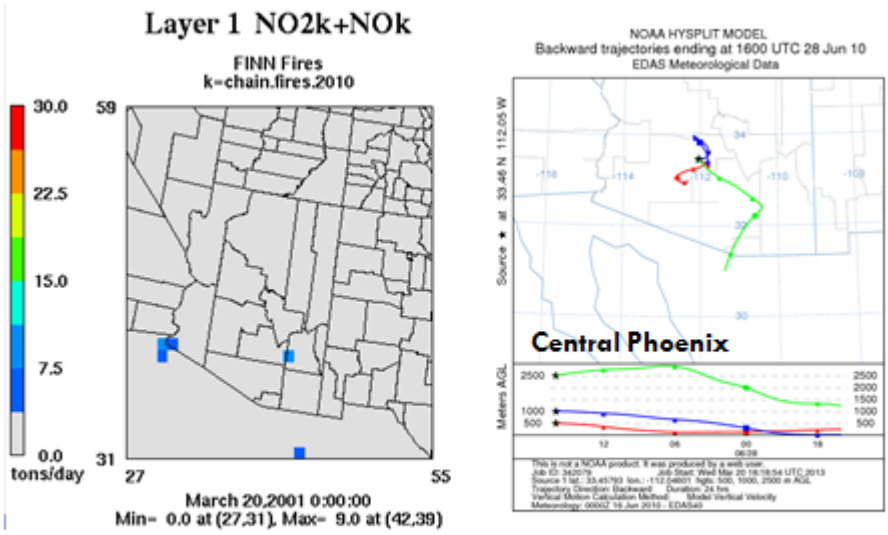
- Back trajectories indicate not a fire impact

Figure A-21. June 23, 2010.



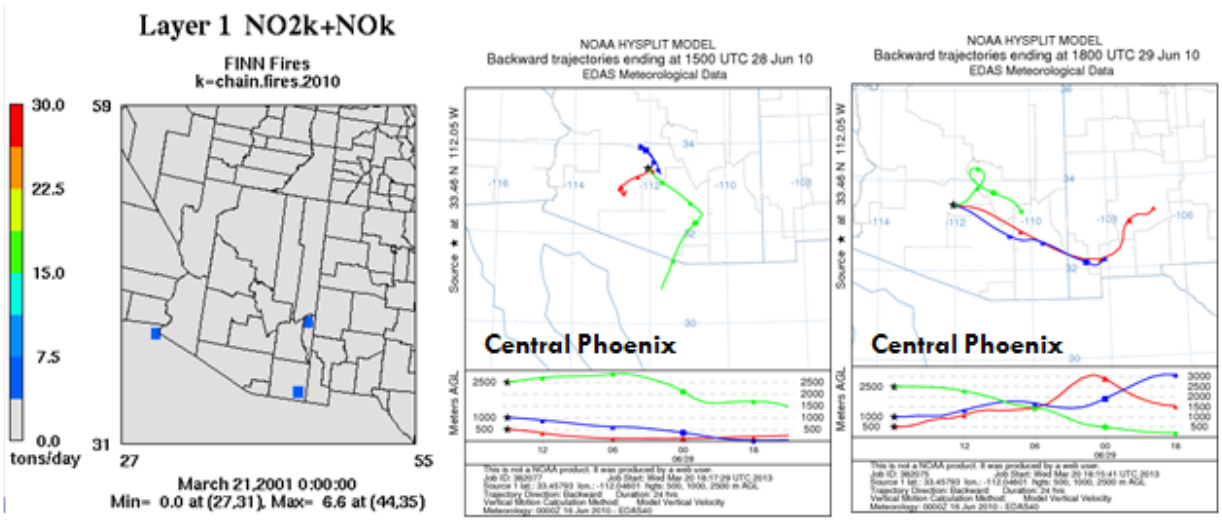
- Back trajectories indicate not a fire impact

Figure A-22. June 24, 2010.



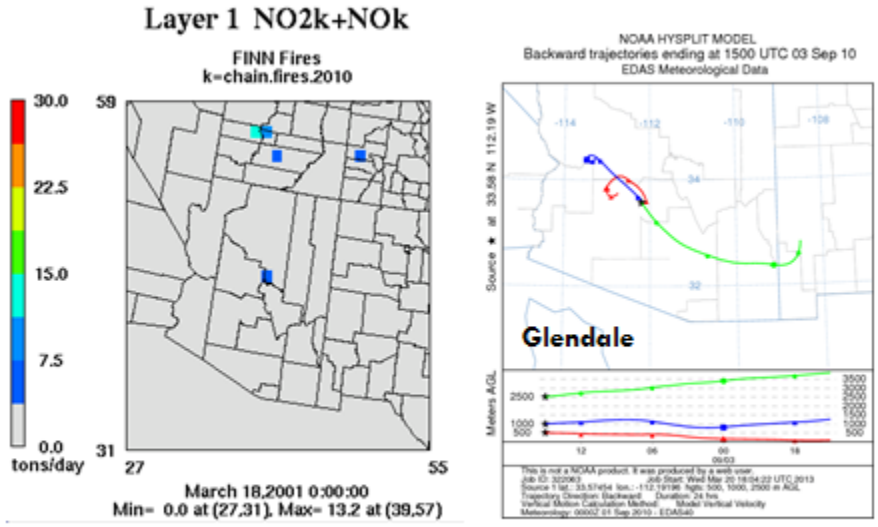
- Possible fire impact

Figure A-23. June 28, 2010.



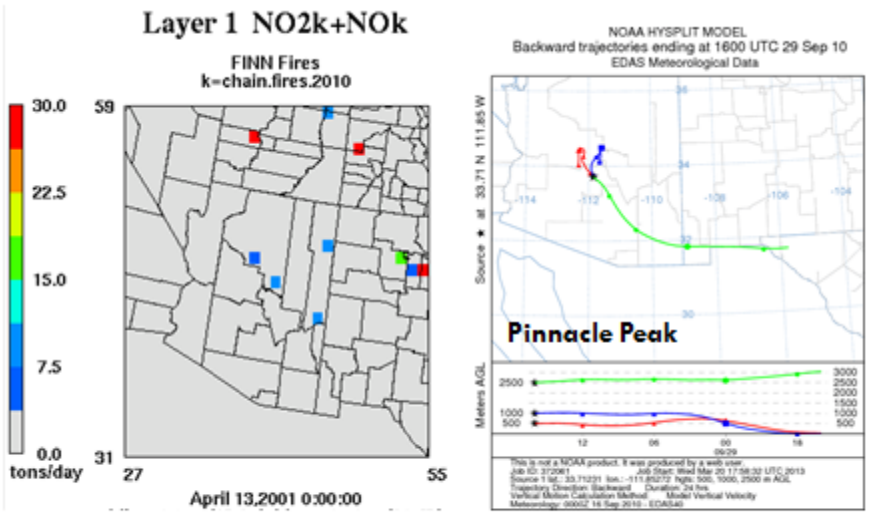
- Back trajectories indicate not a fire impact

Figure A-24. June 29, 2010.



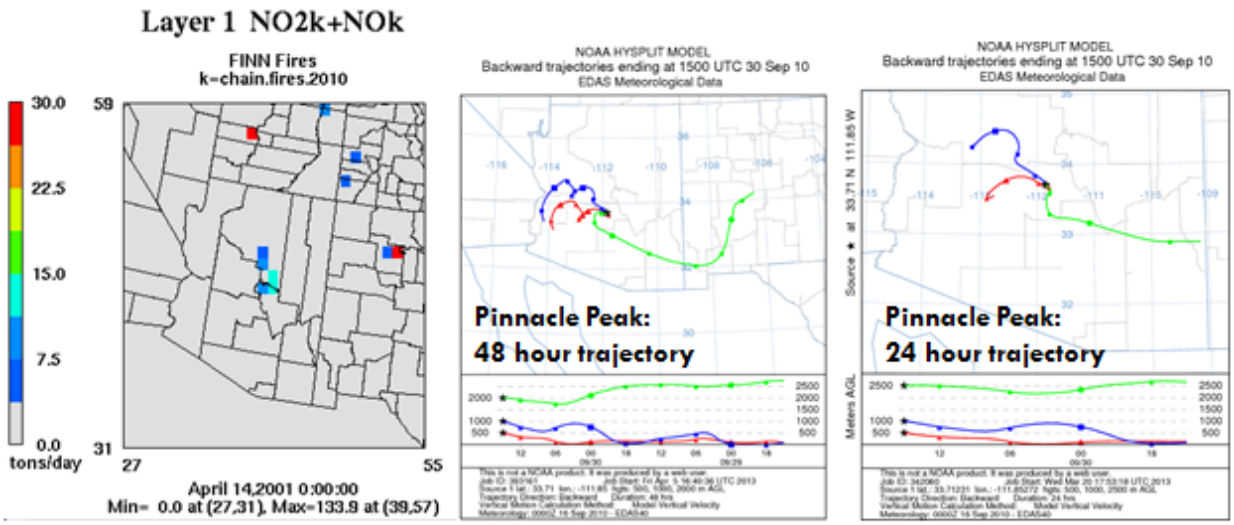
- Back trajectories indicate not a fire impact

Figure A-25. September 3, 2010.



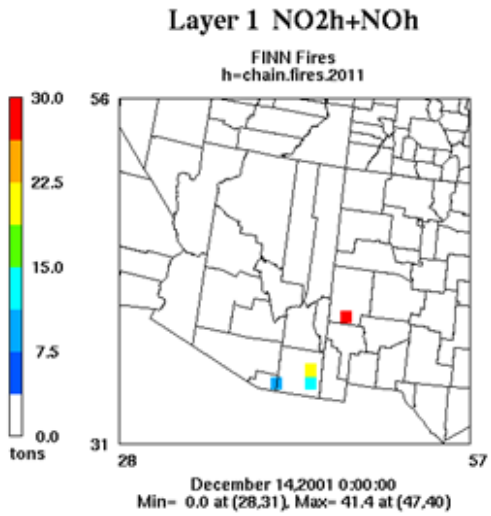
- Possible fire impact
- Near-surface air is stagnant

Figure A-26. September 29, 2010.



- Air is stagnant
- Back trajectories do not suggest impact

Figure A-27. September 30, 2010.



- Blue Point, Cave Creek, Humboldt Mountain and Rio Verde exceed
- Not a fire impact, back trajectories extend over the Phoenix metro area and toward CA

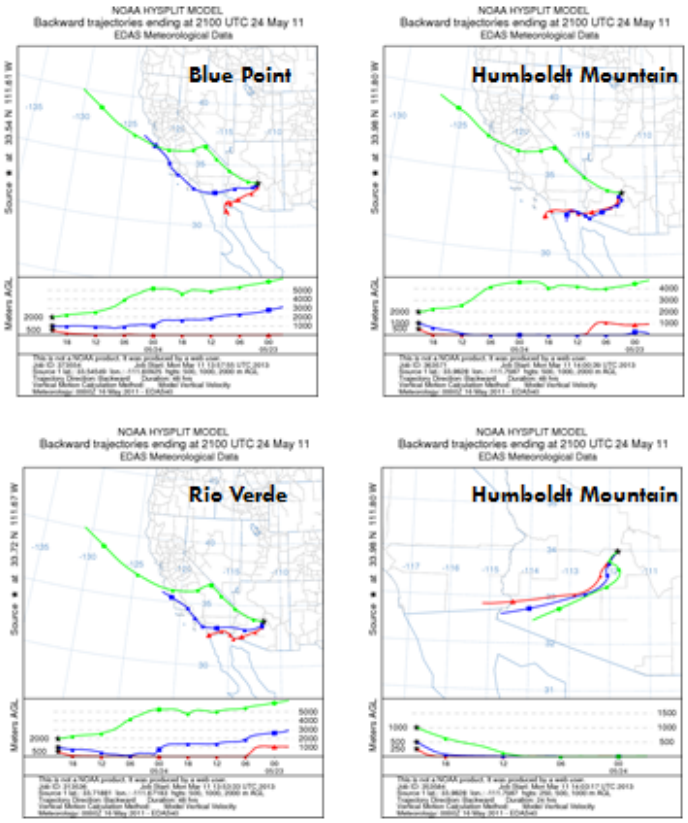
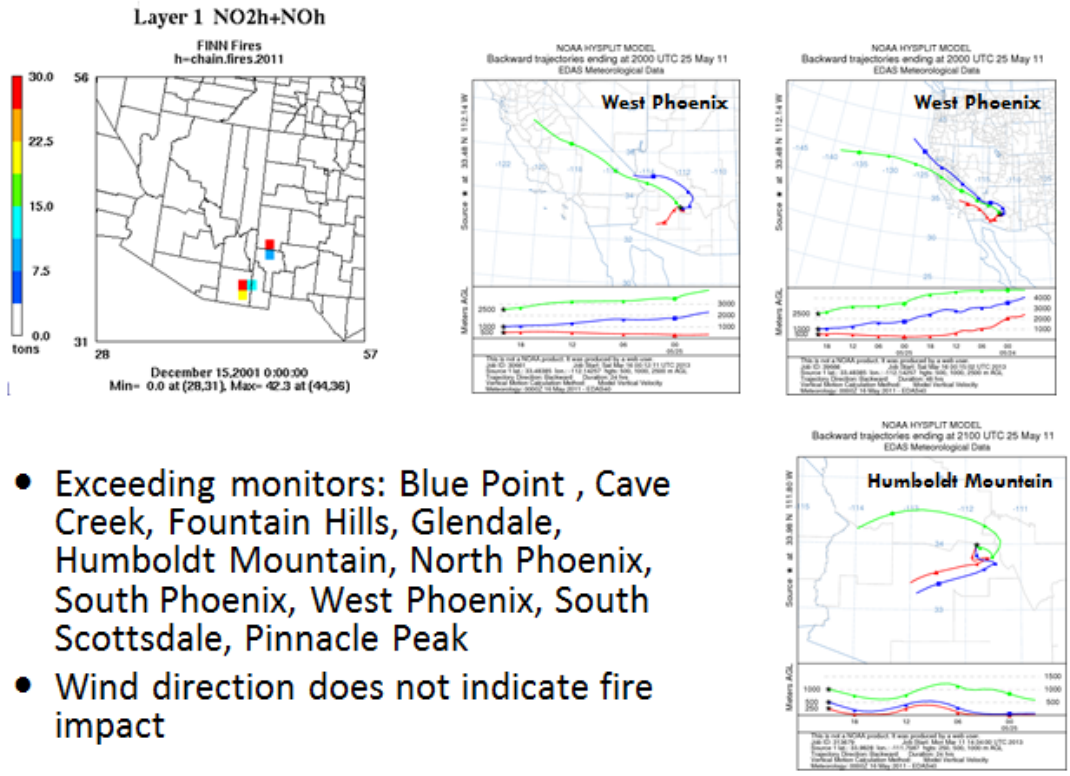
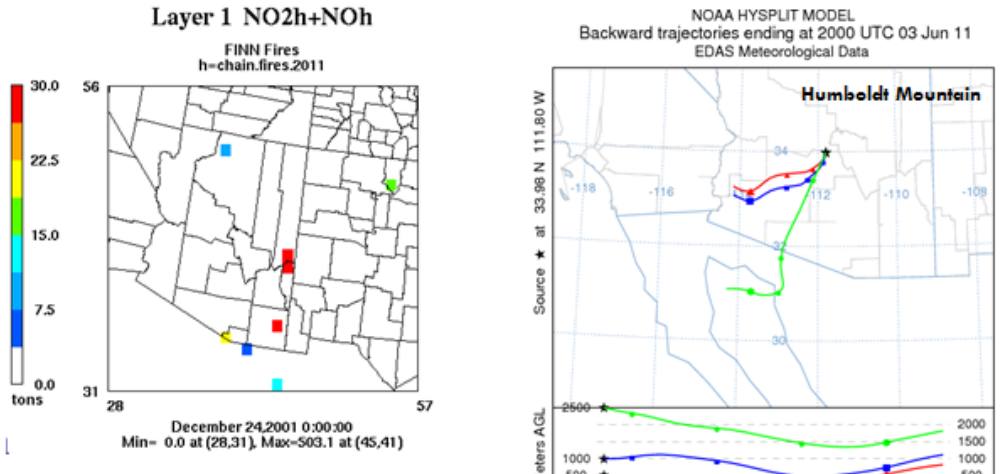


Figure A-28. May 24, 2011.



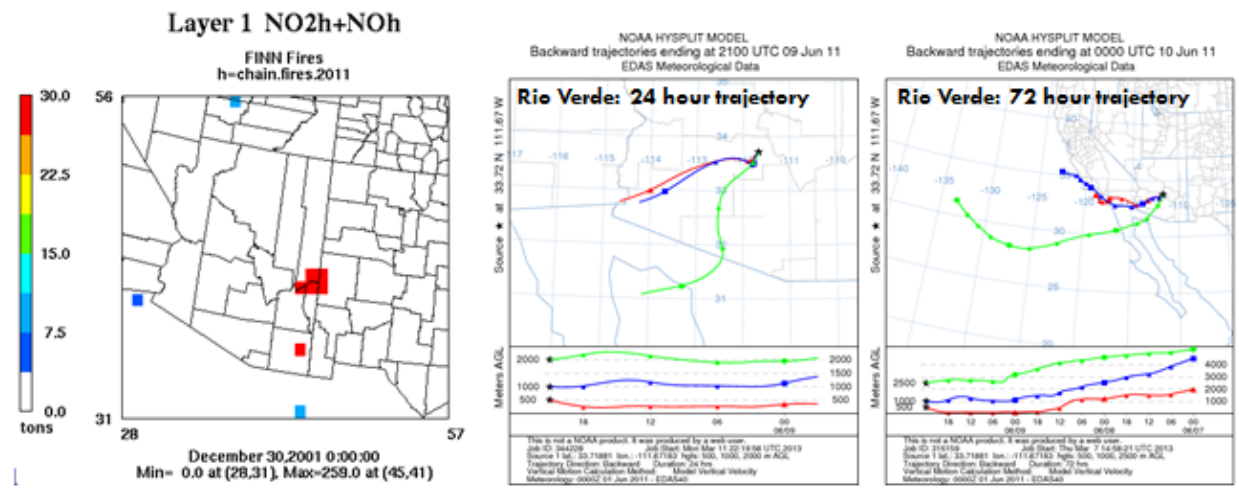
- Exceeding monitors: Blue Point , Cave Creek, Fountain Hills, Glendale, Humboldt Mountain, North Phoenix, South Phoenix, West Phoenix, South Scottsdale, Pinnacle Peak
- Wind direction does not indicate fire impact

Figure A-29. May 25, 2011.



- Humboldt Mountain; wind direction does not indicate a fire impact

Figure A-30. Figure 8 30. June 3, 2011.



Exceeding monitors:

Blue Point	Cave Creek	Central Phoenix	Fountain Hills	Glendale	Humboldt Mountain	North Phoenix	Pinnacle Peak	Rio Verde	South Phoenix	South Scottsdale	Tempe	West Chandler	West Phoenix

- Showing June 8 fires because there are no fires on June 9-suspect that fire complex was obscured from satellite because fires appear there on June 8 and June 10
- Winds blowing plume east away from Phoenix, not a fire impact

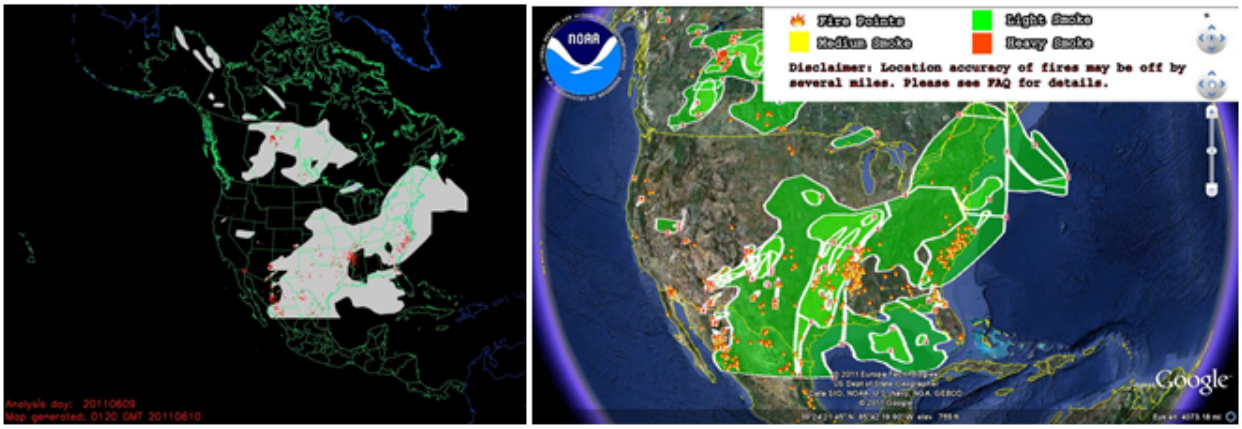
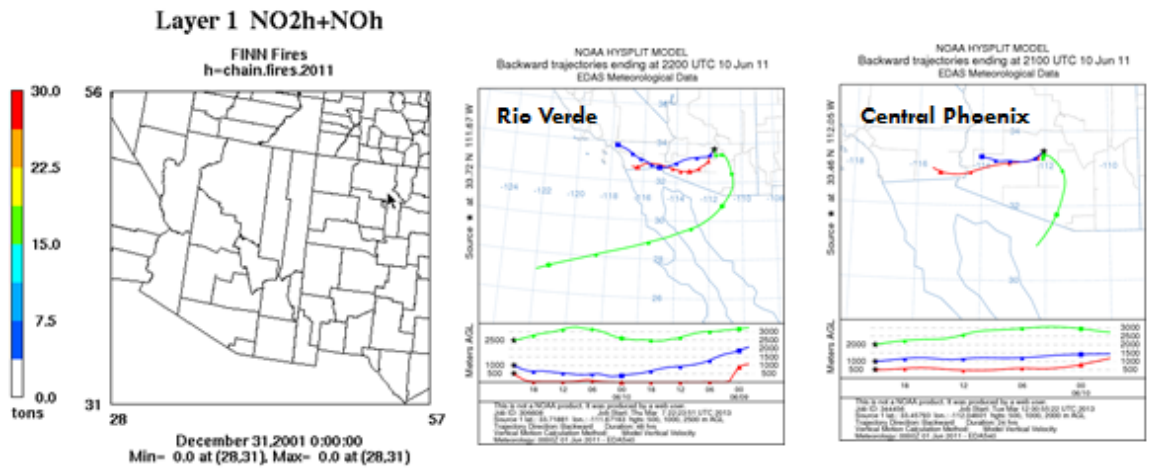


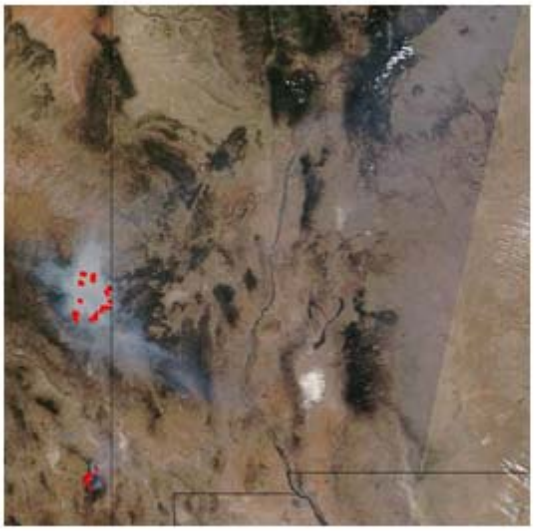
Figure A-31. June 9, 2011. Lower panels: Images obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).



Exceeding monitors

Blue Point	Cave Creek	Central Phoenix	Fountain Hills	Humboldt Mountain	North Phoenix	Pinnacle Peak	Rio Verde	South Phoenix	South Scottsdale		West Phoenix

- Fires obscured from satellite used to derive FINN data
- Other satellite data (below) indicates fires still present near Arizona/New Mexico border
- Wind direction indicates no fire impacts



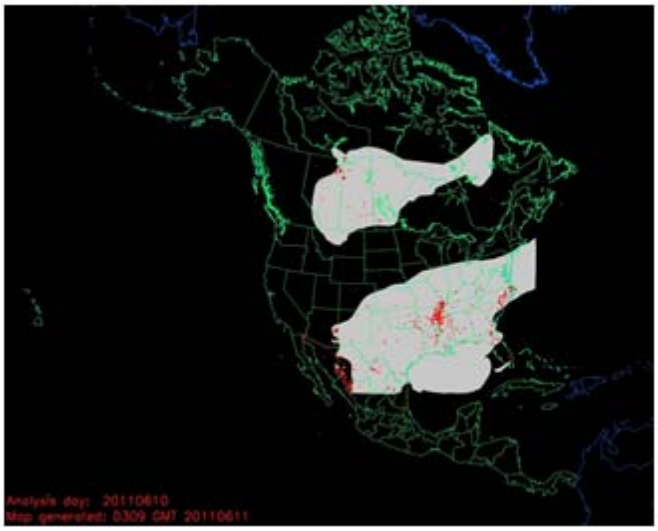
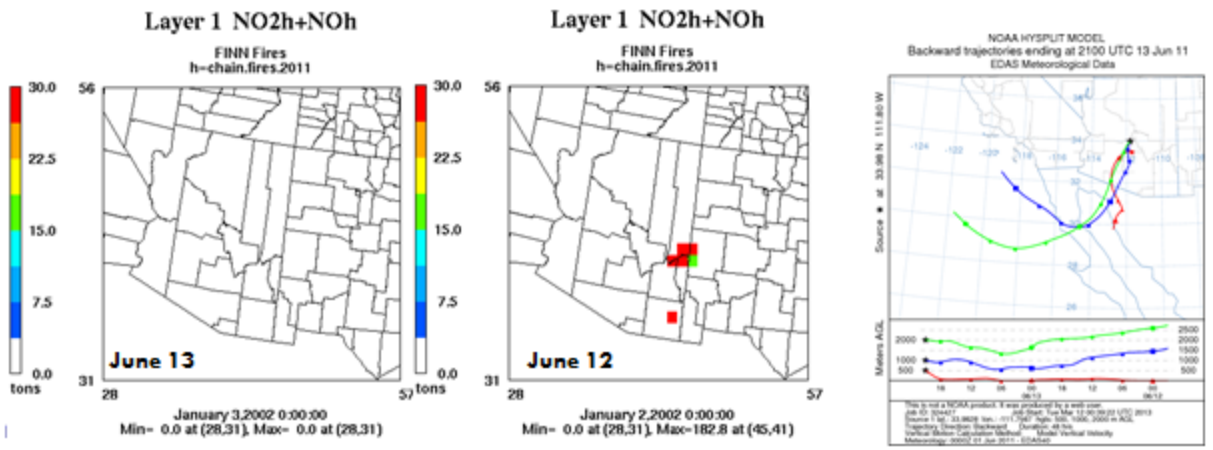


Figure A-32. June 10, 2011. Lower panels: Images obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).



- Humboldt Mountain
- Wind direction indicates not a fire impact

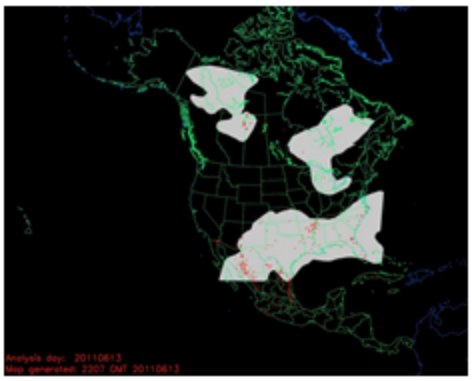
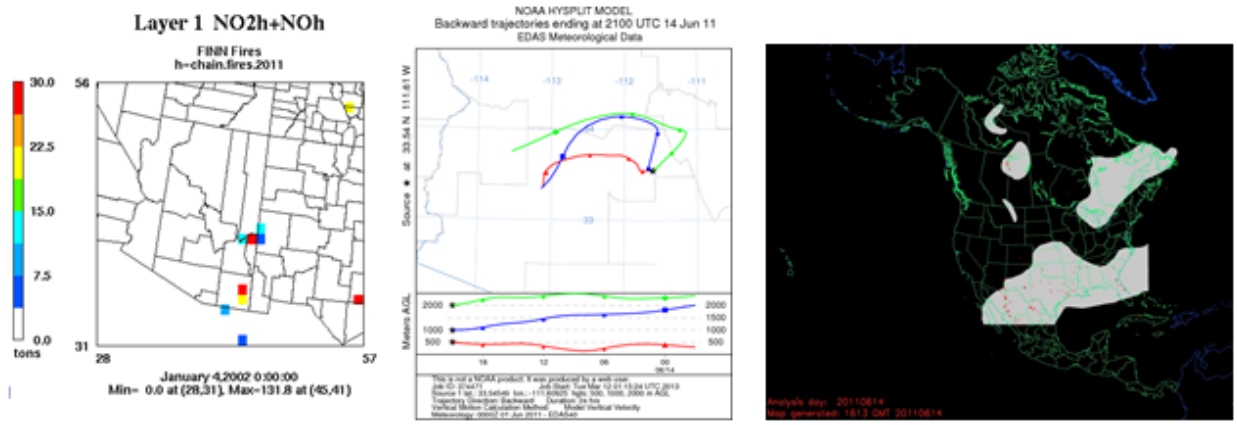


Figure A-33. June 13, 2011. Lower right hand panel: Image obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).



- Blue Point is only exceeding
- Stagnant air, not a fire impact
- Wallow fire still burning, may be obscured from satellite

Figure A-34. June 14, 2011. Right hand panel: Image obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).

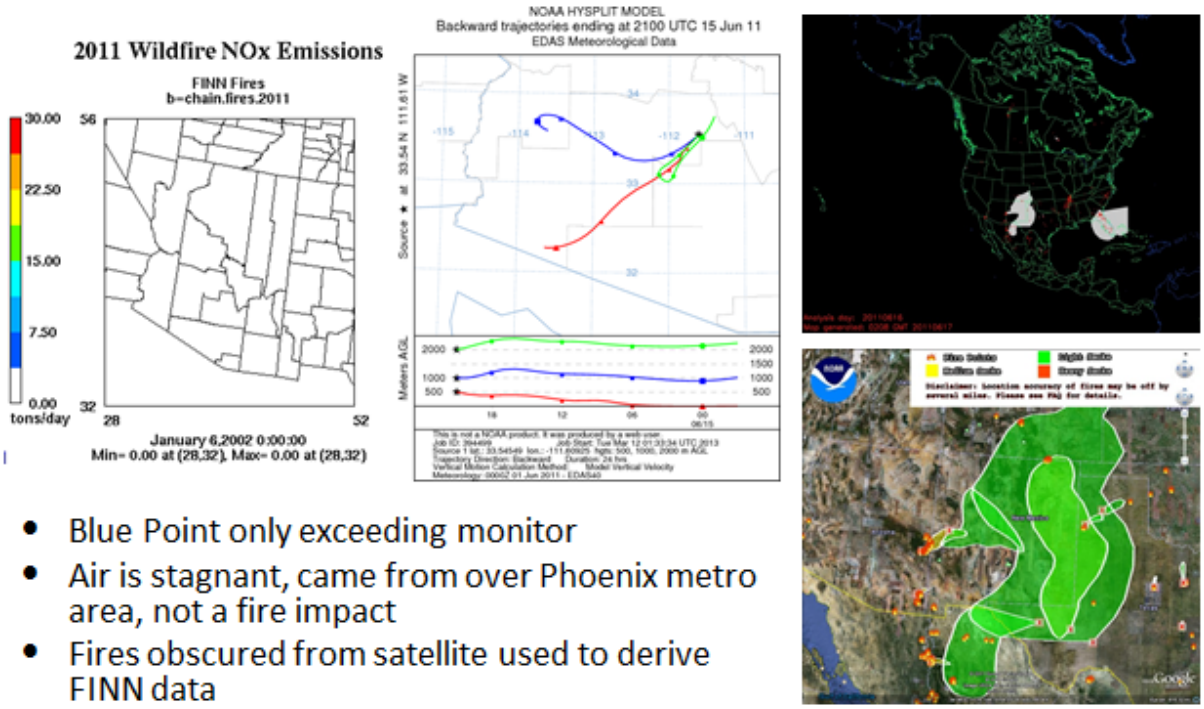


Figure A-35. June 15, 2011. Right hand panels: Images obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).

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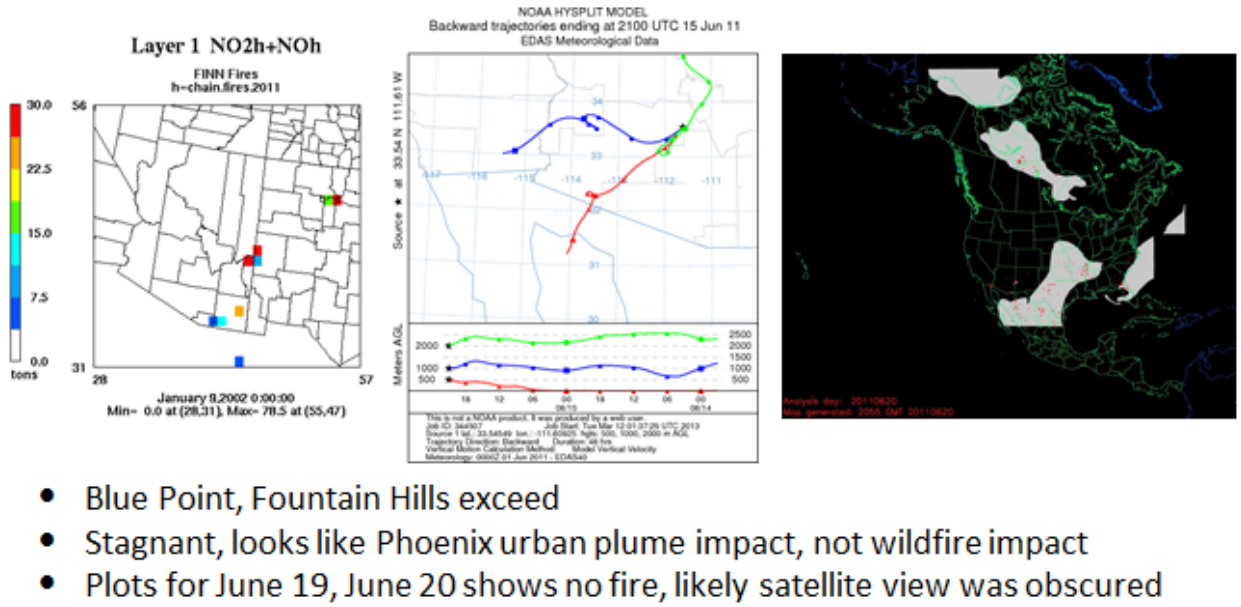
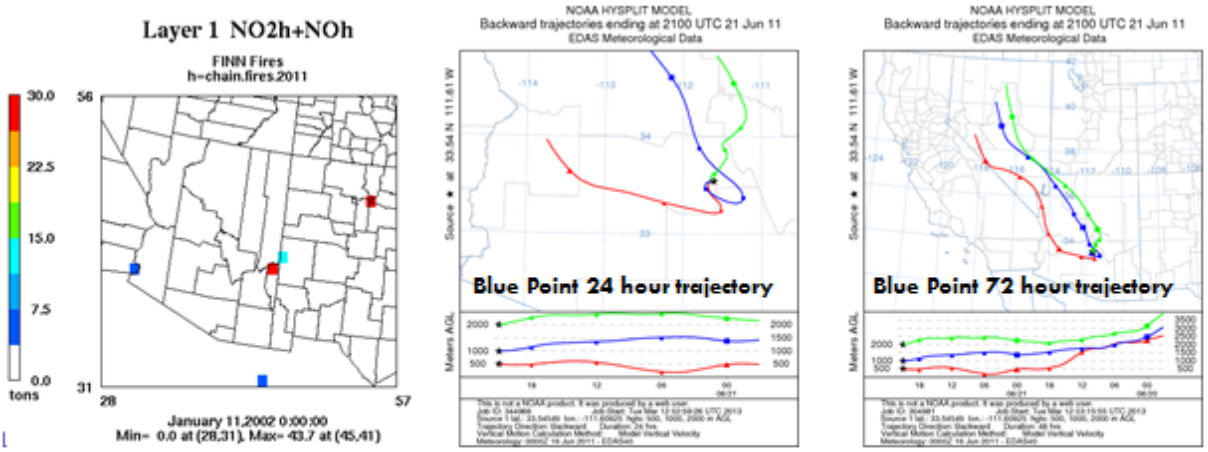
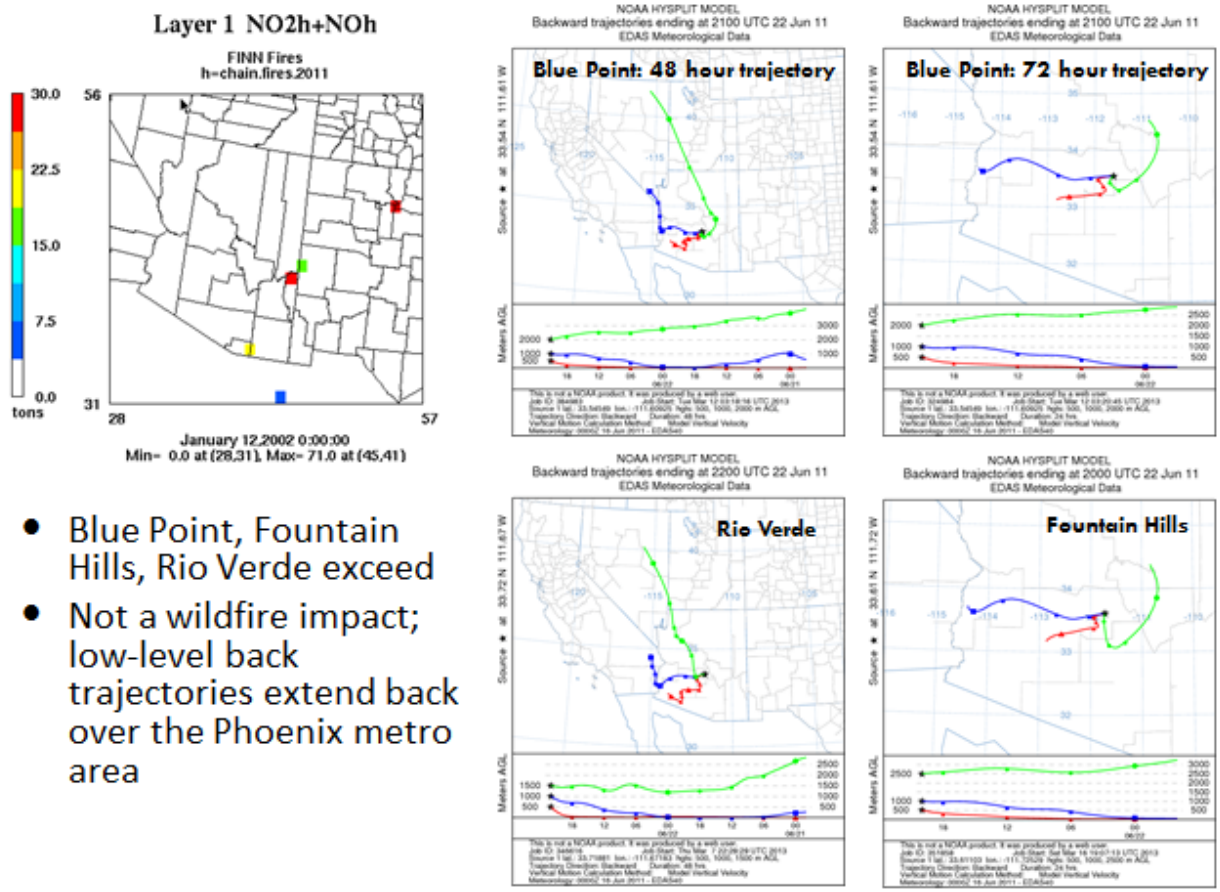


Figure A-36. June 20, 2011. Right hand panel: Image obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).



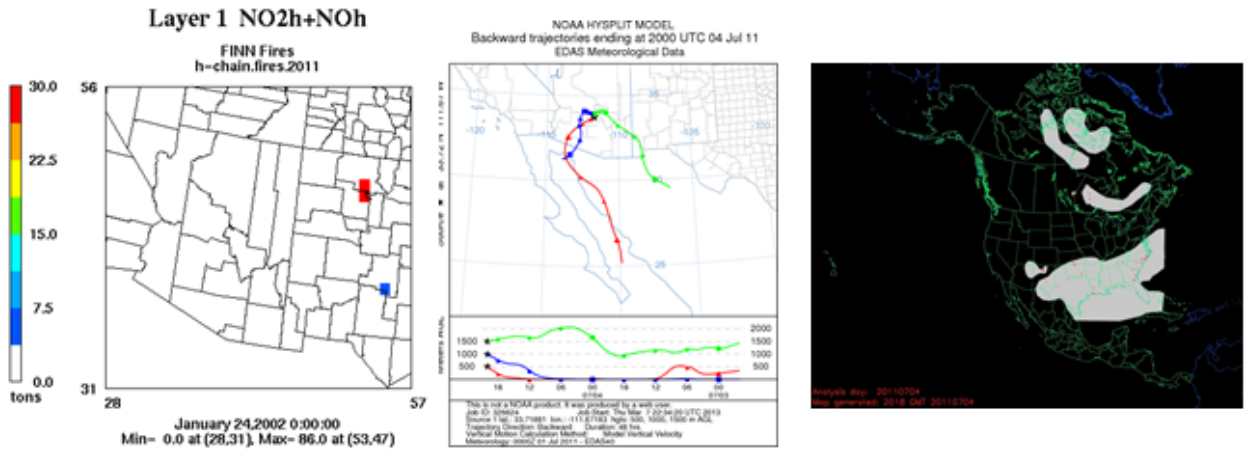
- Blue Point, Fountain Hills, Pinnacle Peak exceed
- Wind direction indicates not a wildfire impact

Figure A-37. June 21, 2011.



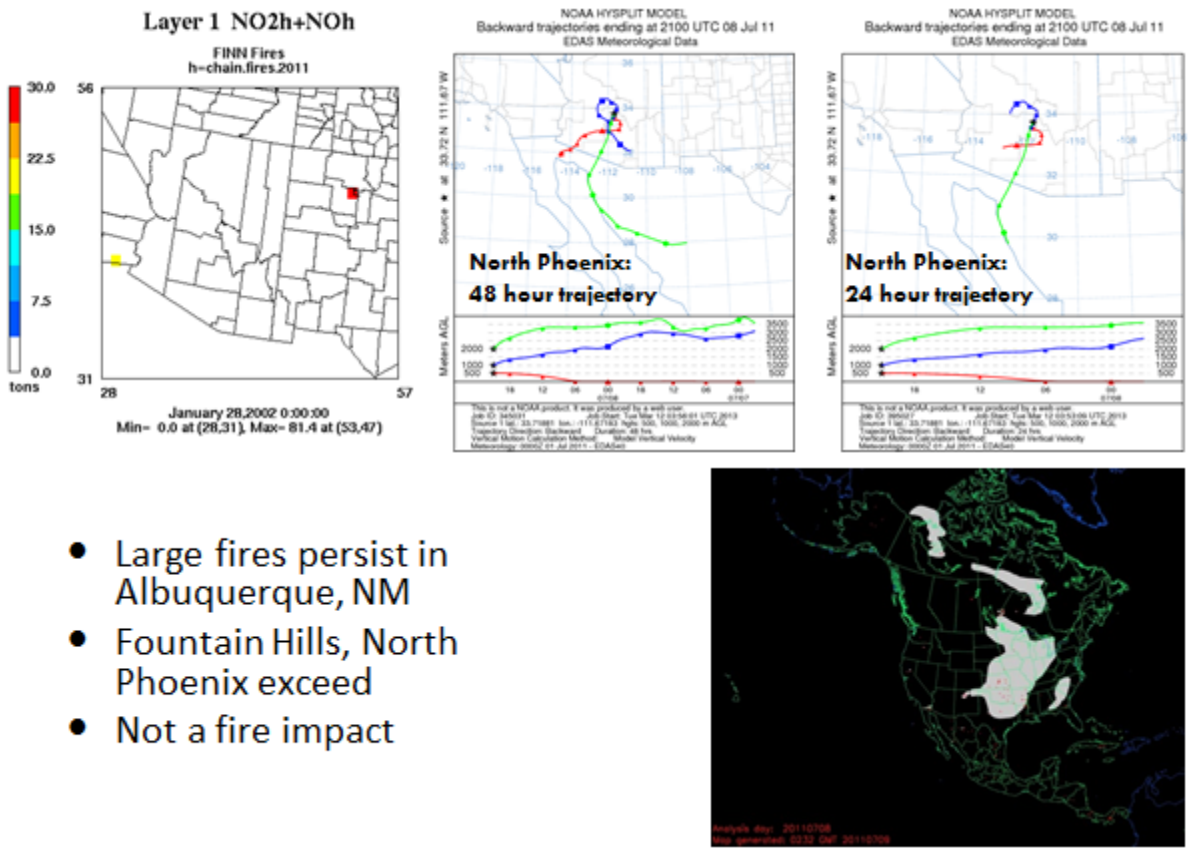
- Blue Point, Fountain Hills, Rio Verde exceed
- Not a wildfire impact; low-level back trajectories extend back over the Phoenix metro area

Figure A-38. June 22, 2011.



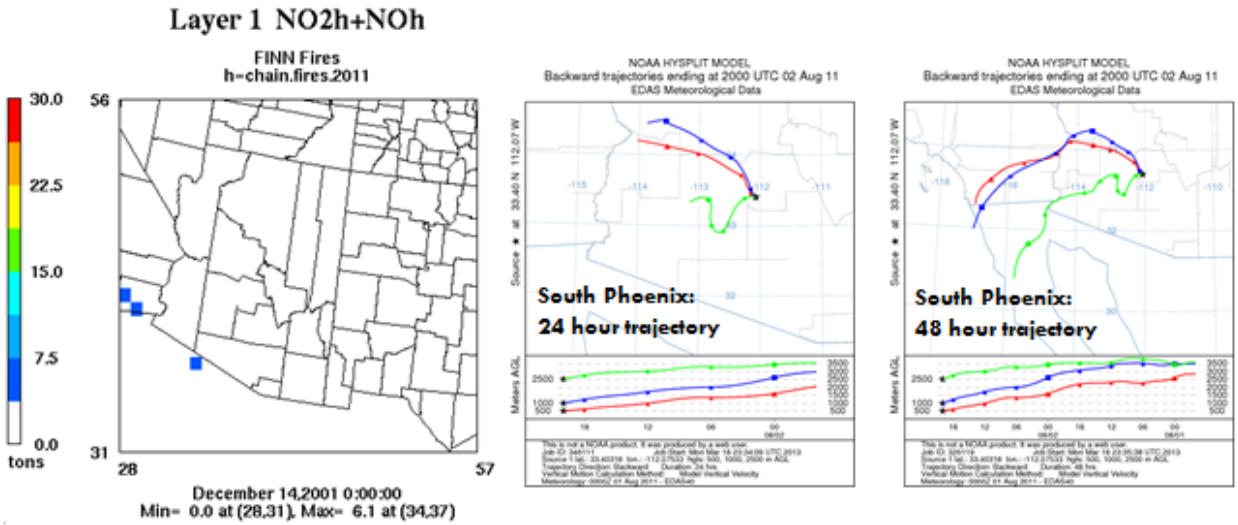
- Large fires in Albuquerque, NM
- Rio Verde exceeds
- Fire impact less likely than urban plume impact

Figure A-39. July 4, 2011. Right hand panel: Image obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).



- Large fires persist in Albuquerque, NM
- Fountain Hills, North Phoenix exceed
- Not a fire impact

Figure A-40. July 8, 2011. Lower right hand panel: Image obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).



- South Phoenix, West Chandler
- No fire south of US-Mexico on border previous day—not a fire impact

Figure A-41. August 2, 2011.

No fires present on August 3-4, 2011.

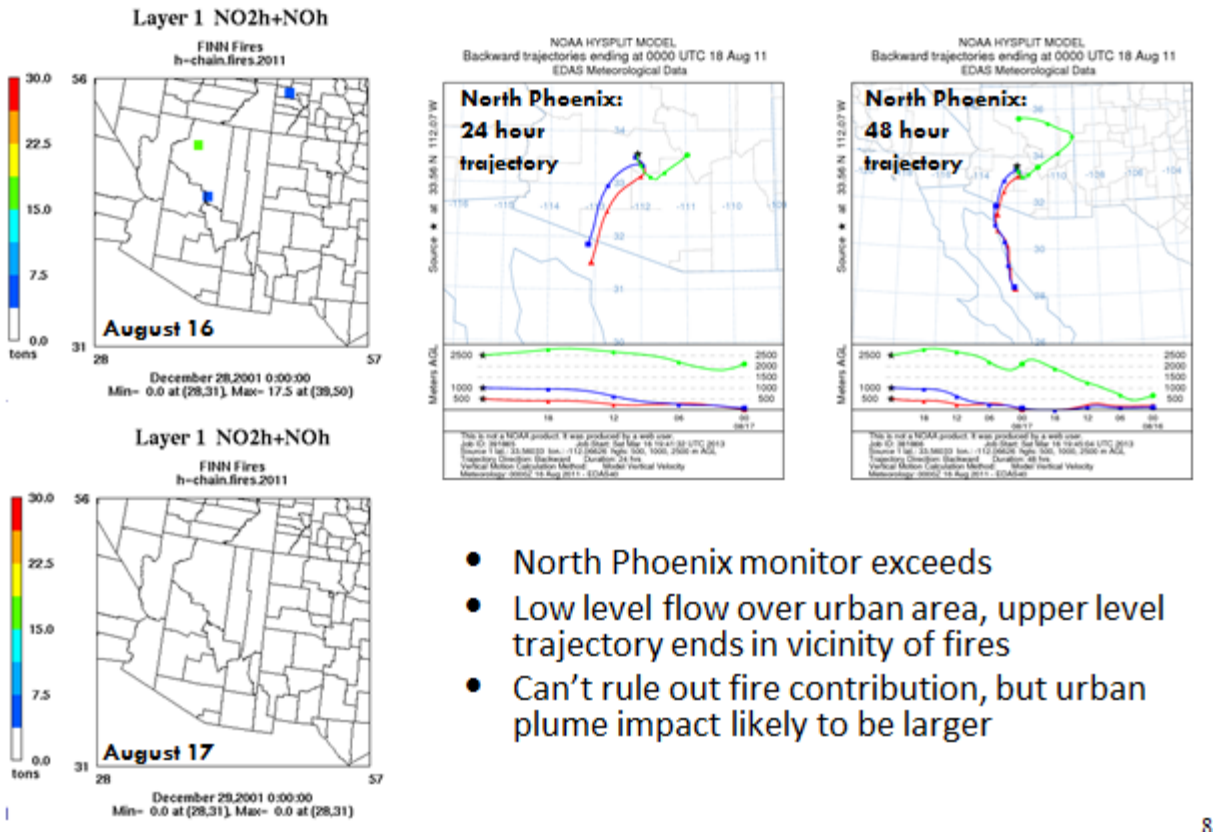


Figure A-42. August 17, 2011.

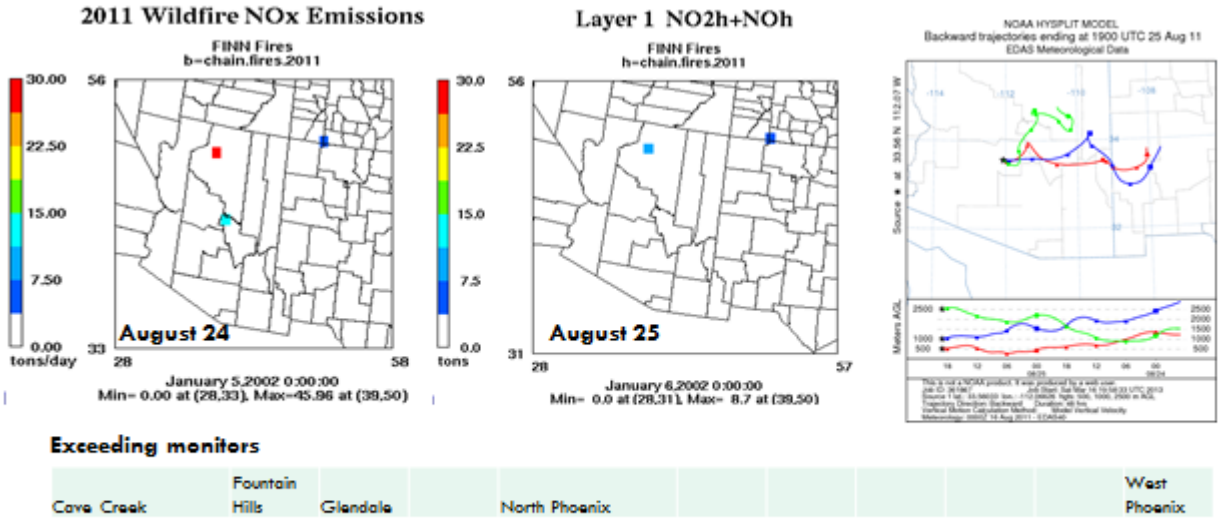
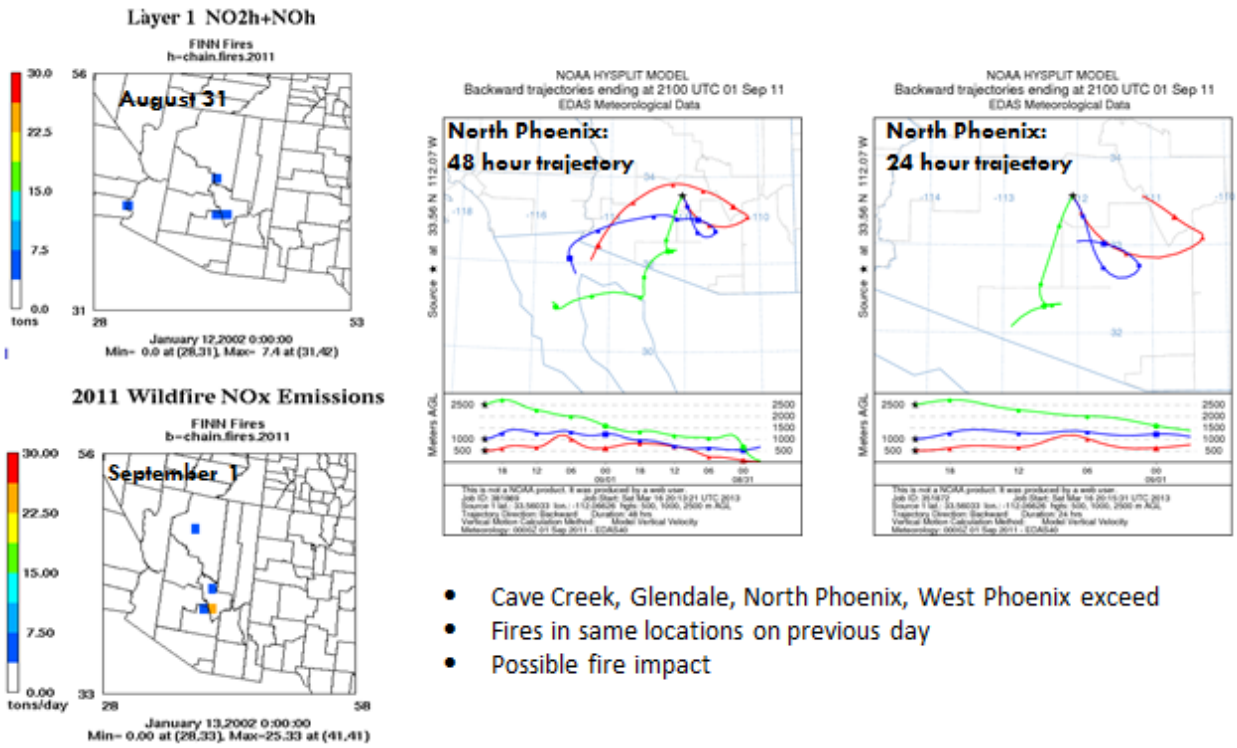


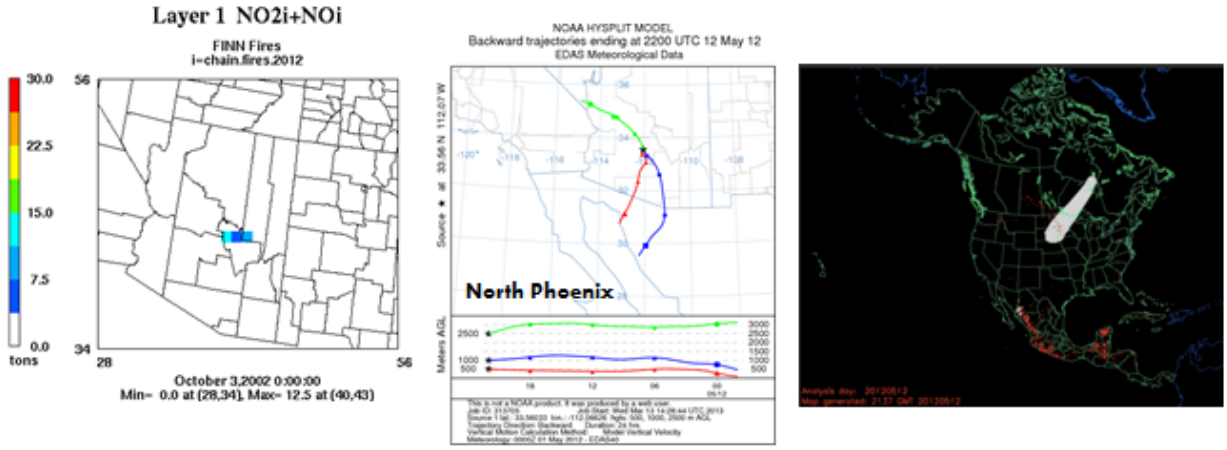
Figure A-43. August 25, 2011.



- Cave Creek, Glendale, North Phoenix, West Phoenix exceed
- Fires in same locations on previous day
- Possible fire impact

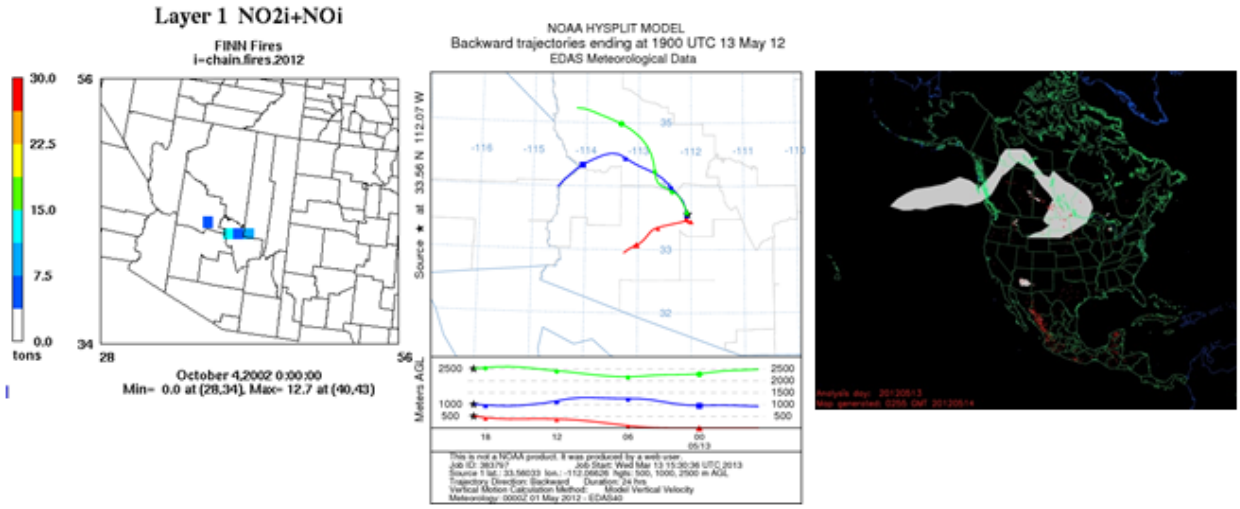
Figure A-44. September 1, 2011.

April 17, April 21, May 10, 2012: No fires.



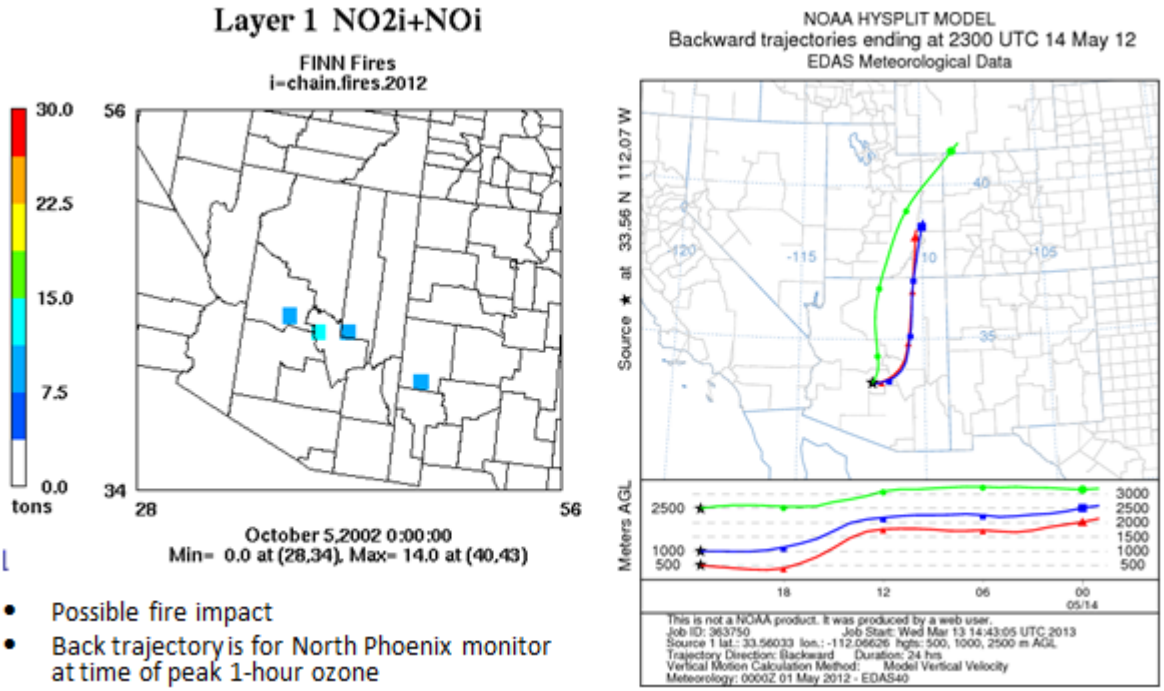
- Back trajectory indicates fire impact unlikely
- Back trajectory is for North Phoenix monitor at time of peak 1-hour ozone

Figure A-45. May 12, 2011. Right hand panel: Image obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).



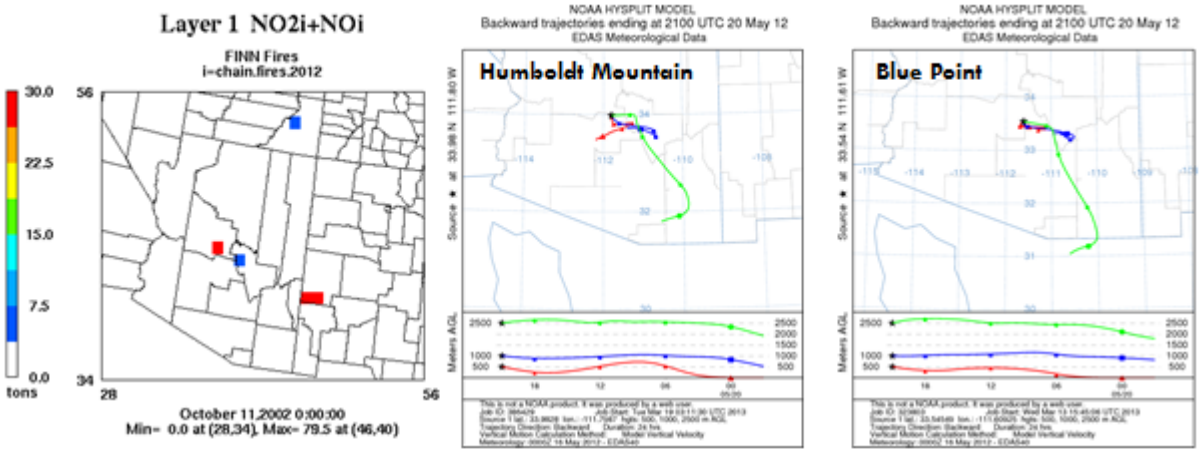
- Possible fire impact
- Back trajectory is for North Phoenix monitor at time of peak 1-hour ozone

Figure A-46. May 13, 2012. Right hand panel: Image obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).



- Possible fire impact
- Back trajectory is for North Phoenix monitor at time of peak 1-hour ozone

Figure A-47. May 14, 2012.



- Humboldt Mountain and Blue Point exceed
- Possible impact from local fires

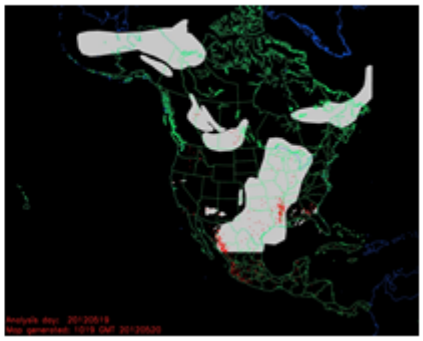
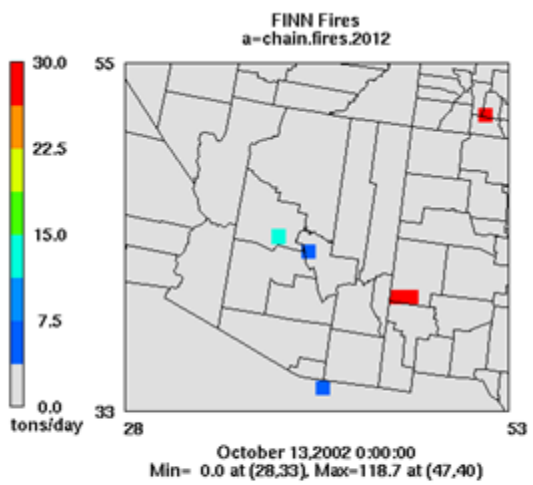
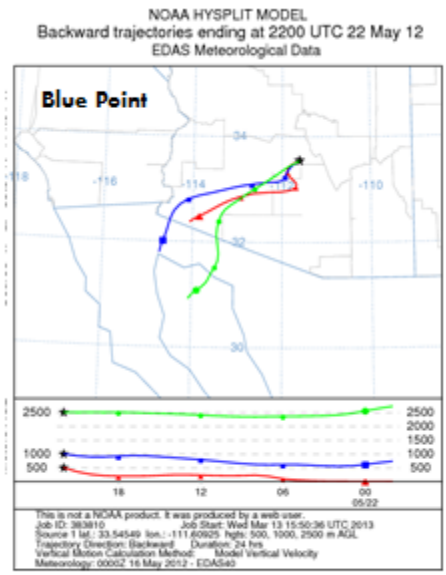


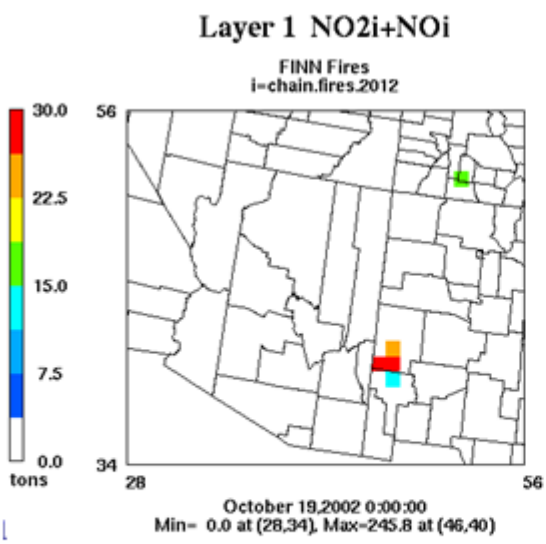
Figure A-48. May 20, 2012. Lower right hand panel: Image obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).

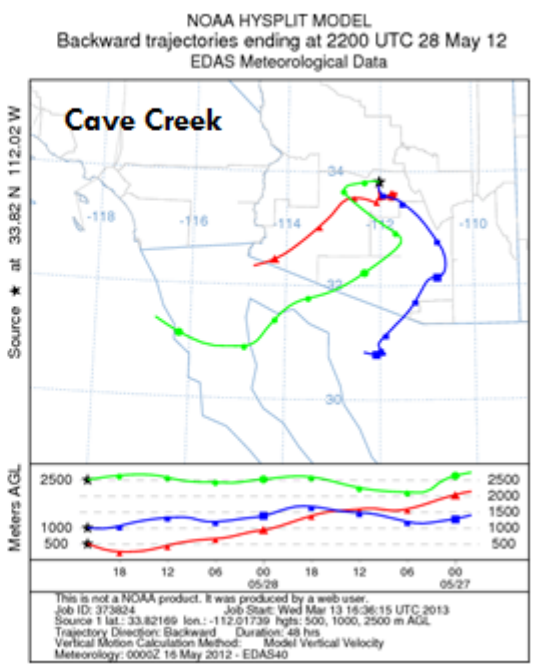




- Not a direct fire impact
- Back trajectory is for Blue Point monitor at time of peak 1-hour ozone

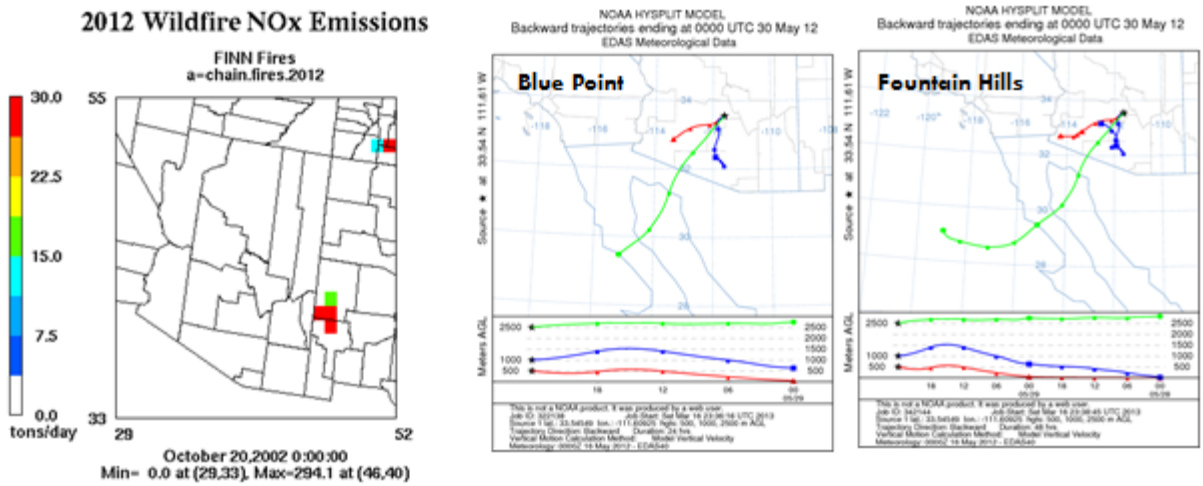
Figure A-49. May 22, 2012.





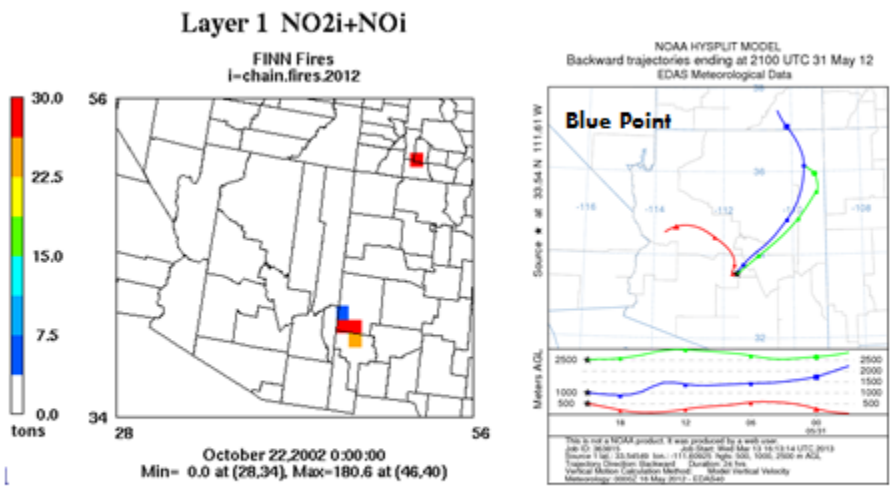
- Whitewater-Baldy Fire Complex near AZ/NM border
- Cave Creek, Humboldt Mountain exceed
- Trajectories indicate not a fire impact

Figure A-50. May 28, 2012.



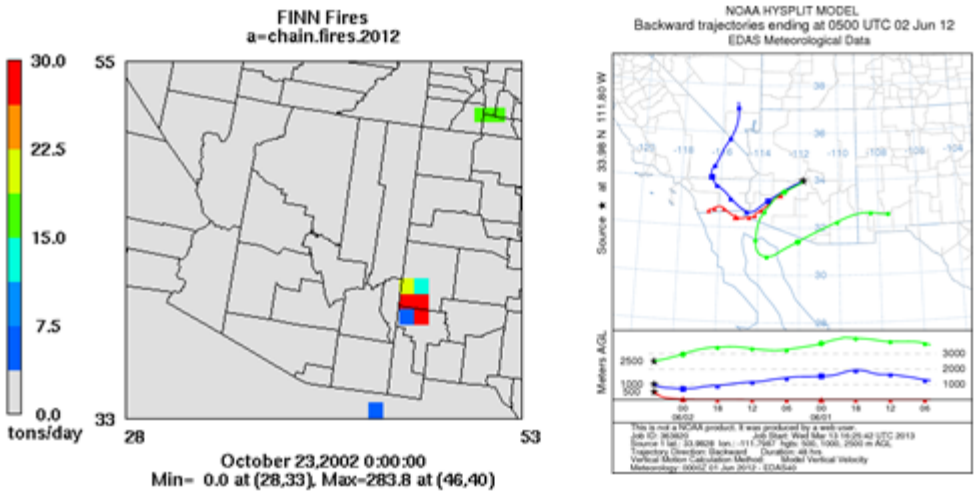
- Blue Point, Fountain Hills exceed
- Not a fire impact

Figure A-51. May 29, 2012.



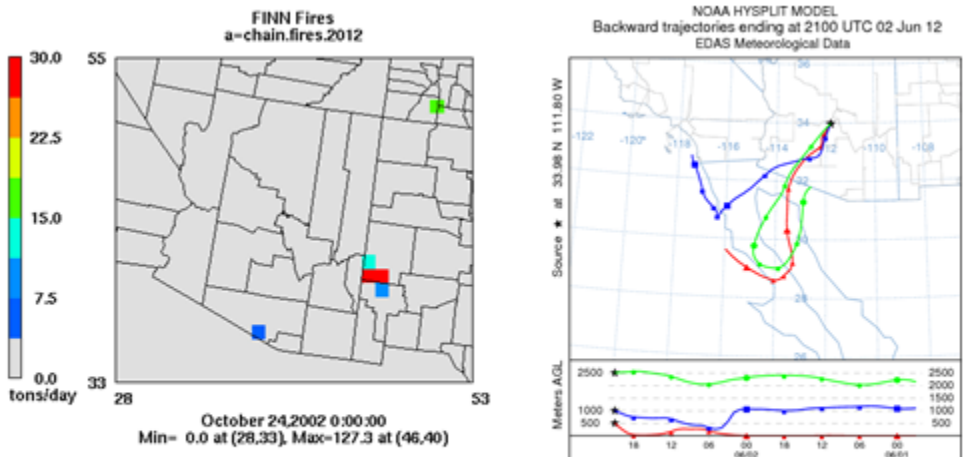
- Back trajectories indicate not a direct fire impact

Figure A-52. May 31, 2012.



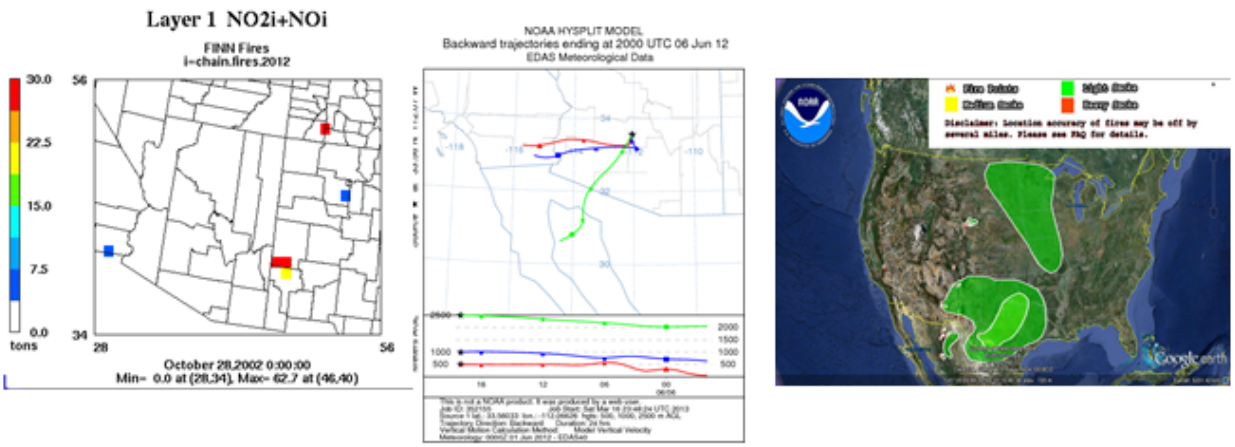
- Possible direct fire impact , but urban plume may also contribute
- Back trajectory is for Humboldt Mountain monitor at time of peak 1-hour ozone

Figure A-53. June 1, 2012.



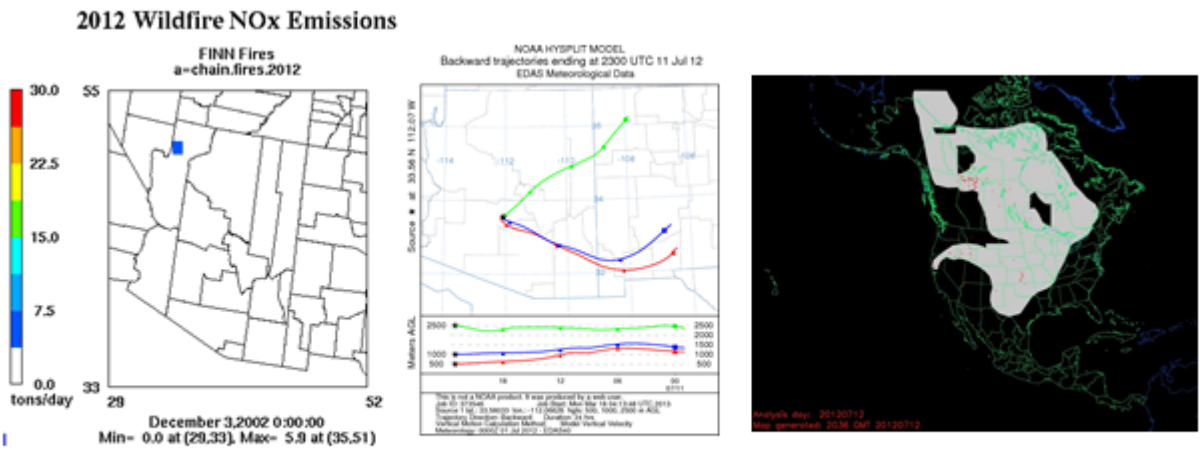
- Cave Creek, Humboldt Mountain exceed
- Back trajectories indicate not a fire impact

Figure A-54. June 2, 2012.



- Wind shifts, Whitewater-Baldy plume now carried east
- Possible fire impact, but impact of local urban plume probably more important

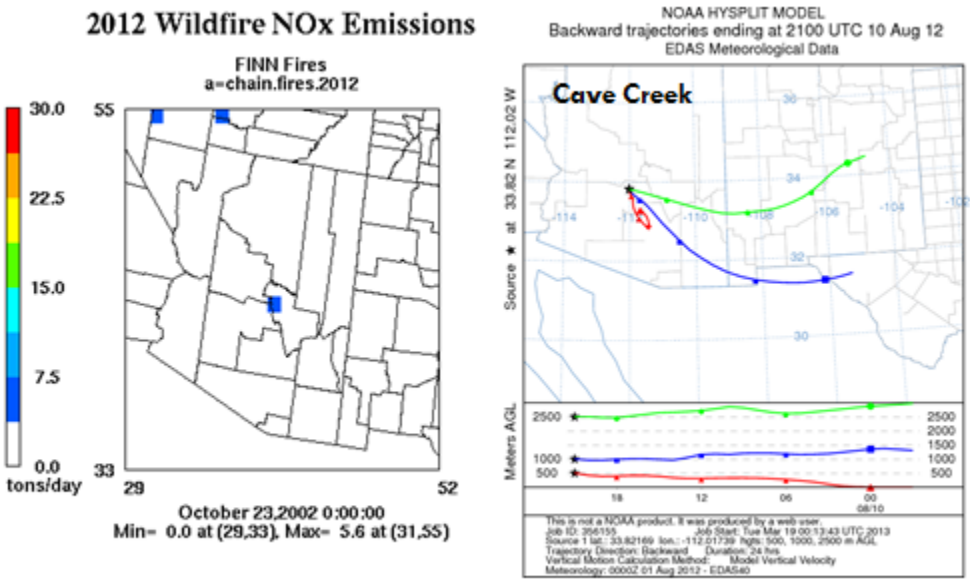
Figure A-55. June 6, 2012. Right hand panel: Image obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).



- Little evidence of fire impacts in Phoenix on June 12
- No fires July 10, 11

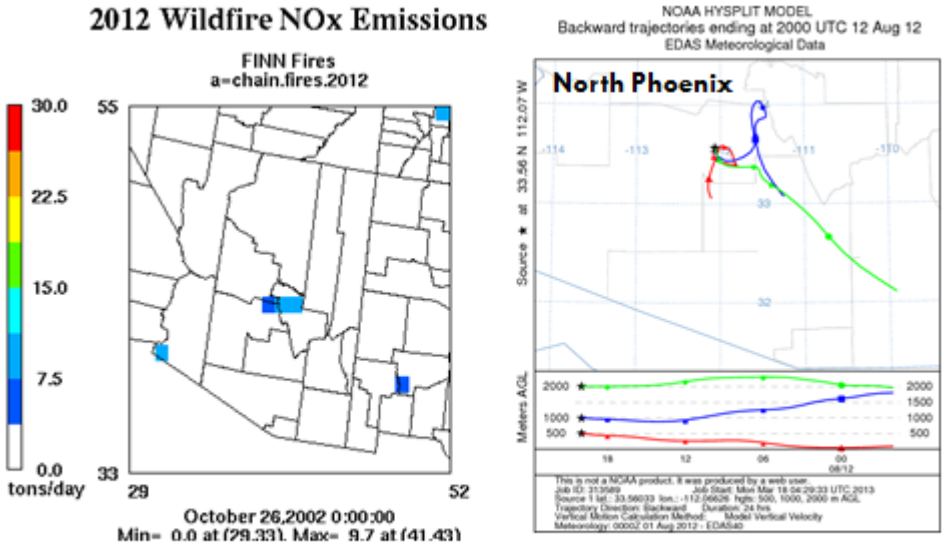
Figure A-56. July 10-12, 2012. Right hand panel: Image obtained from the U.S. Air Quality Smog Blog (http://alg.umbc.edu/usaq).

August 4, 6, 8 ,9, 2012. No fires.



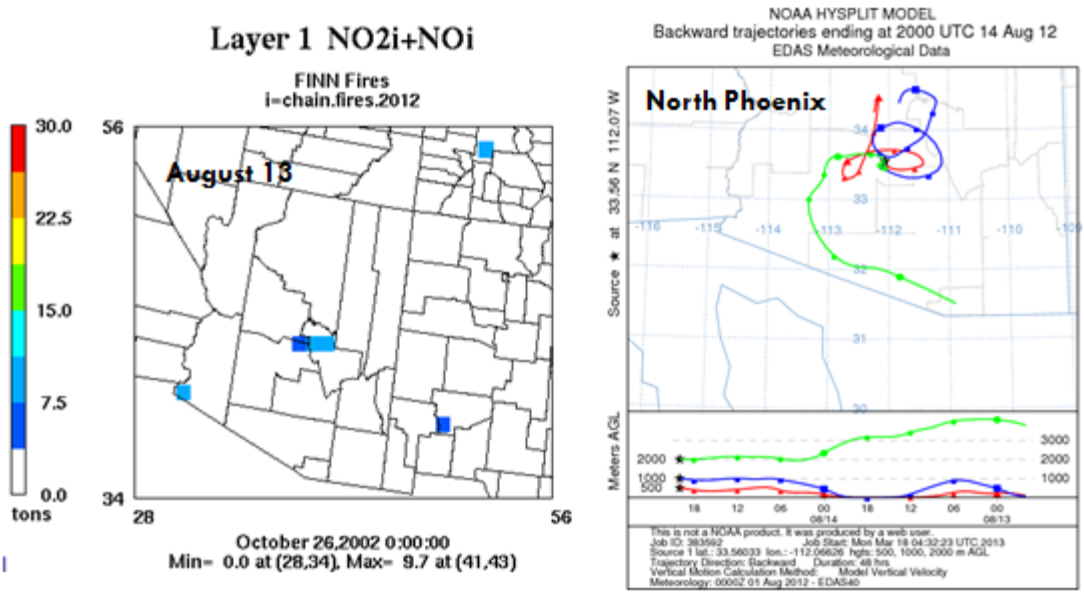
- Possible fire impact

Figure A-57. August 12, 2012.



- Possible impact from nearby fires

Figure A-58. August 12, 2012.



- Satellite detected no fires on August 14, but there are fires August 13 and 15
  - Suspect satellite view was obscured
- North Phoenix exceeds
- Fires nearby, possible fire impact, stagnant air

Figure A-59. August 14, 2012.

August 20, 27, 2012, no fires.

APPENDIX B

Large-Scale Meteorological Fields

Appendix B. Large-Scale Meteorological Fields

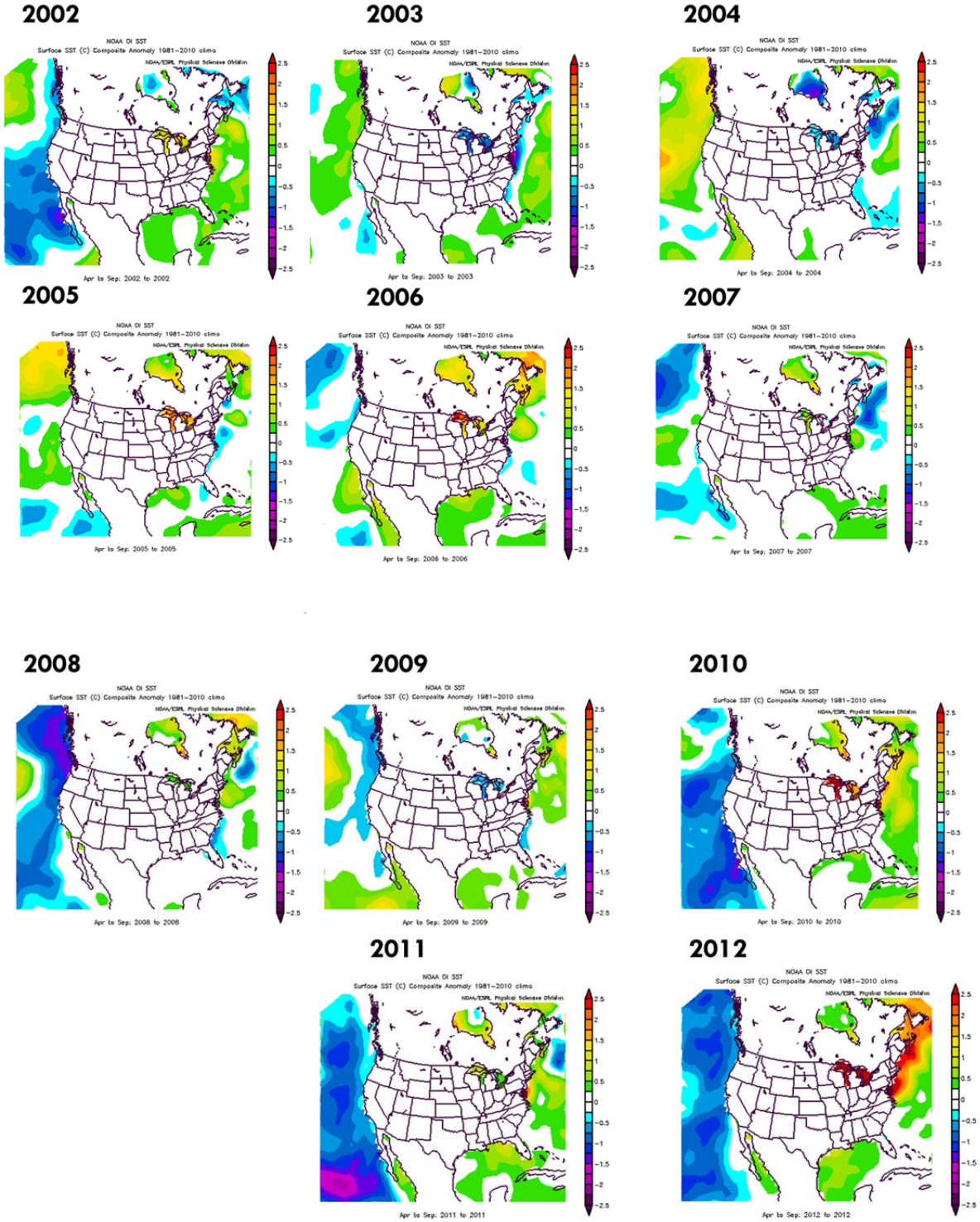


Figure B-1. NOAA OI SST anomaly.

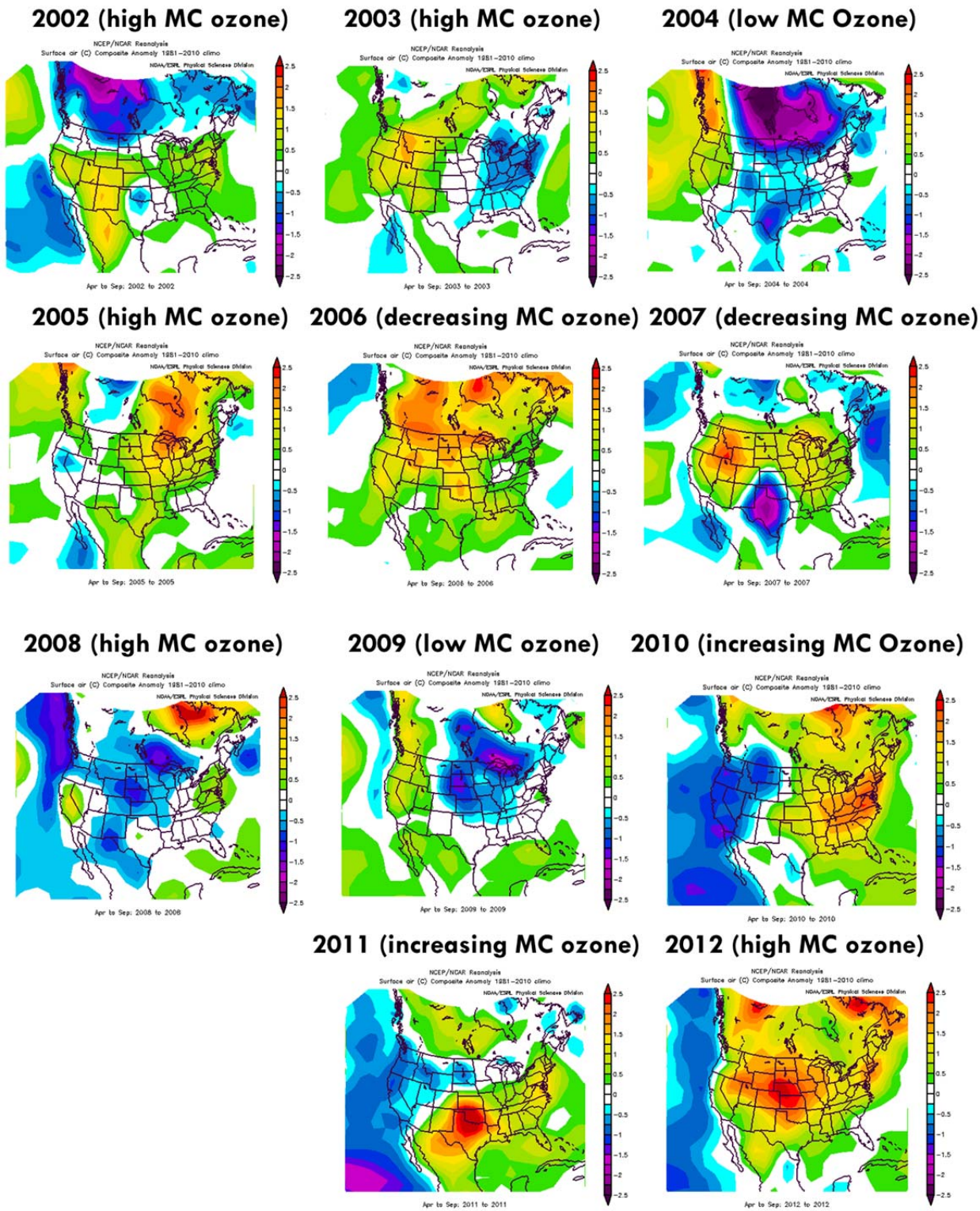


Figure B-2. Ozone Season Surface Air Temperature Anomaly. NCEP/NCAR reanalysis: April-September average anomaly.

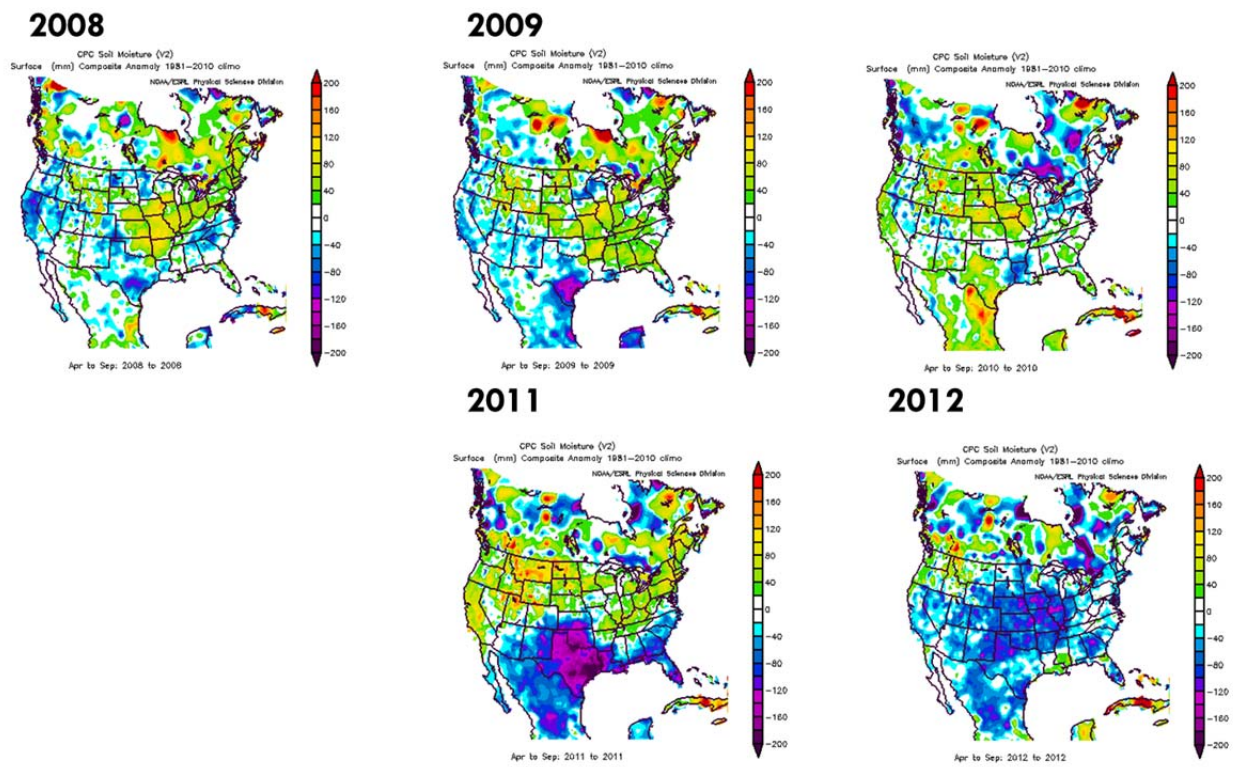


Figure B-3. Soil Moisture Anomaly.

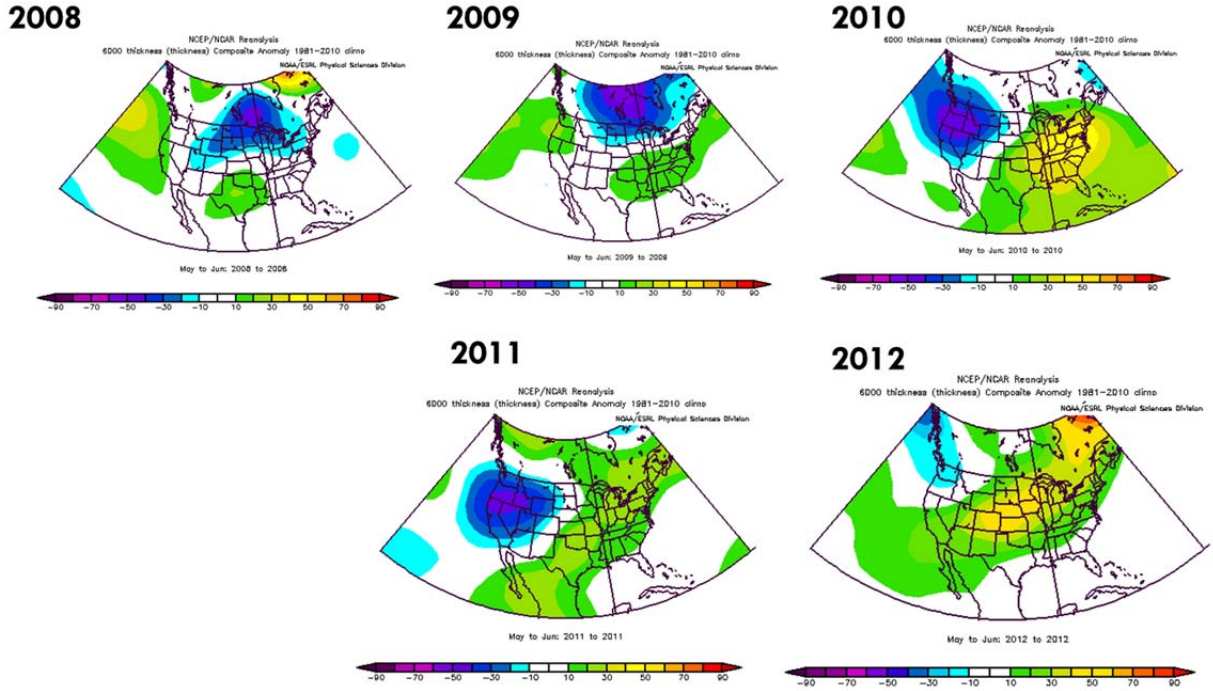


Figure B-4. May-June 1000-500 mb thickness anomaly. NCEP reanalysis.

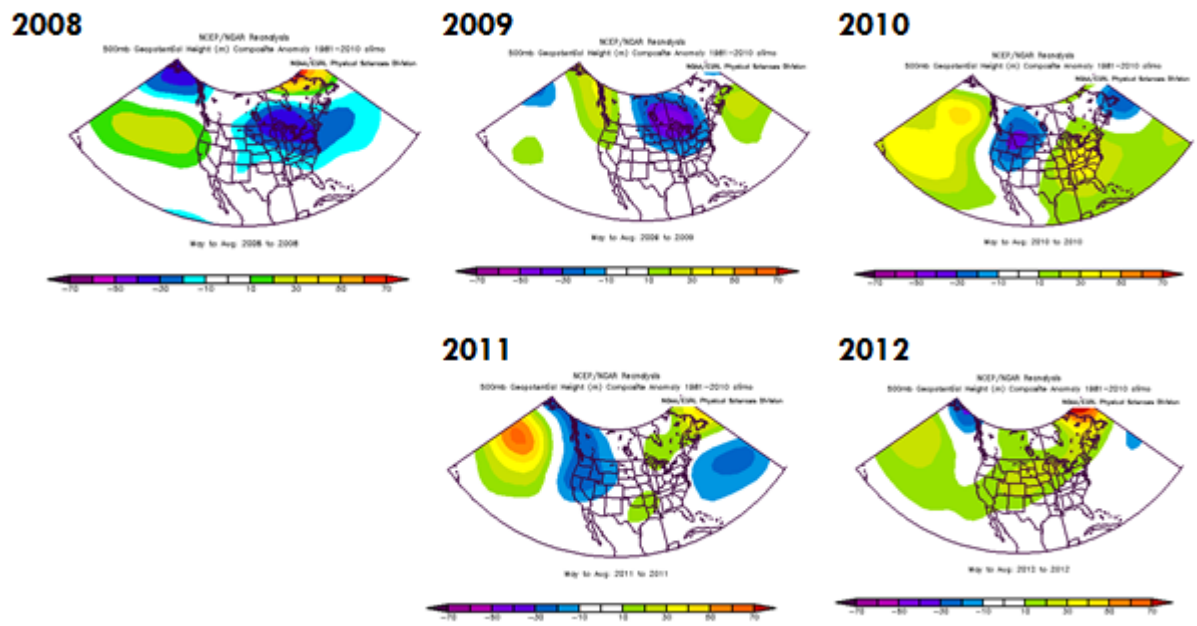


Figure B-5. May-August 500 mb height anomaly. NCEP/NCAR Reanalysis.

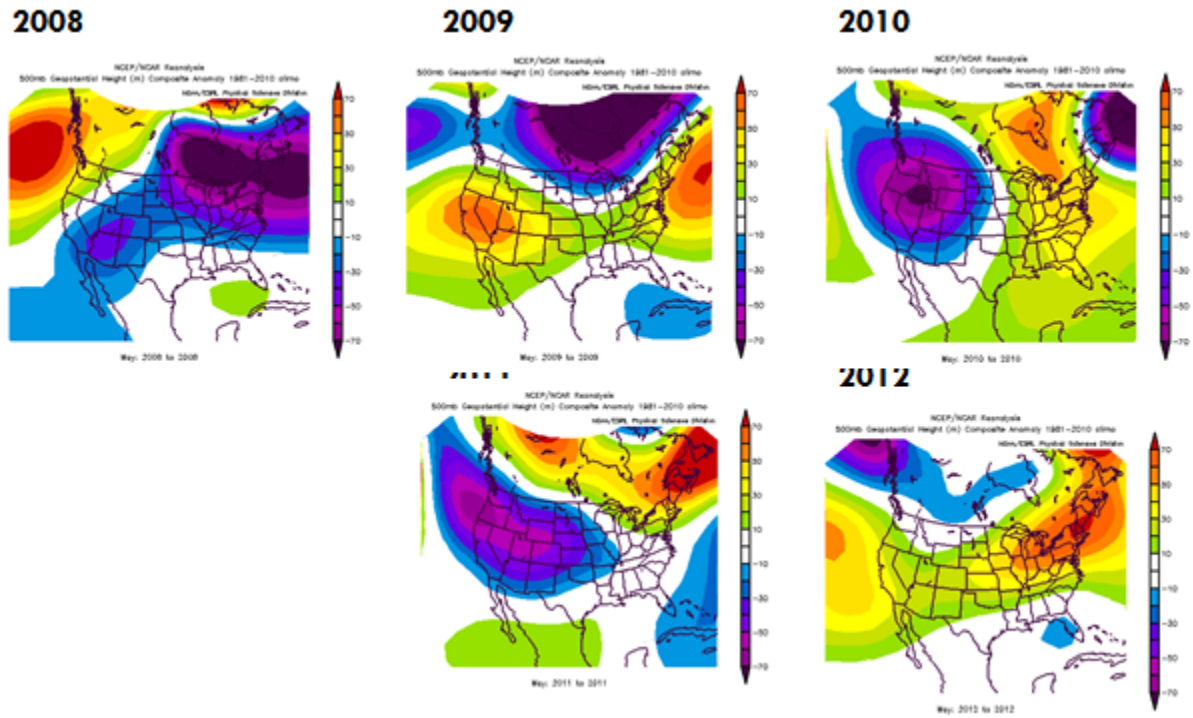


Figure B-6. May 500 mb height anomaly.

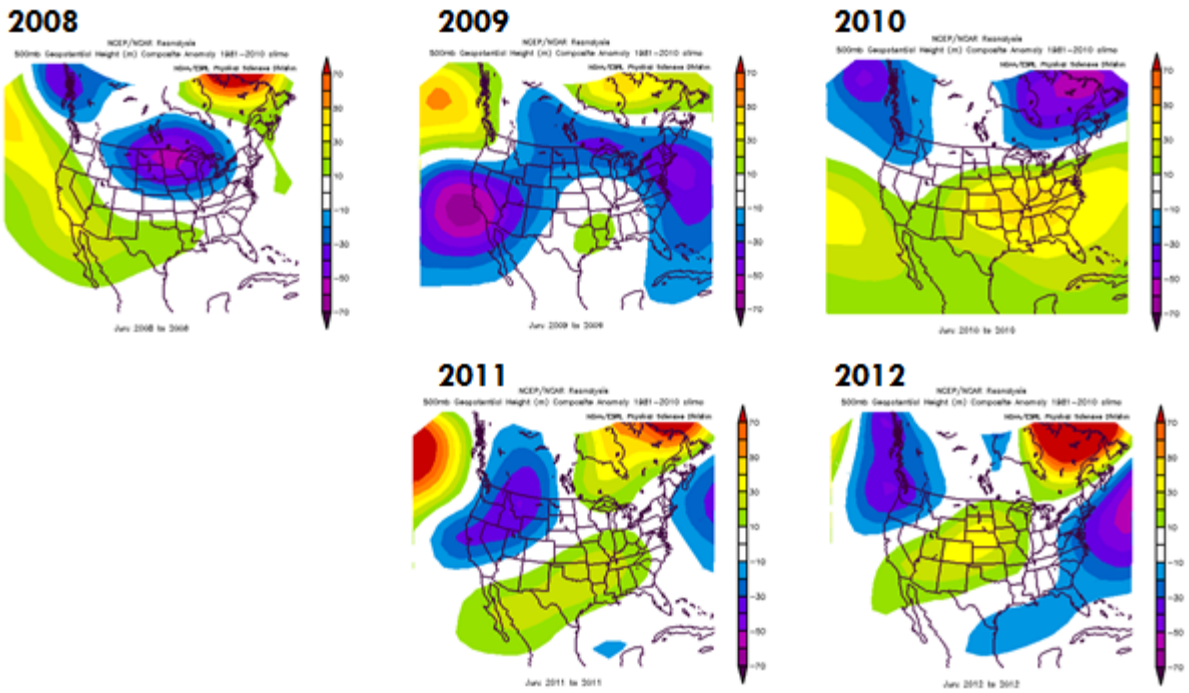


Figure B-7. NCEP/NCAR Reanalysis June 500 mb height anomaly.

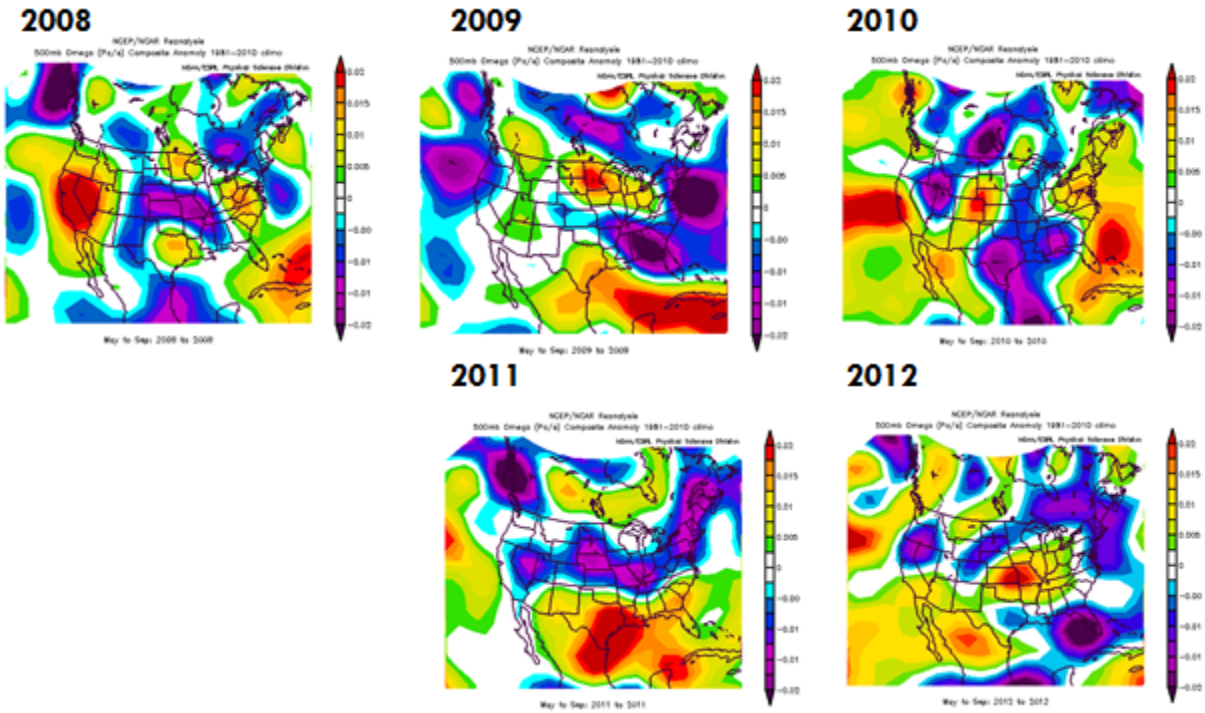


Figure B-8. May-Sept ω(500 mb) Anomaly.

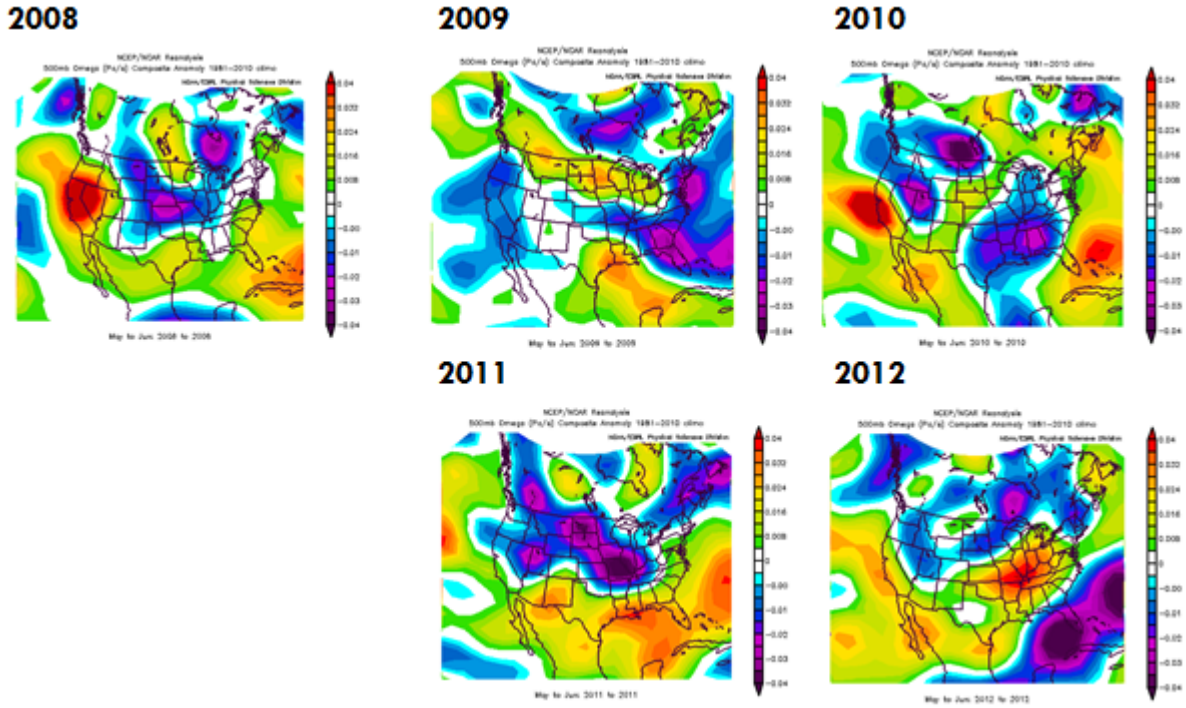


Figure B-9. May-June ω(500 mb) anomaly.

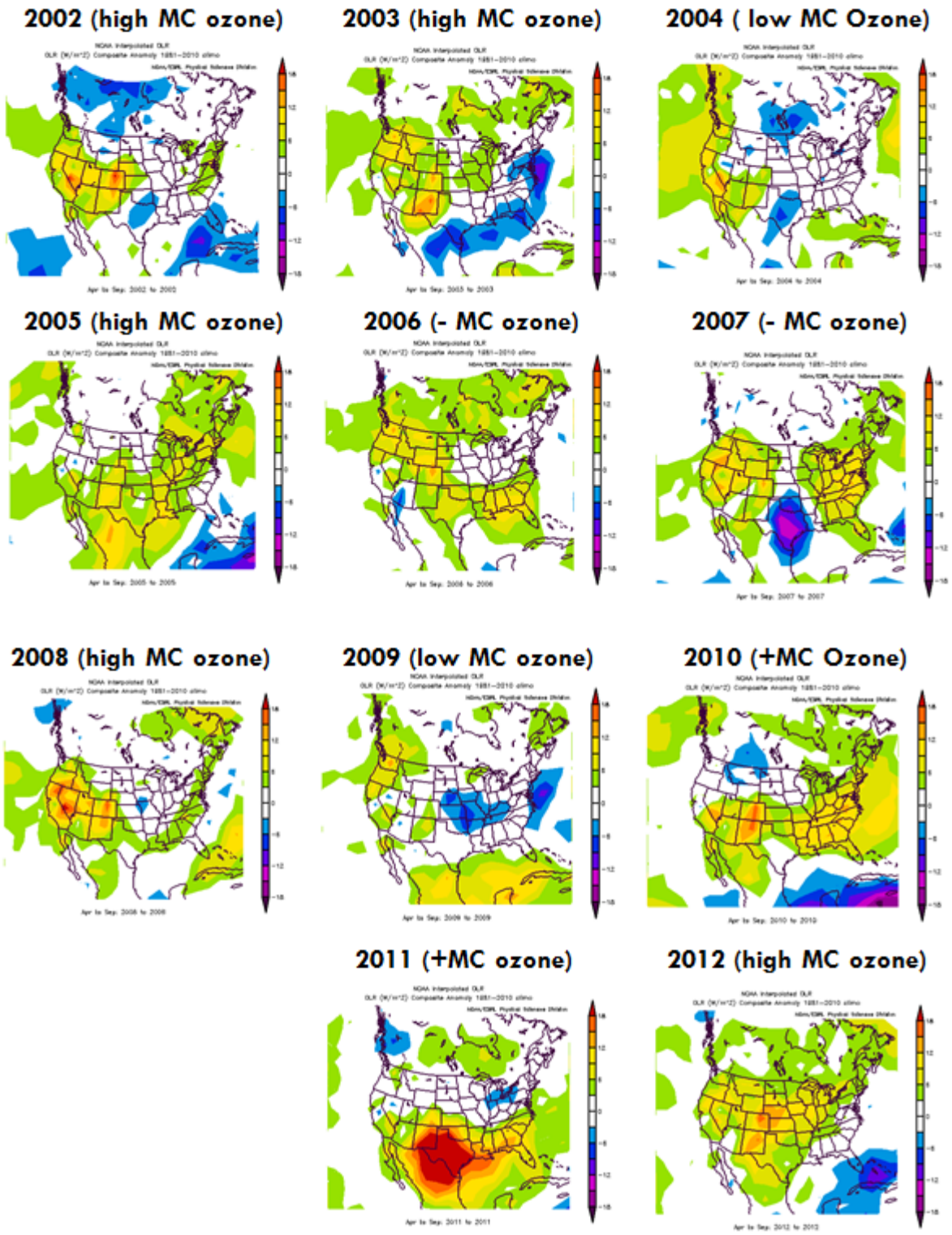


Figure B-10. April-September OLR Anomaly.

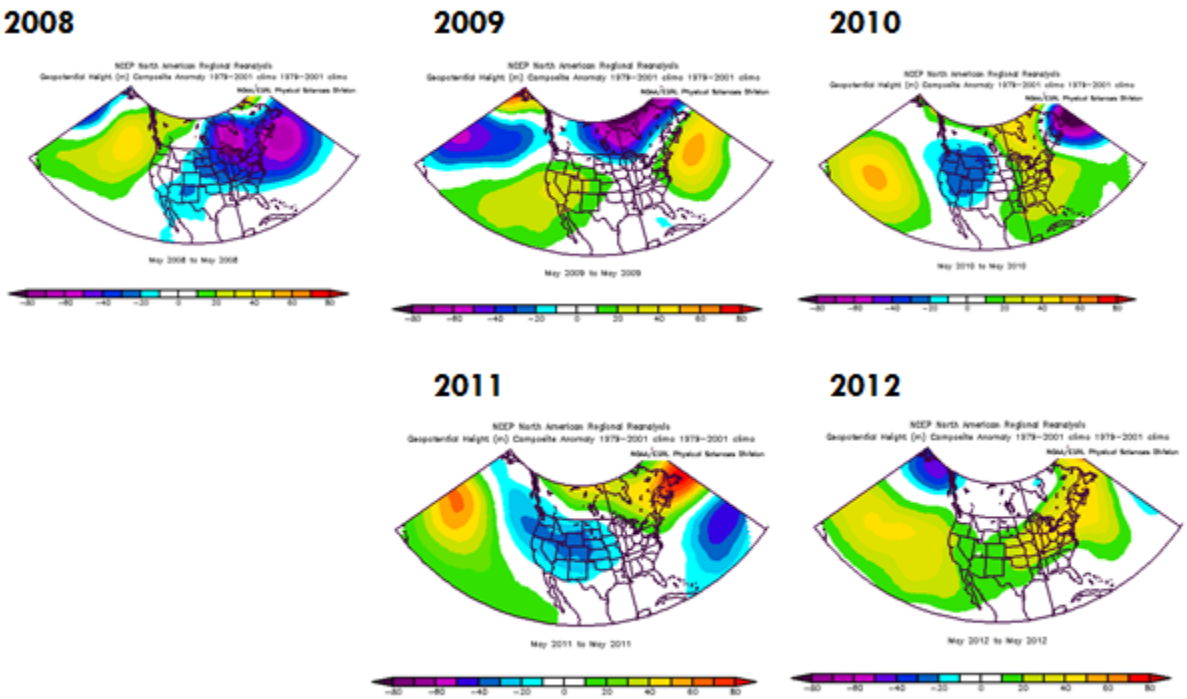


Figure B-11. May 700 mb height anomaly. NARR [http://www.esrl.noaa.gov/psd/cgi-bin/data/narr/plotmonth.pl.](http://www.esrl.noaa.gov/psd/cgi-bin/data/narr/plotmonth.pl)

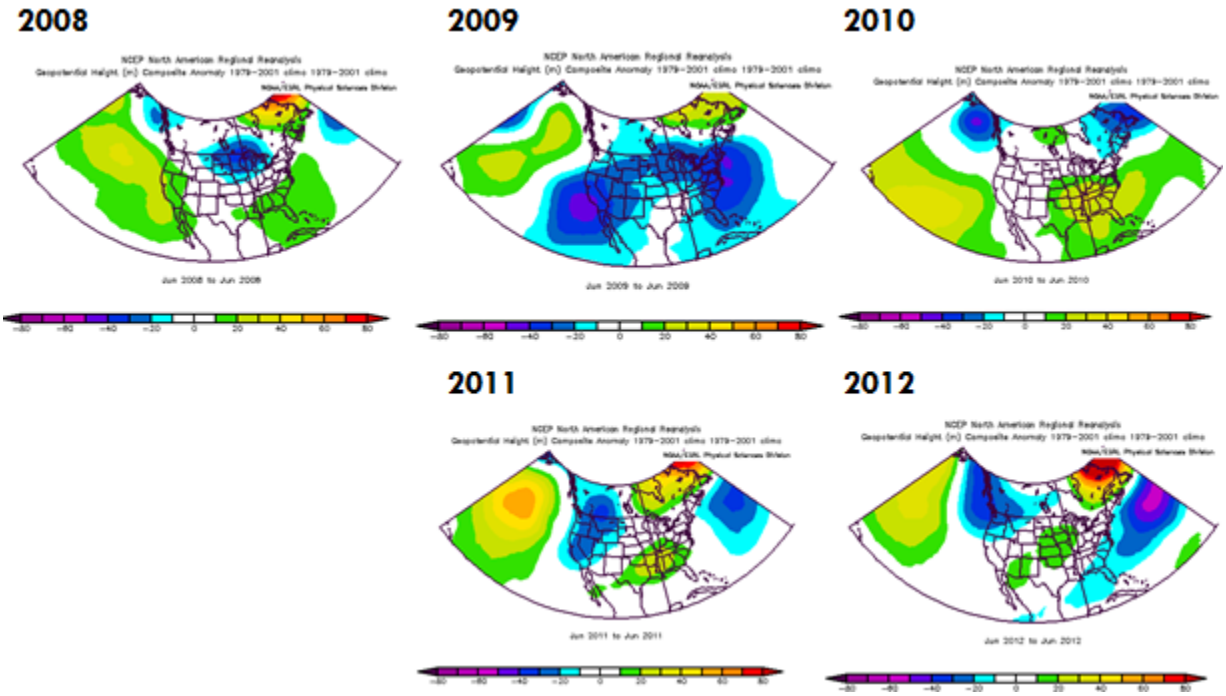


Figure B-12. June 700 mb height anomaly. NARR [http://www.esrl.noaa.gov/psd/cgi-bin/data/narr/plotmonth.pl.](http://www.esrl.noaa.gov/psd/cgi-bin/data/narr/plotmonth.pl)

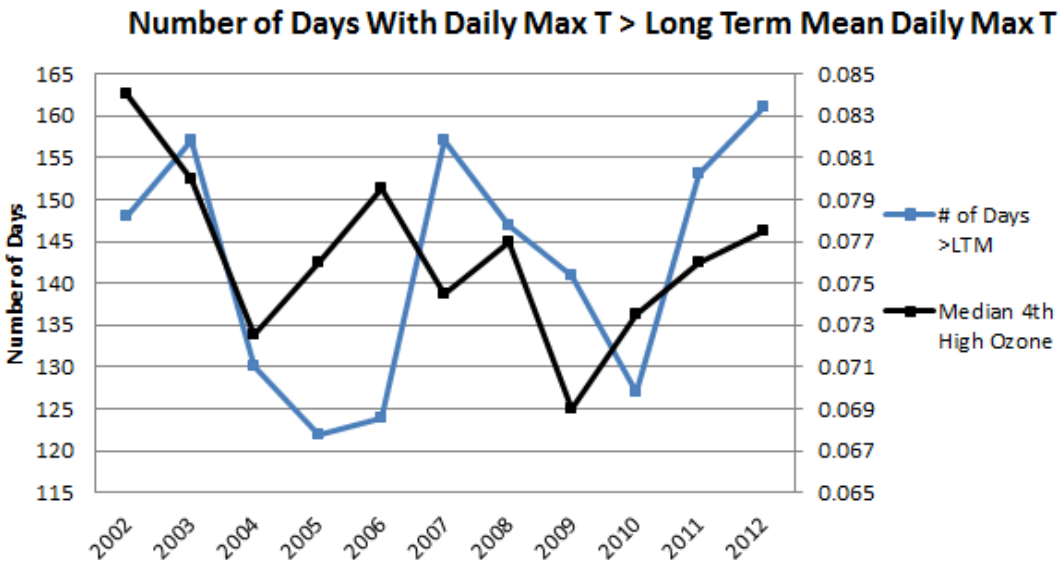


Figure B-13. Daily Max Temperatures Above Long Term Mean. KPHX.

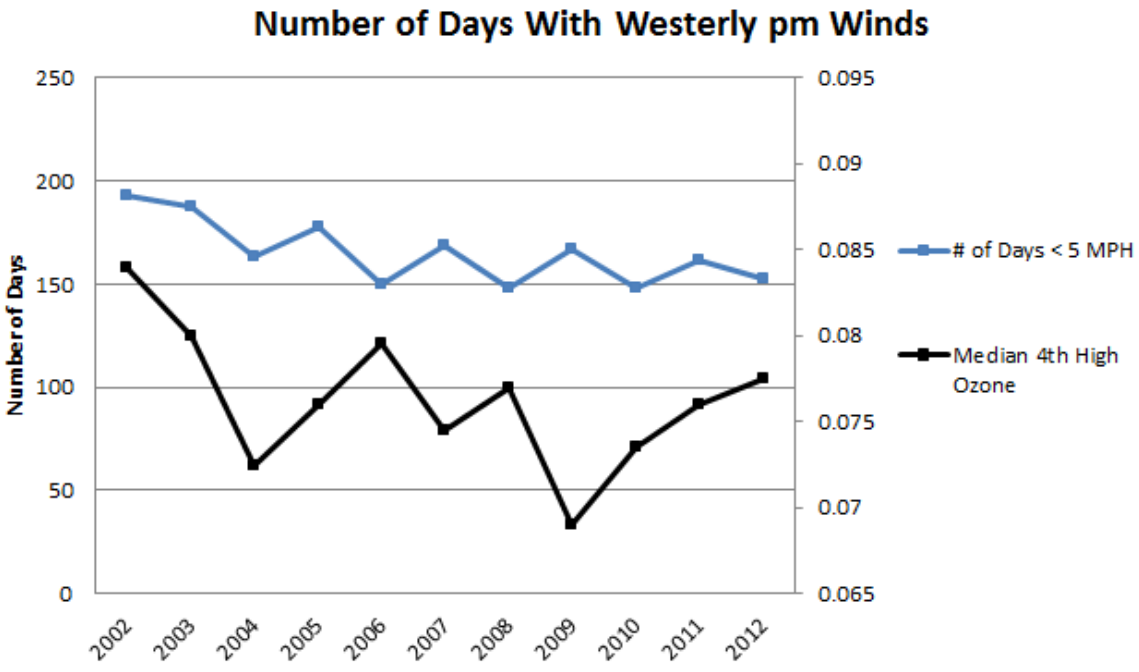


Figure B-14. Days with westerly winds.

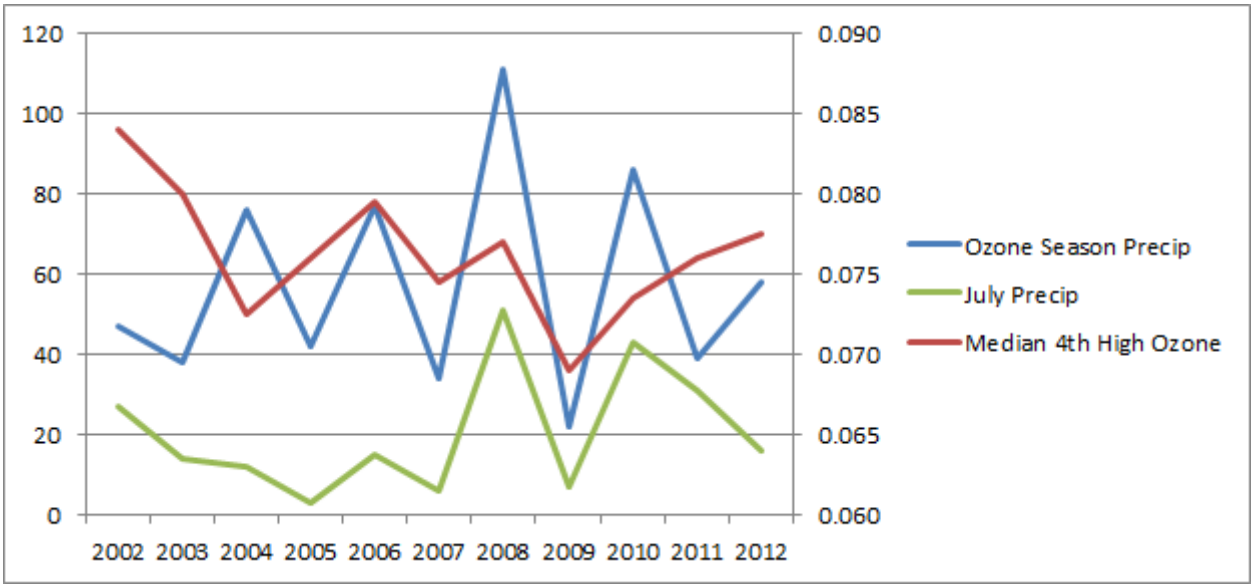


Figure B-15. KPHX precipitation.

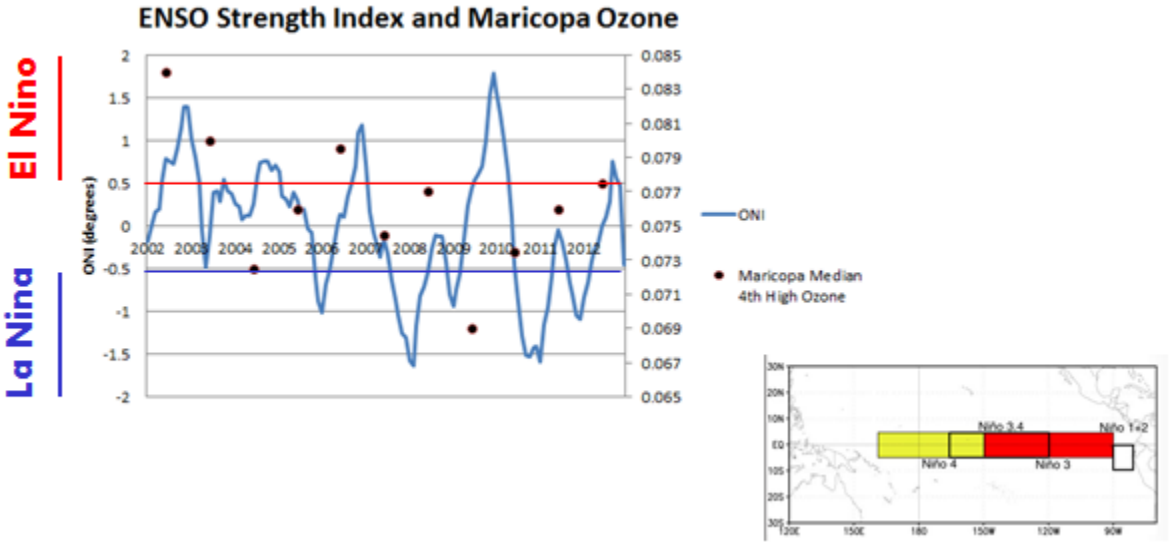


Figure B-16. El Nino-Southern Oscillation (ENSO) phase. Inset panel shows the tropical Pacific ocean region used to determine the sea surface temperature anomalies from which the Oceanic Nino Index (ONI) is derived. The ONI is used to determine the ENSO phase.

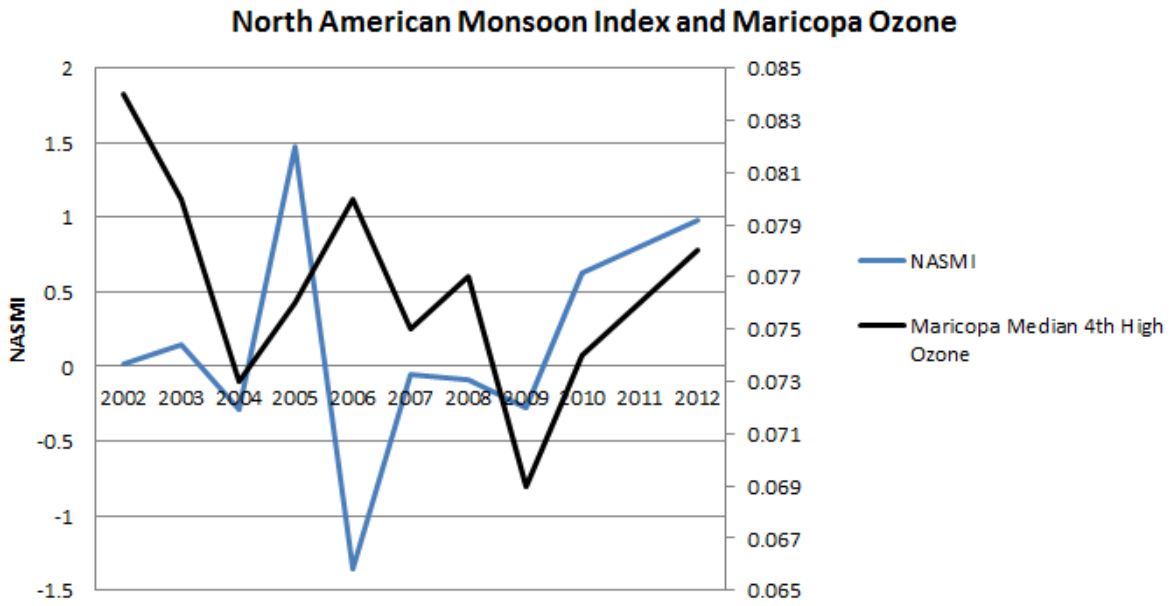


Figure B-17. NAM index.

Index measures seasonal variation of the wind field at 700 hPa over (17.5–35°N, 100–120°W). e.g. Li and Zheng, GRL, (2002).