Beltsville PBL Air Quality Modeling – Atmospheric Chemistry
Applications of 3-Models to Air Quality Analysis and Public Policy
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Objective: The purpose here is to provide students with an outline of some of the measurement and modeling aspects involved with the development of air quality improvement strategies. This is a very broad field that links science, engineering, law and governmental agencies. Here we can't be comprehensive. It's important to note that the language involved in public policy can be very legalistic, sometimes counterintuitive and therefore we suggest that government guidance documents be consulted for any specific application. Both the California Air Resources Board and the US EPA provides websites with detailed regulatory guidance. The California Air Resources Board (ARB-Glossary) provides a starting point.

Criteria, Other Air Pollutants and Their Environmental Effects

The US Clean Air Act was passed first in 1963 and it has been amended several times. The US Clean Air Act has established criteria air pollutants and National Ambient Air Quality Standards (NAAQS). Criteria air pollutants and some of their effects are listed in Table 1 and the US EPA's National Ambient Air Quality Standards are shown in Table 2.

Table 1. Criteria Air Pollutants and Some of Their Health Effects

Criteria Air Pollutant	Effects
Carbon Monoxide (CO)	Poisonous – Binds with hemoglobin preventing it from carrying oxygen. Can be fatal in high concentrations.
Lead (Pb)	Potent neurotoxin
Nitrogen Dioxide (NO_2)	Lung irritant, causes severe irritation or swelling of the respiratory tract. Can be fatal in high concentrations. Ozone, PM and acid precipitation precursor.
Particulate Matter (PM)	May flow deep into lungs. From the lungs it has been suggested that particles may reach the brain and heart where they may cause further damage. PM reduces life expectancy.
Ozone (O_3)	Lung irritant, causes severe irritation or swelling of the respiratory tract.
Sulfur Dioxide (SO_2)	Acid precipitation precursor, Lung irritant.

Nitrogen dioxide and nitric oxide (NO) along with carbon monoxide and volatile organic compounds (VOC) contribute to ozone formation and produce nitric acid (HNO_3). Nitric acid contributes to acid precipitation and inorganic PM formation. The oxidation of sulfur dioxide produces sulfate PM. Sulfate containing PM along with other particulate matter reflect and absorb radiation this affects solar radiation modifying climate. The oxidation of sulfur dioxide in both the gas-phase and aqueous-phase contributes to acid precipitation. Acid precipitation and deposition acidifies lakes and forest ecosystems causing damage. PM also degrades visibility causing adverse economic and safety effects.

Table 2. National Ambient Air Quality Standards for Criteria Air Pollutants.

Pollutant		**Primary /Secondary**	**Averaging Time**	**Mixing Ratio /Concentration**	**Rule**
Carbon Monoxide (CO)		primary	8 hours	9 ppm	Not to be exceeded more than once per year
			1 hour	35 ppm	
Lead (Pb)		primary and secondary	Rolling 3-month average	0.15 μg/m^3	Not to be exceeded
Nitrogen Dioxide (NO_2)		primary	1 hour	100 ppb	98th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		primary and secondary	1 year	53 ppb	Annual Mean
Ozone (O_3)		primary and secondary	8 hours	0.070 ppm	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years
Particle Matter (PM)	$PM_{2.5}$	primary	1 year	12.0 μg/m^3	annual mean, averaged over 3 years
		secondary	1 year	15.0 μg/m^3	annual mean, averaged over 3 years
		primary and secondary	24 hours	35 μg/m^3	98th percentile, averaged over 3 years
	PM_{10}	primary and secondary	24 hours	150 μg/m^3	Not to be exceeded more than once per year on average over 3 years
Sulfur Dioxide (SO_2)		primary	1 hour	75 ppb	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		secondary	3 hours	0.5 ppm	Not to be exceeded more than once per year

(Source: EPA Criteria Air Pollutants)

Federal regulations set the National Ambient Air Quality Standards (NAAQS) for criteria air pollutants but many regions fail to meet them. This failure is known as non-attainment or non-compliance. In the case of non-attainment, local regions, cities and states develop Air Quality Management Plans (AQMP). For example, California is divided into air quality management districts that develop air quality management plans and submit them to the state government; many other states operate with similar local agencies. AQMPs are used to set policies needed to bring the area into compliance with state and national ambient air quality standards.

AQMPs from across a state are incorporated into the State Implementation Plans (SIP) and the SIP is submitted to the U.S. EPA for approval. A SIP is a statewide plan for attaining and maintaining the national ambient air quality standards. SIPs include summaries of emission inventories, air quality monitoring, special air quality studies and other scientific details that are relevant to the state's current air quality situation. Air quality modeling studies are included to evaluate emission control measures and other strategies designed to bring air quality into compliance with federal regulations. Proposed enforcement mechanisms to enforce the control measures and strategies are a component of a SIP.

Development of a State Implementation Plan
Some examples of EPA approved components that may be submitted as part of a State Implementation Plan are listed below (EPA-SIP).

Table 3. EPA documents approved for inclusion in a SIP (EPA-SIP).

SIP Narratives	Part D Nonattainment Area Plans
Particulate Matter Plans	Attainment Demonstrations
Carbon Monoxide Plans	Transportation Control Measures (TCMs)
Ozone Plans	Committal Measures
Visibility Plans	Contingency Measures
Maintenance Plans	15% Rate of Progress Plans
Vehicle Inspection and Maintenance (I/M) SIPs	Emergency Episode Plans
Emissions Inventories	Non-regulatory and Non-TCM Control Measures
Monitoring Networks	State Statutes submitted for the purposes of demonstrating legal authority

It is important to define the region that is to be included in the air quality management plan, but this is usually defined previously by state and local governments and the region may be designated as nonattainment or near nonattainment by the U.S. EPA. Typical significant technical and political issues that affect the planning process include: 1) transportation conformity concerns and motor vehicle emission budgets, 2) pollutant transport from nearby regions, 3) technological limits to emission reductions from local sources, and 4) uncertainties in meeting the federal ozone standard by required dates. Transportation conformity is a requirement of the Clean Air Act that requires approval and federal funding of highway and transportation projects to be consistent with air quality goals established under a SIP.

One of the first actions in the development of an AQMP for a SIP is to determine what are the most important technical and policy questions that need to be addressed, especially for a local region. Some representative questions are listed below.

1. Will the existing policies lead to attainment of the NAAQS by some specific date?
2. What additional emission reductions are needed to meet attainment by that date?
3. How should new control measures (if any) be partitioned between stationary and mobile sources and what is the optimal timing of the new controls?
4. What are the motor vehicle emissions budgets for an area that would be commensurate with an attainment demonstration by the earliest practicable date?
5. What is the extent of impact due to transported pollutants on local air quality?
6. What type and extent of additional VOC and/or NOx controls in other regions to lower the transported pollutants would be beneficial to ozone levels and attainment in the local region? Does the level of transported pollutants from upwind sources prevent the local region from attainment?
7. Do conclusions reached on the basis of data analysis (in this context also known as weight of evidence attainment analysis) agree with those based on air quality modeling?
8. Are the episodes chosen for the modeling representative of typical conditions in the region?
9. Are the episodes adequate to characterize pollutant transport from upwind areas and other areas into the local region?

Data Collection

Routine Monitoring – Most regions with air quality problems will have routine monitoring sites (e.g. EPA-Monitoring). These sites measure mixing ratios of ozone, carbon monoxide, nitrogen dioxide, nitric oxide, sulfur dioxide and particulate matter. The time resolution of the gas measurements may be high, but the gas mixing ratios may be archived as hourly averages. Depending upon the instrumentation used the time resolution measurements of particulate matter may be much lower because PM is often collected on filters over periods ranging from a few hours to a few days. Various techniques are used to determine the number, size, mass and perhaps their concentration of the aerosol particles.

Special Field Studies – These may be conducted over a season, two to three months. For example, a special field studies might be conducted over a summer when ozone concentrations are highest or during the fall and winter when PM concentrations are high (depending upon location). Special field studies are much more intense than routine monitoring. Given the high level of effort and cost, extensive planning is required for a special field study. A number of sites, measurement platforms and instruments must be deployed and coordinated. A number of new networks of ground sites with meteorological towers, multiple aircraft, satellites and even research ships may be deployed along with frequent launches of meteorological sondes and ozonesondes. These provide high temporally and spatially resolved measurements of trace gases and PM. The PM measurements may include measurements of PM physical properties and composition. The goals of a special field study might include assessments of emission inventories and process analysis. The process analysis could include assessments of the effects of meteorology, atmospheric

transport and dispersion, gas-phase atmospheric chemistry, PM/aerosol/cloud chemical and physical processes, and radiation / actinic flux measurements. Extensive data analysis and computer modeling follow a special field study (e.g. Ryerson et al., 2013).

Weight of Evidence Attainment Analysis

There are EPA guidance documents available to guide this critical data analysis step. A weight of evidence analysis begins by characterizing year-to-year variations in monitored concentrations of the pollutant causing nonattainment (usually ozone or PM) over a specified multiyear period. A typical time period might be the most recent five years. For a weight of evidence analysis for the multiyear ozone trends the following statistics would be determined. These statistics may include: annual exceedances of the federal 1-hour and 8-hour ozone standards, annual maximum 1-hour and 8-hour concentrations for each monitoring site and total number of exceedances in nonattainment area; ozone design value for each year (4th high hourly daily maximum over a 3-year period); highest 2nd high daily maximum ozone concentration observed each year; highest running average 2nd high daily maximum ozone concentration, averaged over 3 consecutive years; highest 95th percentile daily maximum ozone concentration; total number of hours with observed concentrations greater than 124 ppb; annual average of the top 30 maximum 1-hour and 8-hour concentrations; and annual seasonal (June to September) average maximum 1-hour and 8-hour concentrations for all days, weekdays, Saturdays, and Sundays. The average timing of the peak 1-hour and 8-hour ozone concentrations for each monitoring site could be determined.

Figure 1 shows an example of a thirty-year trend in ozone concentrations for Los Angeles, Figure 2 shows a cumulative ozone reduction trend in the South Coast Air Basin (SoCAB) and Figure 3 shows the emissions trends in total VOC and NOx emissions in tons per day in the SoCAB.

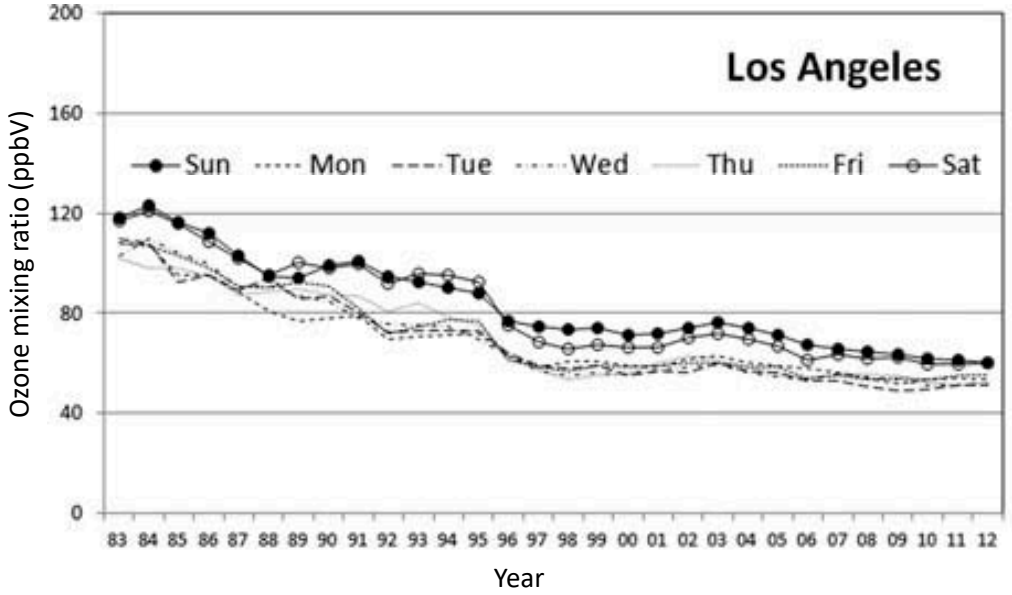


Figure 1. Thirty-year trend in 3-yr running seasonal (June 1 to September 30) mean daily ambient maximum 1-hr ozone by day of week for Los Angeles (Fujita et al., 2016).

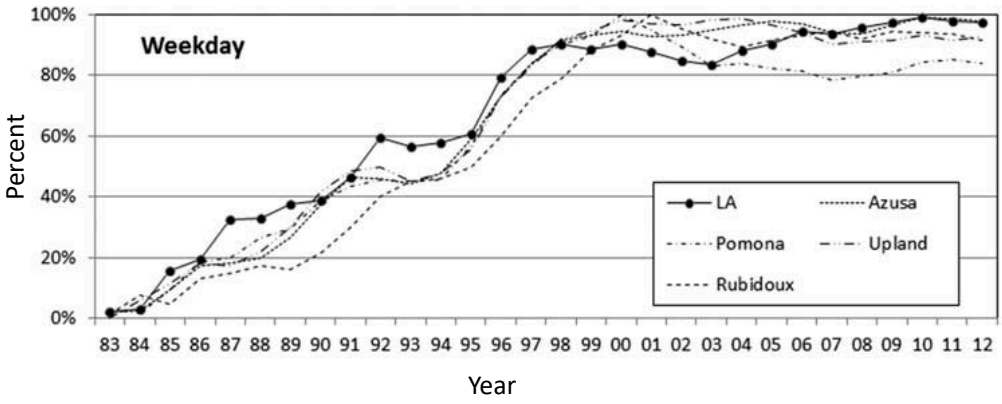


Figure 2. Cumulative ozone reduction trend in the South Coast Air Basin from 1982 to 2012 of (30-yr max − annual max)/(30-yr max − 30-yr min) in percent for weekdays (middle). Ratios are based on 3-yr running averages of the annual means of the daily maximum 1-hr ozone mixing ratios (Fujita et al., 2016).

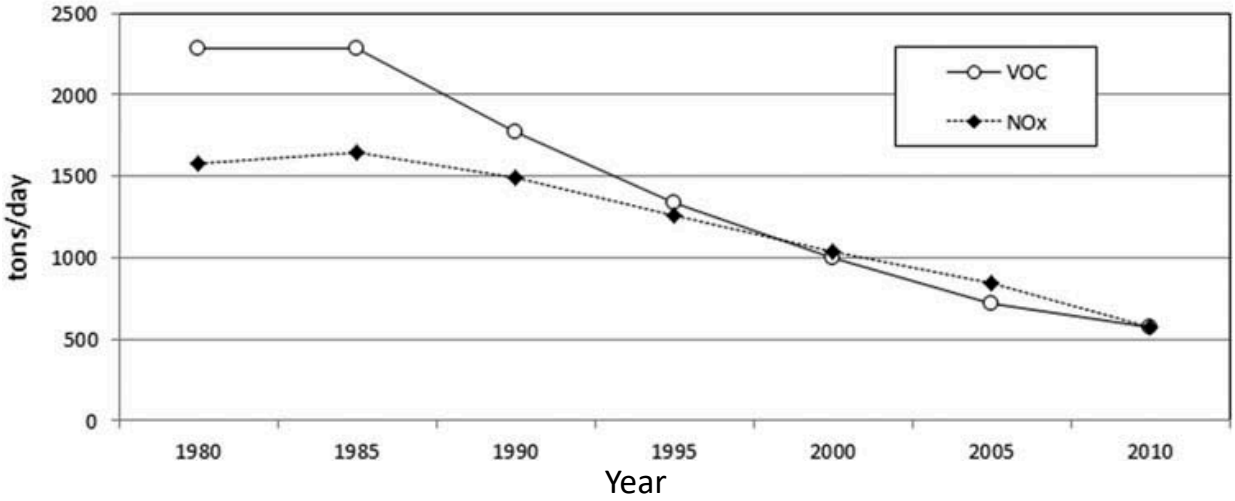
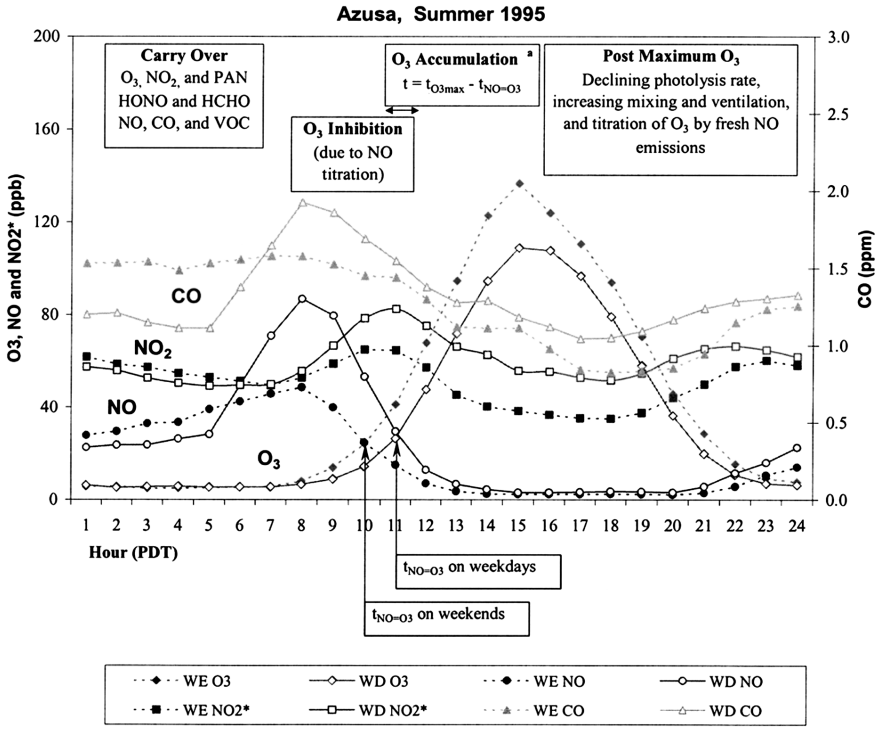


Figure 3. Trends in the total VOC and NO_x emissions in tons per day in the South Coast Air Basin (Fujita et al., 2016).

The objective the analysis presented in Figures 1 to 3 was to compare trends in the ambient concentrations of ozone concentrations with corresponding trends in VOC and NO_x emission inventory data. Routine monitoring data were used in this investigation. Note that if VOC data is not directly available then carbon monoxide data may be used as a partial surrogate for VOC emissions estimations and VOC concentrations. The major finding shown in Figures 1 to 3 is that ozone mixing ratios have not changed very much between 1999 and 2012 even though reductions in VOC and NO_x emissions have occurred. Clearly, this analysis would be important in the development of an air quality management plan and more work is needed to reconcile the trends in VOC and NO_x emissions with ozone trends with respect to current understanding of ozone formation.

Further analysis should take year-to-year variations in meteorology into account. Various curve fitting techniques, Classification of Regression Tree (CART), multi-linear regression, curvilinear regression and other techniques could be used to develop a statistical model for ozone or PM that could be used to develop the air quality management plan. The statistical model should be evaluated through comparison with a randomly selected portion of the data set not used to develop the model. This is very much like the procedure used to evaluate neural networks or other machine learning application. Curvilinear regression may be valuable for including NO_x or VOC in a trend analysis because has the capacity to capture the non-linear relationships of ozone and predictor variables better than multi-linear regression. In any case the statistical model should be used in the development of a general conceptual model of the ozone trends across the assessment region.

The more complete measurement datasets provided by a special study allow an analysis of detailed atmospheric chemistry impacts and chemical transport. Characterization and comparison of the spatial and diurnal patterns of pollutant concentrations including O_3, NO, NO_x, VOC, HCHO and others should be performed to examine the atmospheric chemistry occurring in the region. Figure 4 shows a typical diurnal plot for Azusa, California, which is a polluted site. Notice that ozone mixing ratios are higher on weekends than on weekdays. The weekend ozone is higher even though NO_x (NO_x = NO + NO_2) is lower on weekends than on weekdays. This finding has obvious implications for the development of ozone control strategies (Fujita et al., 2003).



a. O3 accumulation rate = [O3(max) - O3 ($t_{NO=O3}$)]/(t_{O3max} - $t_{NO=O3}$)

Figure 4. Mean summer 1995 diurnal variations of O_3 and NO at Azusa in the South Coast Air Basin during the weekday and weekend (Fujita et al., 2003).

Assess the Effect of Pollutant Transport on Local Air Quality

Results from a special field study may help in the assessment of pollutant transport on local air quality. Detailed chemical and meteorological observations from many upwind and downwind monitoring sites could be analyzed to identify those days in recent years with high air pollutant levels in a nonattainment area. These days could be classified according to their potential for the transport of ozone and PM and their precursors from sources into the nonattainment area. In other words, to classify days according to when air quality is mostly affected by local sources versus days that are more affected by the long-range transport of pollutants.

Meteorological modeling is a key component in the assessment of the effect of pollutant transport on local air quality. The goal of this assessment is to determine if high ozone days in the nonattainment area are strongly associated with days with long range transport. One way would be to run the Weather Research and Forecasting (WRF) model for a season that included the highly polluted days classified by their potential for long range transport. Meteorological modeling can determine and compare modeled and observed flow patterns and boundary layer structure on the synoptic scale and these can be compared with observations.

The WRF simulation could be used to drive a Lagrangian particle dispersion model to visualize regional scale transport with the number of emitted particles scaled to the emission rates of NO_x and VOC. The particles could be tagged according to their emission site. HYSPLIT (HYbrid Single Particle Lagrangian Integrated Trajectory) model is another example of a model that could be used. HYSPLIT is capable of computing trajectories, either forward or backward in time. The HYSPLIT has excellent advection algorithms, updated stability and dispersion equations and an option to include modules for chemical transformation. It requires a set of WRF meteorological simulations over the timeframe. It can be used to determine the relative number of trajectories from a source area that correspond with high pollution episodes in a nonattainment area.

Simulations for the Development of Emission Control Strategies

The Community Multiscale Air Quality Model (CMAQ) and the Comprehensive Air Quality model with Extensions (CAM-X) are two models that are often use for regulatory air quality modeling. These models along with WRF-Chem are more extensively discussed in the unit 3-D Air Quality Models. The WRF model is used to prepare the 3-D meteorological fields needed to run CMAQ and CAM-X. The chosen air quality model is run to simulate a base case. The base case is usually an episode, a season or even a year. The base case must be representative of meteorological and chemical conditions and the high pollutions must be typical according to the past record. The base case is evaluated against observations using statistics presented in the unit on Evaluation of Meteorological and Air Quality Simulations with Observations and this evaluation is known as an operational evaluation.

Operational evaluations consist of comparing concentration estimates from the model to ambient measurements. The key question in an operational model evaluation is to determine the extent of agreement between simulated and measured concentrations of ozone and its precursors. The measured and simulated ozone and its precursor concentrations should agree in their spatial extent and in their timing. Typical statistics for model evaluation include: the

comparisons of predicted and observed daily maximum 1-hr observed ozone concentrations, comparison of 90th percentile concentrations, mean bias (ppb) and mean normalized bias (%) and the mean error (ppb) and mean normalized error (%). Data available from special air quality studies might allow the comparison of model predictions with airborne measurements of VOCs (total VOC, homologous groups, and lumped VOC classes) along boundaries and above the mixed layer and the magnitude and constancy of their mixing ratios in space and time and the same may be done with airborne measurements of NO, and total nitrogen containing species.

Another kind of evaluation is a diagnostic evaluation. Diagnostic evaluations are required to determine if the air quality model is estimating ozone concentrations for the right reasons. The emissions, chemistry and transport are assessed to determine if these are treated correctly within the model. Ratios of chemical species that are sensitive to specific processes within the model may be examined and compared with measurements, for example the ratio of ozone to nitrogenous species such as NO_z or NO_y. NO_z is the sum of nitrogenous compounds produced from the oxidation of NO_x and these include nitric acid (HNO_3), nitrous acid (HONO), dinitrogen pentoxide (N_2O_5), peroxyacetyl nitrate (PAN), alkyl nitrates ($RONO_2$), peroxyalkyl nitrates ($ROONO_2$), the nitrate radical (NO_3), and peroxynitric acid (HNO_4). NO_y is the sum of NO_x and NO_z. NO_y is defined as the sum of NO_x and NO_z.

To be accepted for SIPs, the simulations may need to meet established criteria for accuracy and bias. The requirement to meet accuracy and bias standards may require making many simulations as sensitivity tests of input parameters (topographic resolution, model grid, synoptic fields verses radiosonde network, range and variation of sea/surface temperature, urban effects/roughness, sinks and sources of heat, data assimilation) to improve the model's performance for the base case simulation and to estimate uncertainties in model results. The uncertainties in the attainment and weight of evidence analyses needs to be estimated. The uncertainty associated with the key measurements and parameters associated the attainment and weight of evidence analysis is estimated from the information available. The sensitivity of the results of the attainment and weight of evidence analysis to the key parameters are estimated by varying the parameters over the range of uncertainties to determine how they affect the analysis. The range of possible final results given by varying the key parameters represents an estimate of the "error bars" associated with the attainment and weight of evidence analysis.

When the base case is successfully simulated, sensitivity studies are made with variations in the NO_x and VOC emissions and their initial conditions to generate reduction isopleth plots for selected sites. Figure 5 shows a PM reduction isopleth plot that was generated from a chemical box model. The figure shows isopleths of total particulate nitrate (NH_4NO_3) and ammonium sulfate ($(NH4^+)_2(SO4^=)$). These compounds are the major constituents of inorganic aerosol for the investigated site, Treasure Valley (Boise, Idaho; Stockwell et al.2003). The NO_x and VOC are expressed as percent of the base case emissions. The large dot in the upper right corner represents the base case, the x-axis shows percent reductions in VOC while the y-axis shows percent reductions in NO_x. The figure shows that at current NO_x levels, VOC reductions would be more effective in reducing inorganic PM. At current VOC levels, NO_x reductions actually increase inorganic PM until NO_x is reduced by at least 60%.

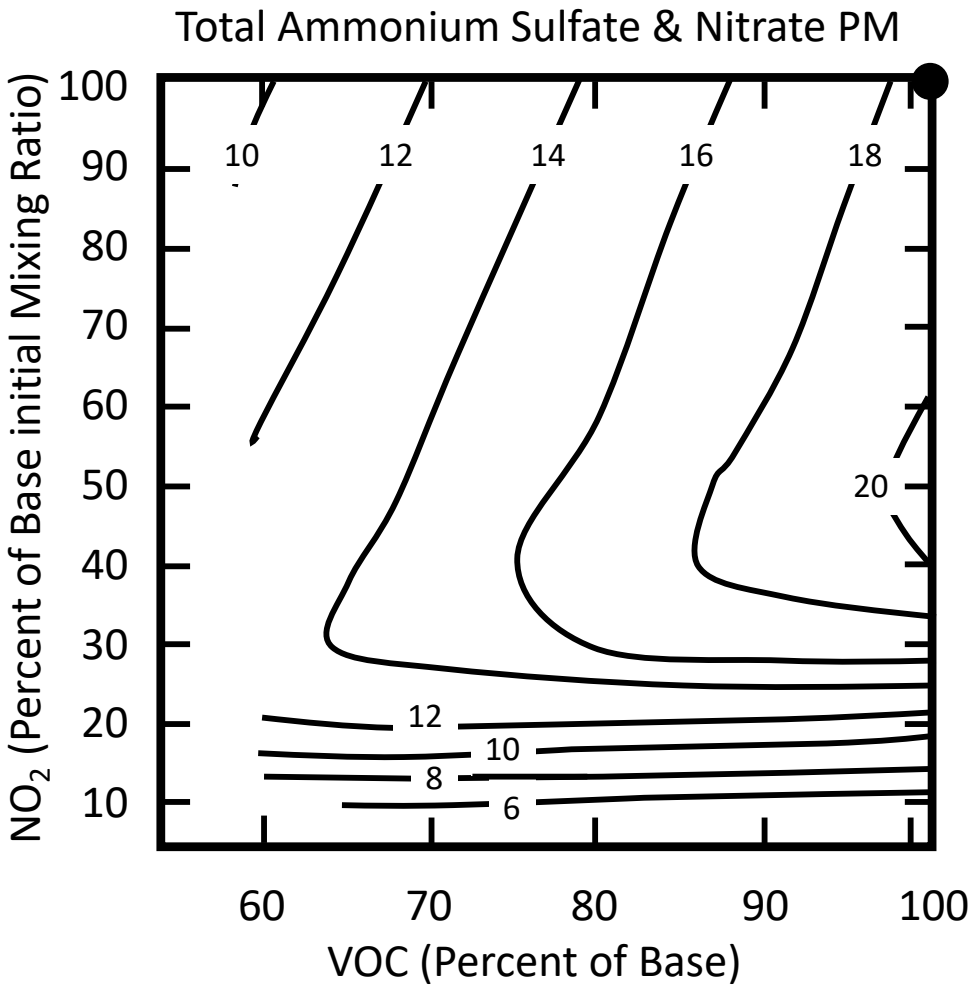


Figure 5. Isopleths of total particulate nitrate (NH_4NO_3) and ammonium sulfate ($(NH4^+)_2(SO4^=)$) expressed as mass concentrations μmg m^{-3}: The large dot in the upper right corner represents the base case. The NO_x and VOC emission rates are expressed as percent of the base case emissions (Stockwell et al.2003).

Air quality models can be used to map historical data and project future mixing ratios. Figure 6 shows isopleths for daily average ozone at Upland-San Bernardino California. Here the x-axis and y-axis show the logs of the initial VOC and NO_x respectively. In the middle of the plot the points show historical average values of VOC and NO_x mixing ratios. The diagonal line is called the ridgeline. The ridgeline divides the top portion where VOC control will be most effective in reducing ozone and the bottom portion were NO_x control will be most effective.

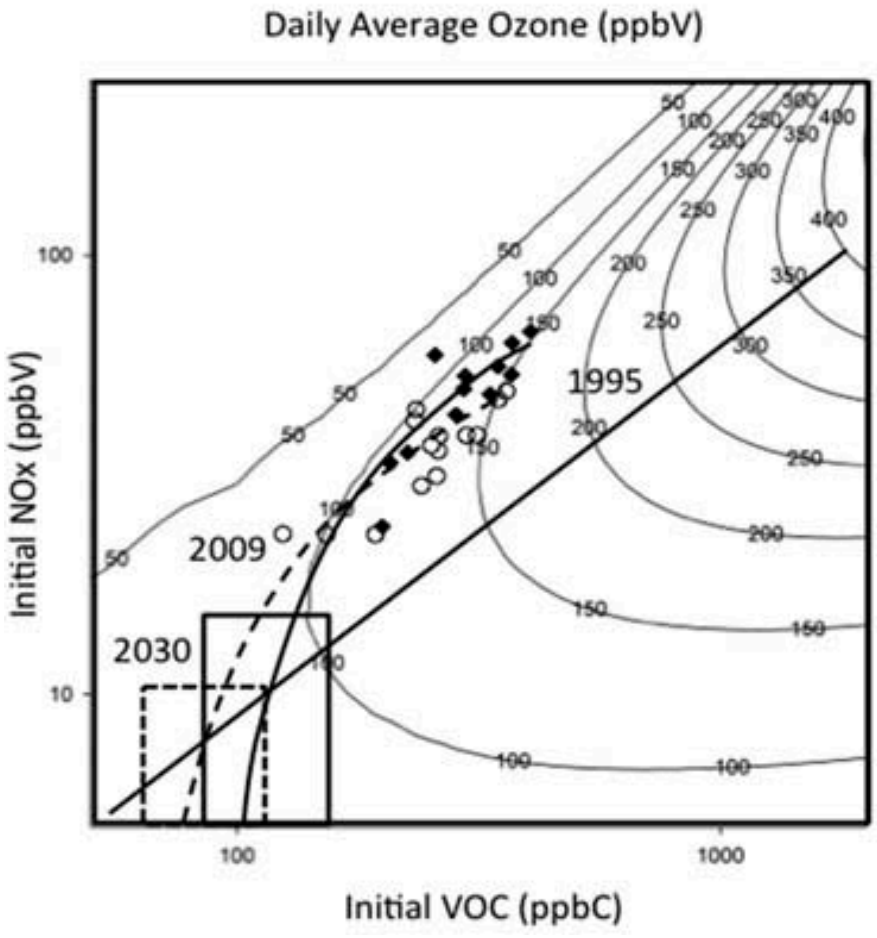


Figure 6. Isopleths for daily average ozone for Upland-San Bernardino. Plotted on the isopleths are average values of VOC and NO_x for the years 1995–2011. The solid diamonds are weekday averages and the open circles are weekends. Projections for 2030 are plotted as rectangles on the isopleths where the solid-line rectangle represents weekdays and the dashed-line rectangle represents weekends. The trend lines for the VOC and NO_x weekday (solid line) and weekend (dashed line) concentrations are plotted (Fujita et al., 2016).

Some other Considerations for Preparing an Air Quality Management Plan for a SIP

An air quality management plan would review progress achieved (or not) in the implementation of previous adopted state and local control measures. An analysis would be made to determine whether all the rules needed to effect emission reductions have been adopted, assess the degree of implementation of local measures and their success or failure. Available information regarding effectiveness or quantitative reconciliation of expected and actual emission reductions would be summarized. A determination of new rules, if required to meet attainment by a target date, would be part of the air quality management plan.

One contributing question is to determine how much emissions from upwind regions limit the effectiveness of local control measures on air quality in the nonattainment area. Given this

limitation, the simulation results would be used to assess control strategies in the nonattainment area. The plan would include a review of current emission inventory data. An evaluation of the effectiveness of VOC and NO_x controls in the nonattainment area would be central to the report. Potential stationary and mobile source control measures needed for attainment would be developed and assessed. Additional emission reductions for mobile and stationary sources would be identified along with future emission control technologies or approaches that are under study or development.

Disclaimer

We must state very clearly that here we are not trying to give advice or provide a template for a SIP development project. Here we are presenting a few selected topics on measurements and modeling that are relevant to SIP and other air quality public policy applications. Please consult EPA, state and local guidance documents for your specific purpose. We and our sponsors accept no liability for the misapplication of anything in this document.

References

ARB California Air Resources Board Glossary, https://ww2.arb.ca.gov/about/glossary

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Assignment

Data for this assignment is available in the Excel spread sheet, O3ISOTABLE.xlsx, which provides a table of maximum ozone mixing ratios in units of ppbV. The top first row corresponds to the x-axis and it gives the log10 of the initial mixing ratios of VOC (Log [VOC, ppbC]) in steps of 0.1 ranging from 2.1 to 4.0. The vertical values in the first column correspond to the y-axis and it gives the log10 of the initial mixing ratios of NO_x (Log [NOx ppbN]) in steps of 0.1 ranging from 0.9 to 2.9. This means that the upper left grid cell of the O_3 mixing ratios corresponds to Log [VOC] = 2.1; Log [NO_x] = 0.9 while the lower right cell corresponds to Log [VOC] = 4.0; Log [NO_x] = 2.9.

1) Use the software platform of your choice to make a contour plot (isopleth plot) of the ozone mixing ratios with Log [VOC] as the x-axis and Log [NO_x] as the y-axis.

2) In what regions of the isopleth plot would VOC control be most effective? In what regions of the isopleth plot would NO_x control be most effective? Please consider adding a ridgeline to your plot.

3) Use what you learned about atmospheric chemistry to explain the shape of the isopleth plot.

4) Parrish and Stockwell (2015) show that air quality and Los Angeles and Beijing have followed similar paths. Discuss the implications for these two cities and other megacities.