

EPA-454/R-99-054  
December 1999

**A Simplified Approach for Estimating Secondary Production  
of Hazardous Air Pollutants (HAPs) Using the OZIPR Model**

**Replaces Section 2.4 in Dispersion Modeling of Toxic Pollutants in Urban  
Areas, EPA-454/R-99-021**

## **Notice**

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## **Acknowledgments**

For their thoughtful comments on this document, the authors wish to thank Deborah J. Luecken, Ned Meyer and Jawad S. Touma of the U. S. Environmental Protection Agency.

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## **Executive Summary**

Title III of the 1990 Amendments to the Clean Air Act stipulates regulation of chemicals classified as hazardous air pollutants (HAPs). These are substances that are either known to cause or suspected of causing a threat of adverse human health effects. These compounds are found in the atmosphere as a result of primary emissions or from the transformation of organic compounds emitted into the atmosphere by stationary or area sources. Carbonyl compounds represent an important class of organic compounds found on the list of HAPs. This study examines three of these compounds, formaldehyde, acetaldehyde, and acrolein, to determine the relative importance of their formation through primary and secondary processes.

Several very complex models exist that include both dispersion and atmospheric chemistry to yield HAPs concentration estimates. However, these models are very expensive to execute, often requiring the use of supercomputers. The goal of this study was to explore whether a simplified approach could provide useful estimates of total HAPs concentrations. The approach taken here was to estimate secondary HAPs production with a stand-alone model, run in a personal computing environment, that incorporated only nondispersive processes, such as photochemistry. The results from this model would then be coupled to those from a relatively simple dispersion model. The study results have been quite encouraging, because in comparison with available monitoring data, the approach used here seems to perform as well as more complex models such as RADM.

The photochemical modeling was done using the OZIPR model, a one-dimensional box model with a time-varying box height. Emissions were added to the box by time of day; factors such as temperature, relative humidity, atmospheric pressure, solar radiation, and deposition were used to determine chemical reaction rates. OZIPR was originally designed to predict ozone concentrations, but the concentrations of other stable intermediate compounds, such as aldehydes, are also calculated during the course of the simulations. The model is generally run only for the daylight hours on a single day. The reaction mechanism used in the current study is based on the widely used SAPRC97 mechanism. The model outputs chemical concentrations as a function of time. These estimates can then be used in conjunction with output from other models that account for dispersion but not for

chemical transformations. The output data from the OZIPR model are presented in several ways (e.g., annual and seasonal averages, time series profiles) to facilitate their use with dispersion models.

Ten study areas were selected for this project: Atlanta, Boston, Chicago, Denver, Houston, Los Angeles, Phoenix, Pittsburgh, Seattle, and Washington D.C. In each study area, urban and rural counties were chosen. The urban counties are centered on the cities in question; the rural counties are near enough to the urban areas to have similar meteorological patterns, but different emissions based on their lower population and distinct land use patterns. As many as 48 model runs were needed to adequately characterize each city.

The results show that secondary formation generally accounted for approximately 90% of the ambient formaldehyde and acetaldehyde and approximately 85% of acrolein; these percentages varied only slightly between cities. Annual averages for the urban secondary formation of formaldehyde ranged from 3.0  $\mu\text{g m}^{-3}$  for Seattle to 13.4  $\mu\text{g m}^{-3}$  for Los Angeles. For acetaldehyde, the corresponding numbers are 5.0  $\mu\text{g m}^{-3}$  for Phoenix to 18.0  $\mu\text{g m}^{-3}$  for Los Angeles; for acrolein, the values are 0.2  $\mu\text{g m}^{-3}$  (five cities) to 0.7  $\mu\text{g m}^{-3}$  for Los Angeles. Generally, the rural values for each of the three HAPs ranged between 30% and 50% less than the urban values. The ambient formaldehyde concentrations were usually greater for southern cities.

Tables of secondary concentrations were also developed for incorporation with dispersion models. These tables are designed to provide an area-wide additive adjustment to concentrations of the compounds as a function of time and season or on an annual basis. Section 8 contains these results.

The user can choose to use the information in this report in the following ways:

1. The most elaborate information can be obtained from running OZIPR using city-specific parameters as described in Section 9 and Appendix A.
2. Tables 8-1 through 8-6 can be used in conjunction with a dispersion model to provide seasonal and hourly adjustments (Tables 8-1 through 8-3) or annually (Tables 8-4 through 8-6) for secondary production.
3. When the location of interest is dissimilar from those studied here and the OZIPR model cannot be run, Section 9 provides guidance on adjusting estimates of aldehyde concentrations for secondary production.

Section 9 discusses each of these approaches.

## **Section 1**

### **Introduction**

Title III of the 1990 Amendments to the Clean Air Act stipulates regulation of chemicals classified as hazardous air pollutants (HAPs). These are substances that either are known to cause or are suspected of causing adverse human health effects. The list includes 189 compounds, many of which are volatile or semivolatile organic compounds. These compounds are found in the atmosphere as a result of primary emissions and the transformation of organic compounds (both hazardous and nonhazardous) emitted into the atmosphere by stationary, area, or mobile sources.

Carbonyl compounds represent an important class of organic compounds (Carlier et al., 1986) found on the list of HAPs. At present, four aldehydes—acetaldehyde, acrolein, formaldehyde, and propionaldehyde—and three ketones—acetophenone, 2-butanone (i.e., methyl ethyl ketone), and methyl-*i*-butyl ketone—are represented. A unique feature of these compounds is that they are emitted directly into the atmosphere (by both natural and anthropogenic means) and formed as products from the oxidation of other emitted hydrocarbons.

Relatively little previous work has been undertaken to evaluate the fraction of ambient carbonyl compounds due to primary versus secondary processes. Grosjean and coworkers (1983) undertook a study of the relative production of carbonyl compounds in the metropolitan Los Angeles area in the early 1980s. Ambient levels as high as 70, 56, and 37 ppbv were measured for formaldehyde, acetaldehyde, and propionaldehyde, respectively. Changes in carbonyl/carbon monoxide (CO) ratios determined for individual pollution events allowed the investigators to estimate that from 44% to 98% of the ambient formaldehyde, acetaldehyde, and other carbonyl compounds resulted from secondary formation. (CO was assumed to be of primary origin only.) Modeling studies by these investigators tended to confirm their results.

In another study, Harley and Cass (1994) ran a photochemical air quality model to predict concentrations for several HAPs, including formaldehyde, acetaldehyde, acrolein, and phenol. (Modeling results for acetone, which is not a HAP, were also presented.) The study was designed to follow the secondary production of the HAPs at various points in the Los Angeles air shed. For the two-day period studied, secondary products were found to contribute significantly to the observed concentrations of these HAPs, particularly in downwind locations where the ozone concentrations

tend to be highest in the afternoon. The results of the model were compared to ambient data obtained as part of the summer 1987 Southern California Air Quality Study and gave only fair agreement.

Both the Grosjean and Harley and Cass studies are subject to a number of limitations. For example, in the Grosjean study CO concentrations did not include contributions from secondary chemistry; thus, the secondary component might have been an underestimate. Second, both studies were conducted in a single city (Los Angeles) under summertime conditions, which is when secondary products are expected to be the greatest. The modeling results were compared to concentrations obtained from individual pollution episodes. Thus, data for seasonal or annual averages may be difficult to extrapolate, especially for other less polluted areas. Moreover, the studies were performed during the early to mid-1980s when ambient volatile organic compound (VOC) emissions were considerably higher than they are today. With the advent of reformulated gasoline, the composition of fuels has changed in several areas of the country, particularly in severe nonattainment areas. Finally, photochemical modeling parameters for formaldehyde and other aldehydes have been improved since the early 1980s. These factors taken together might lead to a different secondary contribution of carbonyl compounds than found in these earlier studies.

The most accurate means of predicting concentrations and sources of HAPs would be to use a full three-dimensional dynamic atmospheric model such as the Urban Airshed Model (UAM), which accounts for emissions, chemistry, and dispersion simultaneously. However, considerable expertise, and in some cases high costs and computing requirements, make these models burdensome to run.

The goal of this study is to determine whether a simplified method for modeling secondary HAPs production can provide reasonable estimates of the levels of these chemicals. The approach taken in this study is to model secondary HAPs production apart from dispersion. The chemistry is modeled using the OZIPR program (the research version of the EPA's Ozone Isopleth Plotting Program). In this study, the OZIPR model is used to estimate the ratio of secondary to primary formation and the concentrations for each target HAP. The results can be applied in several ways, as discussed in Section 9. The chemistry and dispersion are not properly coupled in this approach, but it is considerably simpler to make the calculations in this manner, and the required inputs for meteorology and emissions are less burdensome.

In this study a simplified approach was developed for modeling the concentrations for a subset of aldehydes (i.e., formaldehyde, acetaldehyde, and acrolein) in selected study areas to allow comparison of the primary and secondary formation. While emission inventories exist for these chemicals, the estimation of atmospheric concentration is complicated by the fact that they are highly reactive chemically; that is, all three aldehydes are produced and destroyed in the atmosphere on short time scales. Chemical lifetimes for each of the compounds range between 3 and 6 hours in daylight urban atmospheres. On balance, the production of these HAPs from other organic species

is expected to outweigh their chemical removal, yielding higher atmospheric concentrations than if no chemical reactions occurred.

This report provides justification for the approach taken and discusses the modifications to the base chemical mechanism and other input parameters required to estimate secondary formation for the compounds of interest. The SAPRC chemical mechanism is modified to include additional reactions for modeling acrolein. The overall approach to the study is described in Section 2. Modifications to the chemical mechanism are summarized in Section 3. The distribution of VOCs used in the OZIPR runs is discussed in Section 4. The methods of preparing emission rates and meteorological data for input to the model are discussed in Sections 5 and 6, respectively. Section 7 details the method used for distinguishing primary from secondary formation and describes the preparation of OZIPR input files; a more detailed explanation of the preparation of input files is given in Appendix A. Section 8 contains the results of the study and discusses their use in adjusting estimates of primary production for the three aldehydes. Section 9 explains the practical use of the results obtained from this study.

Finally, a word of caution about this study. EPA is interested in obtaining comparative annual-average estimates of ground level concentrations of the 188 HAPs that are considered to be important air toxics. The estimates—to be comparable—must include both concentrations associated with HAPs directly emitted (primary production) and indirectly produced via atmospheric processes (secondary production). The Agency also is interested in obtaining these estimates for relatively large geographical domains, such as urban or metropolitan areas. Obtaining accurate annual average estimates for pollutants that undergo chemical transformations in the ambient air is very difficult. This report, then, addresses topics in which there remains a number of significant uncertainties. Some examples of these uncertainties are: (1) ozone photochemistry in the winter, which usually is not addressed; and (2) using chemical mechanisms which accurately predict ozone, but with relatively less attention paid to the ability to predict the carbonyl species. Other difficulties include temporal differences inherent in short-term modeling of ozone episodes, which is usually done, versus the need for long-term averages associated with the modeling of point and area sources to evaluate their chronic cancer and non-cancer potential.

In practice, there is a great incompatibility between the extensive amount of resources needed to exercise photochemical models, applied to episodes of limited duration, and the problem at hand: the estimation of annual average concentrations for certain photochemically active chemicals using relatively unsophisticated emission inventories. Added to this is the context within which results using the described methodology will be used. That is, results will likely be used in concert with unit risk factors to estimate the risk of getting cancer if subjected to long term exposure to the concentrations calculated with the approach. Thus, it is important that the report results are used in the context within which the described estimates are being made. It is easy to identify features in

the methodology which fall short of the most scientifically rigorous treatment; however, based on the results of this study, EPA staff believes that it is unlikely that the most rigorous treatment of secondary-production processes would substantially improve our ability to predict ground-level HAPs concentration given the current state of scientific knowledge and available data. Thus, it will take a significant amount of scientific and technical research to substantially reduce uncertainty in these estimates. Until that work is accomplished, EPA staff believes that it is important to address the issue using the best information available, and this study utilizes the most current knowledge of the subject.

## Section 2

### General Approach for Estimating Secondary Formation of Target HAPs

The approach taken in this study was to separate the modeling of chemistry and dispersion, focusing on the photochemical formation of secondary HAPs. Chemical transformations of confined urban and rural atmospheres were modeled using the OZIPR program. In general, any comprehensive model describing reactive transformation in a large area should couple chemistry and dispersion to achieve proper spatial and temporal chemical distributions. However, in addition to the computing power required, chemical and meteorological inputs to such three-dimensional models are quite demanding, especially in terms of the mass emissions of VOCs as a function of time and location. While a three-dimensional model might be suitable for a research study of a limited number of episodes, the simplified approach described here, because of its limited input requirements, is far more amenable to examining a broad range of cities, seasons, and meteorological conditions.

The OZIPR model is a one-dimensional box model with a time-varying box height (i.e., the height of the mixing layer). This model was originally designed to predict ozone concentrations; however, the concentrations of other relatively stable intermediate compounds, especially aldehydes, are necessarily determined during the course of the calculations. Moreover, since carbonyl compounds and ozone result mainly from photochemical secondary processes, the model may be expected to provide reasonable estimates for carbonyl compounds.

The OZIPR model, which is generally run for daylight hours on a single day, calculates solar radiation from the zenith angle of the sun based on date, location, and time of day. Inputs include initial concentrations and hourly emission rates for the relevant chemical species and the meteorological parameters for temperature, humidity, mixing heights, and atmospheric pressure. To allow flexibility in using the model, the chemical species and reactions are not fixed in the program code, but are provided as inputs to the model when it is run. The modeling runs take advantage of this feature by allowing modification to a standard chemical mechanism that includes reactions affecting the target HAPs, such as acrolein.

The hourly emissions input data are typically obtained from emissions inventories. Temperature, barometric pressure, and relative humidity are provided by the National Weather Service. For this study, mixing height data were supplied by EC/R, Inc.

The OZIPR model was designed to be quite flexible, with the user controlling the specific details of the model run through an *input file*. All of the model runs done for this study used the same compiled program code with the only difference between runs found in the input file; the changing input file reflected, for example, different cities and meteorology. Thus, individual changes to the scenarios were easily implemented. The OZIPR user's guide (Gery and Crouse, 1990) provides a more general explanation on how to run the model, and information provided in Section 7 and Appendix A explains the purpose and structure of the input files and other information used to estimate the primary and secondary HAP production.

To obtain an adequate representation of conditions across the United States, 10 study areas were selected: Atlanta, Boston, Chicago, Denver, Houston, Los Angeles, Phoenix, Pittsburgh, Seattle, and Washington, DC. In each study area, urban and rural counties were selected to allow reasonably defined emissions data to be used. When multiple counties were selected in one study area, they were treated as effectively one larger county by calculating average emissions over the total area. The urban counties were centered on the selected cities; the rural counties were close enough to the urban areas to have similar weather but different emissions based on their lower population and distinct land-use patterns. The counties were selected to be representative and did not include all possible counties in each study area. The land areas of each county were used in calculating emission factors (mass per unit area per hour). Table 2-1 lists the study areas and provides geographic information for each.

Up to 48 runs were made for each study area. There were four seasons: winter (December–February), spring (March–May), summer (June–August); and autumn (September–November). For each season, two or three typical days, differing in meteorology, were used. To determine primary and secondary formation, two runs were made for each urban and rural area; one run included primary emissions of the target HAPs and one did not.

**Table 2-1. Counties Selected in Each Study Area**

<b>Study Area</b>	<b>County</b>	<b>State</b>	<b>FIPS Code</b>	<b>Type</b>	<b>Area (km<sup>2</sup>)</b>
Atlanta	Fulton	GA	13121	Urban	1369.3
Atlanta	DeKalb	GA	13089	Urban	694.9
Atlanta	Cobb	GA	13067	Urban	881.2
Atlanta	Walton	GA	13297	Rural	852.8
Boston	Norfolk	MA	25021	Urban	1035.0
Boston	Suffolk	MA	25025	Urban	151.6
Boston	Plymouth	MA	25023	Rural	1720.9
Boston	Rockingham	NH	33015	Rural	1800.7
Chicago	Cook	IL	17031	Urban	2449.3
Chicago	McHenry	IL	17111	Rural	1564.7
Denver	Denver	CO	08031	Urban	397.0
Denver	Clear Creek	CO	08019	Rural	1024.2
Denver	Elbert	CO	08039	Rural	4793.8
Houston	Harris	TX	48201	Urban	4478.1
Houston	Colorado	TX	48089	Rural	2494.3
Los Angeles	Los Angeles	CA	06037	Urban	10515.3
Los Angeles	Orange	CA	06059	Urban	2045.3
Los Angeles	Ventura	CA	06111	Rural	4781.0
Phoenix	Maricopa	AZ	04013	Urban	23838.5
Phoenix	Pinal	AZ	04021	Rural	13908.3
Pittsburgh	Allegheny	PA	42003	Urban	1891.3
Pittsburgh	Westmoreland	PA	42129	Rural	2648.5
Seattle	King	WA	53033	Urban	5506.6
Seattle	Snohomish	WA	53061	Rural	5413.6
Washington, DC	DC	DC	11001	Urban	159.1
Washington, DC	Arlington	VA	51013	Urban	67.0
Washington, DC	Alexandria	VA	51510	Urban	39.6
Washington, DC	Loudoun	VA	51107	Rural	1346.6

### **Section 3**

## **Modifications to the Chemical Mechanism**

To determine the secondary formation of the aldehydes under consideration, a chemical mechanism is required to quantitatively describe the transformation of VOCs and NO<sub>x</sub> to photochemical products. OZIPR has been structured to permit the use of arbitrary chemical mechanisms. There are three major chemical mechanisms used in a wide range of oxidant formation applications in the United States: Carbon Bond IV (CBIV), RADM II, and SAPRC97. In CBIV, VOCs are grouped together in quasi-chemical units, whereby individual VOCs lose their chemical identity. Since this application requires individual species, such as acetaldehyde and acrolein, CBIV would not be appropriate here. SAPRC97 was selected for this study since it is the most up to date mechanism available; it has been placed in the public domain and allows detailed conversion of VOCs to products including formaldehyde (HCHO) and acetaldehyde (ALD2). Input parameters to SAPRC97 are straightforwardly generated from ambient measurements of 6–9 a.m. nonmethane hydrocarbons. However, modifications to the mechanism are required to include the formation and loss processes for acrolein.

SAPRC97, developed by Dr. W.P.L. Carter at the University of California–Riverside, is based largely on the SAPRC93 mechanism and earlier versions, with updates for more accurate rate constants (Carter, 1990; Carter and Lurmann, 1991; detailed information on the mechanism can be found at the following Web address: [www.cert.ucr.edu/~carter/saprc97.htm](http://www.cert.ucr.edu/~carter/saprc97.htm)). The SAPRC mechanism consists of 134 reactions. Of these reactions, the first 38 reactions represent standard reactions of inorganic species applicable in all tropospheric systems. The balance of reactions represent reactions of organic radicals and stable organic compounds. Many of the organic compounds are combined according to the monikers found in Section 4. However, the compounds of interest in this study retain their identity. In the SAPRC97 mechanism, 22 reactions lead to formation and 5 reactions lead to removal of formaldehyde (HCHO). Similarly for acetaldehyde (ALD2), 18 reactions lead to formation and 3 reactions lead to removal. The most important removal processes for formaldehyde and acetaldehyde are reactive loss with the hydroxyl radical (OH) and photolytic loss. Removal of acetaldehyde from the atmosphere by reaction with OH is approximately 60% faster than for formaldehyde. By contrast, photolysis is somewhat more significant for formaldehyde than for acetaldehyde due to formaldehyde's greater absorption and more efficient

quantum yield in the actinic region of the solar spectrum. Photolysis is a function of the sun's zenith angle and thus is highly dependent on the time of day and the season. However, the mechanism contains no formation or removal reactions for acrolein.

The mechanism was modified to allow formation and removal of acrolein. Only one hydrocarbon readily found in the atmosphere, 1,3-butadiene (BDIE in the mechanism), is known to lead to acrolein formation. The five reactions summarized in Figure 3-1 were added to the mechanism along with associated rate constants (units:  $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ ) in Arrhenius form ( $A e^{-E_a/RT}$ ), where A is the pre-exponential factor,  $E_a$  is the activation energy for the reaction, R is the gas constant, and T is the temperature. Rate constants for the OH reaction were based on values taken from Atkinson (1989).

**Figure 3-1. Chemical reactions added to basic mechanism to account for formation and destruction of acrolein.**

---

{ 135 }	ACRO + OH	=	#1.9900E-11;
{ 136 }	ACRO + O3	=	#2.8000E-18;
{ 137 }	ACRO + NO3	=	#1.2000E-15;
{ 138 }	BDIE + OH	= ACRO	#1.4800E-11 @ 448;
{ 139 }	BDIE + O3	= ACRO	#3.3000E-14 @ -2500;

---

The extremely rapid reaction of OH with 1,3-butadiene causes reaction 138 to dominate the removal of 1,3-butadiene during daylight hours. (Reaction numbers refer to reactions found in Figure 3-2.) The reaction of 1,3-butadiene with the nitrate radical is negligible and is not included in the mechanism. The stoichiometry for the formation of acrolein is shown to be 1:1 on a molar basis. While relatively few product studies have been performed to verify this stoichiometry, it would not be possible to form more than one molecule of acrolein per molecule of 1,3-butadiene reacted. Products are not assigned for secondary reactions of acrolein (reactions 135–137), since relatively little reliable information is available from the reaction products from its ozone and radical reactions. Given the extremely low concentration of acrolein in the system, it is expected that inclusion of acrolein products would not increase the reactivity of the system. The complete reaction scheme for the generation and removal of formaldehyde, acetaldehyde, and acrolein (i.e., SAPRC97 with modifications) is presented in Figure 3-2. An explanation of the terminology used in Figure 3-2 can be found in Appendix A and the OZIPR user's guide (Gery and Crouse, 1990).

**Figure 3-2. Modified SAPRC97 mechanism for determining secondary formation of formaldehyde, acetaldehyde, and acrolein. This listing represents the contents of the file, CAL97.MEC, named in the OZIPR input file.**

! The SAPRC97 mechanism, with two added species: 1,3-butadiene (BDIE) and acrolein (ACRO).

!

MECH [CM] >

CNUM=

ALK4 = 4.5,  
 ALK7 = 7.0,  
 ETHE = 2.0,  
 PRPE = 3.0,  
 TBUT = 4.0,  
 TOLU = 7.0,  
 XYLE = 8.0,  
 TMBZ = 9.0,  
 HCHO = 1.0,  
 ALD2 = 2.0,  
 RCHO = 3.0,  
 ACRO = 3.0,  
 BDIE = 4.0,  
 NRHC = 1.0;

REACTIONS =

```

{1} NO2      =      NO      +      O      #0.016667 /L1;
{2} O        =      O3      #1.0500E+03 @ -1282.0;
{3} O + NO2  =      NO      #6.5000E-12 @ -120;
{4} O + NO2  =      NO3     #1.1100E-13 @ -894.0;
{5} NO + O3  =      NO2     #2.0000E-12 @ 1400.0;
{6} NO2 + O3 =      NO3     #1.4000E-13 @ 2500.0;
{7} NO + NO3 = 2*NO2     #1.7000E-11 @ -150.0;
{8} NO + NO  = 2*NO2     #8.1500E-20 @ -528.0;
{9} NO2 + NO3 = N2O5     #4.6200E-13 @ -273.0;
{10} N2O5    =      NO2     +      NO3    #1.3300E+15 @ 11379;
{11} N2O5 + H2O = 2*HNO3   #1.0000E-21;
{12} NO2 + NO3 =      NO     +      NO2    #2.5000E-14 @ 1228.0;
{13} NO3     =      NO      #0.016667 /R1;
{14} NO3     =      NO2     +      O      #0.016667 /R2;
{15} O3      =      O       #0.016667E-03 /R3;
{16} O3      =      O1D    #0.016667E-03 /R4;
{17} O1D + H2O = 2*OH     #2.2000E-10;
{18} O1D     =      O       #7.2000E+08;
{19} NO + OH  =      HONO   #4.0300E-13 @ -833.0;
{20} HONO    =      NO      +      OH     #0.016667 /R5;
{21} NO2 + H2O =      HONO  + -1* NO2 + HNO3 #4.0000E-24;
{22} NO2 + OH  =      HNO3   #9.5700E-13 @ -737.0;
{23} HNO3 + OH =      NO3    #6.4500E-15 @ -818;
{24} CO + OH  =      HO2     #2.400E-13;
{25} OH       =      HCHO    + RO2R + RO2  #28.3^2 @ 1280.0;
{26} O3 + OH  =      HO2     #1.6002E-12 @ 941.0;
{27} NO + HO2 =      NO2    +      OH     #3.7000E-12 @ -242.0;
{28} NO2 + HO2 =      HNO4   #1.0200E-13 @ -773.0;
{29} HNO4    =      NO2    +      HO2    #4.3500E+13 @ 10103;
{30} HNO4 + OH =      NO2    #1.3000E-12 @ -380;
{31} O3 + HO2 =      OH      #1.1000E-14 @ 500.0;
{32} HO2 + HO2 =      H2O2   # 2.200E-13 @ -619.0;
{33} HO2 + HO2 + H2O = H2O2 # 3.100E-34 @ -2818.0;
{34} NO3 + HO2 =      HNO3   # 2.200E-13 @ -619.0;
{35} NO3 + HO2 + H2O = HNO3 # 3.100E-34 @ -2818.0;
{36} H2O2    = 2*OH        # 0.016667E-03 /R6;
{37} H2O2 + OH =      HO2    # 3.3000E-12 @ 200.0;
{37a} HO2 + OH =           # 4.6000E-11 @ -230;
{38} RO2 + NO =      NO      # 4.2000E-12 @ -181.0;
{39} RCO3 + NO =      NO      # 4.2000E-12 @ -180.0;
{40} RCO3 + NO2 =      NO2    # 2.8000E-12 @ -180.0;
{41} RO2 + HO2 =      HO2    # 3.4000E-13 @ -800;
{42} RCO3 + HO2 =      HO2    # 3.4000E-13 @ -800;
{43} RO2 + RO2 =           # 1.0000E-15;
{44} RO2 + RCO3 =           # 1.8600E-12 @ -530;
{45} RCO3 + RCO3 =           # 2.8000E-12 @ -530;
{46} RO2R + NO =           NO2 + HO2    # 4.2000E-12 @ -181.0;
{47} RO2R + HO2 =          ROOH    # 3.4000E-13 @ -800;

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{48} RO2R + RO2      = 0.5*HO2 + RO2      # 1.0000E-15;
{49} RO2R + RCO3    = 0.5*HO2 + RCO3    # 1.8600E-12 @ -530;
{50} ROOH           = HO2 + OH      # 0.016667E-03 /R7;
{51} HCHO           = 2*HO2 + CO    # 0.016667E-03 /R8;
{52} HCHO           = CO           # 0.016667E-03 /R9;
{53} HCHO + OH      = HO2 + CO      # 1.125000E-12^2.0 @ -648;
{54} HCHO + NO3     = HNO3 + HO2 + CO # 2.8000E-12 @ 2516;
{55} HCHO + HO2     = RO2R + RO2     # 1.0000E-14;
{56} ALD2           = CO + HCHO + HO2 + RO2R + RO2 # 0.016667E-03 /R10;
{57} ALD2 + OH      = MCO3 + RCO3    # 5.55000E-12 @ -311;
{58} ALD2 + NO3     = HNO3 + MCO3 + RCO3 # 1.40000E-12 @ 1860;
{59} MCO3 + NO      = NO2 + HCHO + RO2R + RO2 # 4.2000E-12 @ -180;
{60} MCO3 + NO2     = PAN           # 2.8000E-12 @ -180;
{61} MCO3 + HO2     = ROOH + HCHO    # 3.4000E-13 @ -800;
{62} MCO3 + RO2     = 0.5*HO2 + HCHO + RO2 # 1.8600E-12 @ -530;
{63} MCO3 + RCO3    = HO2 + HCHO + RCO3 # 2.8000E-12 @ -530;
{64} PAN           = MCO3 + NO2 + RCO3 # 2.0000E+16 @ 13542;
{65} RCHO           = ALD2 + HO2 + CO + RO2R + RO2 # 0.016667E-03 /R11;
{66} RCHO + OH      = RCO3 + PCO3    # 8.5000E-12 @ -252;
{67} RCHO + NO3     = HNO3 + PCO3 + RCO3 # 1.4000E-12 @ 1860;
{68} PCO3 + NO      = NO2 + ALD2 + RO2R + RO2 # 4.2000E-12 @ -180;
{69} PCO3 + NO2     = PPN          # 8.4000E-12;
{70} PCO3 + HO2     = ROOH + ALD2    # 3.4000E-13 @ -800;
{71} PCO3 + RO2     = 0.5*HO2 + ALD2 + RO2 # 1.8600E-12 @ -530;
{72} PCO3 + RCO3    = HO2 + ALD2 + RCO3 # 2.8000E-12 @ -530;
{73} PPN           = PCO3 + NO2 + RCO3 # 1.6000E+17 @ 14073;
{74} ACET           = MCO3 + HCHO + RCO3 + RO2R + RO2 # 0.016667E-03 /R12;
{75} ACET + OH      = RO2R + RO2 + MCO3 + RCO3 + HCHO # 4.81E-13 ^ 2.0 @ 230;
{76} MEK           = MCO3 + ALD2 + RCO3 + RO2R + RO2 # 0.016667E-03 /R13;
{77} MEK + OH       = 1.5*R2O2 + 1.5*RO2 + 0.5*MCO3 + 0.50*ALD2
                    + 0.5*HCHO + 0.5*PCO3 + RCO3 # 2.9200E-13^2.0 @ -414;
{78} GLYX           = 0.13*HCHO + 1.87*CO # 0.016667E-03 /R14;
{79} GLYX + OH      = 0.6*HO2 + 1.2*CO + 0.4*GCO3 + 0.4*RCO3 # 1.1400E-11;
{80} GLYX + NO3     = HNO3 + 0.6*HO2 + 1.2*CO + 0.4*GCO3
                    + RCO3 # 1.4000E-12 @ 1860;
{81} GCO3 + NO2     = GPAN          # 2.8000E-12 @ -180.0;
{82} GCO3 + NO      = NO2 + HO2 + CO    # 4.2000E-12 @ -180.0;
{83} GPAN          = GCO3 + NO2 + RCO3 # 2.00E+16 @ 13542.0;
{84} GCO3 + HO2     = ROOH + CO      # 3.40E-13 @ -800;
{85} GCO3 + RO2     = 0.5*HO2 + CO + RO2 # 1.8600E-12 @ -530;
{86} GCO3 + RCO3    = HO2 + CO + RCO3 # 2.8000E-12 @ -530;
{87} MGLY          = MCO3 + HO2 + CO + RCO3 # 0.016667E-03 /R15;
{88} MGLY + OH      = MCO3 + CO + RCO3 # 1.7200E-11;
{89} MGLY + NO3     = HNO3 + MCO3 + CO + RCO3 # 1.4200E-12 @ 1860;
{90} ALK4 + OH      = 0.19*HCHO + 0.31*ALD2 + 0.170*RCHO + 0.34*ACET + 0.44*MEK
                    + 0.070*RO2N + 0.930*RO2R + 0.600*R2O2 + 1.600*RO2 # 1.05E-11 @ 353;
{91} ALK7 + OH      = 0.02*HCHO + 0.03*ALD2 + 0.25*RCHO + 0.36*ACET + 0.88*MEK
                    + 0.180*RO2N + 0.820*RO2R + 0.840*R2O2 + 1.840*RO2 # 1.62E-11 @ 288;
{92} ALKN + OH      = NO2 + 0.155*MEK + 1.05*RCHO + 0.48*ALD2 + 0.16*HCHO
                    + 1.390*R2O2 + 1.390*RO2 # 2.19E-11 @ 708;
{93} RO2N + NO      = ALKN          # 4.20E-12 @ -181;
{94} RO2N + HO2     = ROOH + MEK     # 3.4000E-13 @ -800;
{95} RO2N + RO2     = RO2 + 0.5*HO2 + MEK # 1.0000E-15;
{96} RO2N + RCO3    = RCO3 + 0.5*HO2 + MEK # 1.8600E-12 @ -530;
{97} R2O2 + NO      = NO2          # 4.2000E-12 @ -181;
{98} R2O2 + HO2     = ROOH          # 3.4000E-13 @ -800;
{99} R2O2 + RO2     = RO2          # 1.0000E-15;
{100} R2O2 + RCO3   = RCO3         # 1.8600E-12 @ -530;
{101} ETHE + OH     = RO2R + RO2 + 1.56*HCHO + 0.22*ALD2 # 1.9600E-12 @ -438;
{102} ETHE + O3     = HCHO + 0.12*HO2 + 0.42*CO # 9.1400E-15 @ 2580;
{103} ETHE + O      = HCHO + HO2 + CO + RO2R + RO2 # 1.0400E-11 @ 792;
{104} ETHE + NO3    = NO2 + 2*HCHO + R2O2 + RO2 # 5.4300E-12 @ 3041;
{105} PRPE + OH     = RO2R + HCHO + ALD2 + RO2 # 4.8500E-12 @ -504;
{106} PRPE + O3     = 0.65*HCHO + 0.5*ALD2 + 0.285*CO + 0.06*OH + 0.165*HO2
                    + 0.135*RO2R + 0.135*RO2 # 1.32E-14 @ 2105.0;
{107} PRPE + O      = 0.6*ACET + 0.4*HCHO + 0.2*ALD2 + 0.2*HO2
                    + 0.6*RO2R + 0.4*CO + 0.6*RO2 # 1.18E-11 @ 324;
{108} PRPE + NO3    = NO2 + HCHO + ALD2 + R2O2 + RO2 # 5.00E-12 @ 1935;
{109} TBUT + OH     = RO2R + 2*ALD2 + RO2 # 1.0100E-11 @ -549;
{110} TBUT + O3     = ALD2 + 0.15*CO + 0.27*RO2R + 0.12*OH + 0.21*HO2
                    + 0.270*RO2 + 0.300*HCHO # 9.08E-15 @ 1137;
{111} TBUT + O      = MEK + 0.4*HO2 # 2.2600E-11 @ -10;
{112} TBUT + NO3    = NO2 + 2*ALD2 + R2O2 + RO2 # 1.0000E-11 @ 975;
{113} TOLU + OH     = 0.16*CRES + 0.16*HO2 + 0.84*RO2R + 0.4*DIAL
                    + 0.840*RO2 + 0.144*MGLY + 0.114*GLYX # 2.1E-12 @ -322.0;

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{114} DIAL + OH = PCO3 + RCO3 #3.0000E-11;
{115} DIAL = HO2 + CO + MCO3 + RCO3 #0.016667E-03 /R16;
{116} XYLE + OH = 0.17*CRES + 0.17*HO2 + 0.83*RO2R + 0.83*RO2
+ 0.65*DIAL + 0.316*MGLY + 0.095*GLYX #1.66E-11 @ -116;
{117} TMBZ + OH = 0.17*CRES + 0.17*HO2 + 0.83*RO2R + 0.83*RO2
+ 0.49*DIAL + 0.86*MGLY #6.2E-11;
{118} CRES + OH = 0.2*MGLY + 0.15*RO2P + 0.85*RO2R + RO2 #4.2000E-11;
{119} CRES + NO3 = HNO3 + BZO #2.1000E-11;
{120} BZO + NO2 = NPHE #1.3000E-11 @ -300;
{121} BZO + HO2 = PHEN #3.4000E-13 @ -800;
{122} BZO = PHEN #1.0E-03;
{123} PHEN + OH = 0.2*GLYX + 0.15*RO2P + 0.85*RO2R + RO2 #2.6300E-11;
{124} PHEN + NO3 = HNO3 + BZO #3.6000E-12;
{125} NPHE + NO3 = HNO3 + BZN2 #3.6000E-12;
{126} BZN2 + NO2 = #1.3000E-11 @ -300;
{127} BZN2 + HO2 = NPHE #3.4000E-13 @ -800;
{128} BZN2 = NPHE #1.0000E-03;
{129} RO2P + NO = NPHE #4.2000E-12 @ -181.0;
{130} RO2P + HO2 = ROOH #3.4000E-13 @ -800;
{131} RO2P + RO2 = 0.5*HO2 + RO2 #1.0000E-15;
{132} RO2P + RCO3 = 0.5*HO2 + RCO3 #1.8600E-12 @ -530;
{133} NRHC = NRHC #1.0000E+00;

{135} ACRO + OH = #1.9900E-11;
{136} ACRO + O3 = #2.8000E-18;
{137} ACRO + NO3 = #1.2000E-15;
{138} BDIE + OH = ACRO #1.4800E-11 @ 448;
{139} BDIE + O3 = ACRO #3.3000E-14 @ -2500;

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< (MECH)

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## Section 4

### VOC Species—Reactivity Parameters

For the model to predict city-specific secondary formation of formaldehyde, acetaldehyde, and acrolein, a distribution of the VOCs emitted into the atmosphere in the selected urban areas was required; data collected in the mid-1980s were used as the basis for establishing the distribution. This study also used data found in the EPA report by Seila and others (1989). The distribution of hydrocarbons has probably not changed substantially in the past 10 years, with the exception of a moderate increase in the level of oxygenated hydrocarbons due to use of reformulated fuels. In the study by Seila et al. (1989), identifications were made for 34 paraffins (ethane to *n*-decane), 14 olefins (ethene to  $\alpha$ -pinene, including 1,3-butadiene and isoprene), 14 aromatic hydrocarbons (benzene to 1,2-dimethyl-3-ethylbenzene), and acetylene. Beyond these specific compounds, those investigators adopted techniques to classify the remaining unidentified peaks in terms of their hydrocarbon class (i.e., paraffin, olefin, or aromatic). Since flame ionization detection, which has a constant carbon response for all hydrocarbons, was employed for quantification, concentrations could be assigned to compounds for which there was no unique identity. Thus, concentrations for unidentified chromatographic peaks could be attributed to the appropriate class of paraffins, olefins, or aromatics. The report also provided summations for the total sum of paraffins, olefins, aromatics, acetylene, and unidentified hydrocarbons. From the report, data were obtained for 6 of the 10 cities. For these cities, the number of chromatographic measurements during the 6–9 a.m. time frame are given as follows: Atlanta (21 measurements), Boston (8), Chicago (10), Denver (13), Houston (36), and Washington, DC (32).

Data for Los Angeles were obtained from an analysis done by the California Air Resources Board during the 1997 Southern California Air Quality Study (Lonneman, personal communication). For the remaining three study areas (Pittsburgh, Phoenix, and Seattle), there are no known sources of city-specific VOC speciation available, and, therefore, cities of similar characteristics, for which data are available, were used. The following substitutions were made: Akron for Pittsburgh, Salt Lake City for Phoenix, and Boston for Seattle.

Given the information available for these study areas, it was possible to classify virtually the entire carbon mass of VOCs according to the SAPRC97 mechanism classification scheme. This

scheme combines all organic compounds into 14 groups, given below, which account for the total VOC mass.

ALK4 – low molecular weight alkanes

ALK7 – high molecular weight alkanes

ETHE – ethene

PRPE – propene

BDIE – butadiene

TBUT – high molecular weight alkenes

TOLU – low molecular weight reactive aromatic hydrocarbons

XYLE – intermediate molecular weight aromatic hydrocarbons

TMBZ – high molecular weight aromatic hydrocarbons

HCHO – formaldehyde

ALD2 – acetaldehyde

RCHO – high molecular weight carbonyl compounds

ACRO – acrolein

NRHC – nonreactive hydrocarbons

The groups were generated according to the chemical characteristics of similar types of compounds. The main criteria for grouping were reaction rate and the general identity of the chemical products. For example, ALK4 represents C<sub>4</sub> and C<sub>5</sub> alkanes, two of which are *n*-butane and isopentane. These compounds have rate constants of approximately  $3 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . The products from the reactions, while not identical, give compounds having similar OH reactivity. On the other hand, ALK7 compounds generally have higher OH rate constants and potentially give different types of products than those formed from ALK4 compounds. For example, *n*-hexane can give hydroxy products that result from isomerization reactions.

The procedure for classifying the hydrocarbons into the 14 groups is as follows: Except for Seattle, each city has a unique distribution. For the six cities with hydrocarbon data from the study by Seila et al. (1989), an average distribution of the hydrocarbons was calculated from the tabular hydrocarbon data for each city. Each individual chromatogram making up the average was then compared with the average distribution for that city. The chromatogram showing the least deviation in the components was then used as the basis for determining the distribution for that city. (This

approach was taken because there was no electronic version of the data available.) The following combinations were then used to place the hydrocarbons into their appropriate groups:

ALK4 – The low molecular weight hydrocarbons were taken to be the sum of the concentrations for isobutane, *n*-butane, isopentane, and *n*-pentane.

ALK7 – The high molecular weight alkanes were taken as the sum of the paraffin concentration (provided in the report) minus the concentrations for ethane, propane, isobutane, *n*-butane, isopentane, and *n*-pentane. To this value was added one-half of the unidentified hydrocarbon concentration.

ETHE – The ethene concentration was used.

PRPE – The propene concentration was used.

BDIE – The 1,3-butadiene concentration was used.

TBUT – The high molecular weight alkenes ( $>C_3$ ) were taken as the sum of the olefin concentration minus the concentrations for ethene, propene, and 1,3-butadiene. Isoprene was included in this classification.

TOLU – The low molecular weight aromatic hydrocarbons were taken to be the sum of the toluene and ethylbenzene concentrations. Ethylbenzene was included in this classification rather than with XYLE since its OH rate constant is closer to toluene than the xylene isomers.

XYLE – The intermediate weight aromatic hydrocarbons include (*m* + *p*)-xylene and *o*-xylene concentrations.

TMBZ – The high molecular weight aromatic hydrocarbons were taken as the total aromatic hydrocarbon concentration minus the concentrations for benzene, toluene, ethylbenzene, (*m* + *p*)-xylene, and *o*-xylene. To this value was added one-half of the unidentified hydrocarbon concentration.

HCHO – The formaldehyde concentration was taken to represent 2% of the total hydrocarbons by carbon fraction.

ALD2 – The acetaldehyde concentration was taken to represent 2% of the total hydrocarbons by carbon fraction.

RCHO – The high molecular weight carbonyl concentration ( $>C_2$ ) was taken to be 0.9% of the total hydrocarbons by carbon fraction.

ACRO – The acrolein concentration was taken to represent 0.1% of the total hydrocarbons

by carbon fraction.

NRHC – The nonreactive hydrocarbons were taken to be the sum of the concentrations for acetylene, ethane, propane, and benzene. These compounds all have OH rate constants on the order of  $1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  or less.

To account for the 5% carbonyl concentration, the hydrocarbon distribution was scaled by a factor of 0.95. Finally the individual reactivity components were summed to a precision of 0.01 to ensure that the total distribution gave unity. Adjustments were not required to account for round-off error. The resultant reactivity factors on a city-by-city basis are given in Table 4-1.

The Los Angeles data were calculated differently because hydrocarbon data were available from a different database that contained a finer speciation. Similar procedures as above were used to combine the individual compounds into the 14 groupings of VOCs. The Los Angeles chromatograms also had a 15% oxygenate component (e.g., alcohols, ethers, esters). Since these are slowly reacting compounds, they were divided into the ALK4 and ALK7 classifications. The Los Angeles data set also provided concentrations for carbonyl compounds. The total aldehyde component was found to be 5.1%, a value consistent with our previous assumption. For consistency with the other cities, the aldehyde component for Los Angeles was distributed similarly to that described above.

**Table 4-1. Reactivity Factors Used for the 10 Cities Under Consideration. All values are in percent.**

Parameter	Atlanta	Boston	Chicago	Denver	Houston	Los Angeles	Phoenix	Pittsburgh	Seattle	Washington
ALK4	21.74	19.7	17.14	24.61	27.94	16.68	17.14	18.54	19.7	19.1
ALK7	21.26	20.9	27.2	24.69	20.73	31.99	28.71	21.73	20.9	21.64
ETHE	3.28	4.35	2.28	4.85	3.56	2.72	3.46	3.8	4.35	4.19
PRPE	1.13	1.31	1.46	1.05	1.91	4.86	1.35	1.1	1.31	1.67
BDIE	0.11	0.23	0.24	0.15	0.25	0.27	0.3	0.24	0.23	0.35
TBUT	9.51	10.62	12	6.28	7.21	5.8	7.46	11.67	10.62	8.26
TOLU	8.33	9.04	8.51	7.86	5.11	5.3	8.04	5.74	9.04	10.34
XYLE	5.19	5.44	5.29	4.76	3.33	3.86	5.62	4.36	5.44	10.01
TMBZ	14.21	11.89	14.14	9.48	10.18	8.87	9.26	11.12	11.89	8.96
HCHO	2	2	2	2	2	2	2	2	2	2
ALD2	2	2	2	2	2	2	2	2	2	2
RCHO	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
ACRO	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
NRHC	10.24	11.52	6.74	11.27	14.78	14.59	13.43	16.7	11.52	10.48

## Section 5

### Emissions Data and Boundary Conditions

Hourly emissions data (in units of  $\text{kg km}^{-2} \text{h}^{-1}$ ) were provided as inputs to the OZIPR model for VOCs,  $\text{NO}_x$ , CO, formaldehyde, acetaldehyde, acrolein, and 1,3-butadiene. The total VOC mass is partitioned into species according to the fractions given in the reactivity table, which is part of the OZIPR input file (see Section 7 or Appendix A for details). The emissions data consist of two parts: anthropogenic and biogenic emissions. For the present study, the anthropogenic emissions came from emissions inventories, while the biogenics came from running the BEIS-2 (Biogenic Emissions Inventory System) model. Both types of emissions data were supplied by DynTel Corporation.

The anthropogenic emissions data consisted of 24-hour values for each of four seasons for each pollutant and county. The units were kilograms per hour for total VOCs and moles per hour for other pollutants (CO, NO,  $\text{NO}_2$ , formaldehyde, acetaldehyde, acrolein, and 1,3-butadiene). The pollutant  $\text{NO}_x$  in OZIPR represents the sum of NO and  $\text{NO}_2$ . The data were converted to emission densities ( $\text{kg km}^{-2} \text{h}^{-1}$ ) by dividing by the area of each county (see Table 2-1). The biogenic emissions were in the form of hourly emissions for each day of the year, for each of four species—*isoprene*, *monoterpenes*, other VOCs, and NO. Seasonal averages were calculated for each species. The first three species were added to the anthropogenic VOC emissions to obtain the total VOC emissions, while the NO was added to the anthropogenic  $\text{NO}_x$  emissions to obtain the total  $\text{NO}_x$  emissions. All emissions data were provided as county-wide average rates; in the cases where there were two or more counties of the same type (urban or rural) in a given study area, multicounty averages (weighted by area) were used.

The emissions data are input to OZIPR via the MASS option, which is described in Section 7 and also in Appendix A. The OZIPR model expects a series of hourly emission rates; for the current study the first hour is for 8–9 a.m. and the twelfth (and last) is for 7–8 p.m.

The value provided for each hour represents the average emission rate for that hour across all the days in the given season. The units required for the MASS option are  $\text{kg km}^{-2} \text{h}^{-1}$ .

In addition to the hourly emissions, the initial conditions must be specified. This consists of both the concentrations inside the box (the volume of air being modeled) and the concentrations in

the aloft air. The aloft air is the air mass above the box being modeled; when the mixing height increases, some of the aloft air is mixed into the box. In the present set of runs, four species are initialized aloft: CO, ozone, VOC, and NO<sub>x</sub>. Inside the box, nine species are specified—the four aloft species, the three target HAPs, 1-3 butadiene, and nitrous oxide (HONO). The initial concentrations of the target HAPs were set to fixed fractions of the total VOCs. The initial concentrations (both in the box and aloft) for total VOCs and NO<sub>x</sub> are based on concentrations extracted from runs of the Urban Airshed Model (the lowest level was used for the surface concentrations, and an upper level for the aloft concentrations). This model was run only for the summer; it was assumed that the VOC and NO<sub>x</sub> concentrations are similar in other seasons. Urban surface-level CO was varied seasonally, based on data for 8 a.m. measurements extracted from the AIRS database. There were no CO monitors in any of the rural counties; initial (8 a.m.) concentrations were set to 0.2 ppm. Aloft CO was also set to a level of 0.2 ppm. Surface-level HONO was set to a value of 0.001 ppm. Aloft ozone was seasonally varied, based on surface-level measurements from the AIRS database. Inside the box, initial ozone levels were set to zero, as ozone levels are depleted throughout the night by surface contact and do not have much effect on the early morning chemistry.

The OZIPR model is more sensitive to hourly emissions than to initial concentrations. In test runs, even relatively large changes in initial concentrations (a factor of 2, for example) result in fairly small changes (10% or less) in both ozone and HAP concentrations late in the day. However, the OZIPR model is quite sensitive to meteorological inputs.

## Section 6 Meteorological Data

The OZIPR model requires hourly temperature and humidity data, along with daily average pressure and twice-daily mixing heights. Temperature, relative humidity, and atmospheric pressure data were taken from values reported by the National Weather Service (NWS) at airport monitoring sites for each city. Hourly data from the years 1992–1995, inclusive, were used. Station identification numbers are supplied in Table 6-1.

Mixing height data were supplied by EC/R, Inc. The data were generated from measurements obtained from daily morning and afternoon weather balloon soundings; at all stations, observations were made at midnight and noon, Greenwich mean time. As with the other meteorological data, the years 1992–1995 were used. The mixing height stations are indicated in Table 6-2.

**Table 6-1. NWS Stations Used for OZIPR Meteorological Input**

<b>City (Airport)</b>	<b>Station Number</b>
Atlanta	13874
Boston	14739
Chicago	94846
Denver (Stapleton)	23062
Houston	12960
Los Angeles	23174
Phoenix	23183
Pittsburgh	94823
Seattle	24233
Washington, DC (National)	13743

**Table 6-2. Mixing Height Stations Used for OZIPR Meteorological Input**

City	Station	Station Number
Atlanta	Athens, GA	13873 (1992–1994)
Atlanta	Peachtree City, GA	53819 (1995)
Boston	Chatham, MA	14684
Chicago	Peoria, IL	14842
Denver	Denver, CO	23062
Houston	Lake Charles, LA	03937
Los Angeles	San Diego, CA	03190
Phoenix	Tucson, AZ	23160
Pittsburgh	Pittsburgh, PA	94823
Seattle	Quillayute, WA	94240
Washington, DC	Sterling, VA	93734

### 6.1 Approach to the Utilization of Meteorological Data with OZIPR

The desired outputs from this study were annual and seasonal estimates of secondary production of the HAPs of interest. The limited time resolution (at best, seasonal) of the input emissions data precluded running OZIPR on a daily basis. For these reasons, it was decided to run the model on a seasonal basis; however, even within a given season meteorological conditions can vary substantially. These shifting weather conditions, in turn, can affect the secondary production of HAPs. Since estimates were to be applied only over long time periods, the focus was on common or typical meteorological conditions.

The seasons were defined as

- Winter – December, January, and February
- Spring – March, April, and May)
- Summer – June, July, and August
- Autumn – September, October, and November

To accommodate the variability within seasons while at the same time avoiding excessive calculations, it was decided to use at most three typical days per season. To identify the more common types of days, cluster analysis was carried out on a seasonal basis on the meteorological variables. To be counted as a typical day, a cluster had to contain at least 30 days (out of approximately 365 days [4 years with three months each]). The OZIPR model was then run for each of the typical days in each season, and afterwards seasonal averages of secondary HAP production were calculated by averaging the results for the typical days weighted by their frequency of occurrence (i.e., the number of days in each cluster). The averaging could also be done by dividing each season into more, smaller clusters, but this would require more time and effort and would be of limited value since other inputs (particularly emissions) were not available on a daily basis.

## **6.2 Typical Day Determination**

The following algorithm describes how typical days were determined for each season to supply the meteorological input to OZIPR. Before clustering days together, the hourly meteorological data need to be expressed on a daily basis. To this end, the arithmetic mean for temperature, humidity, and pressure for each day for the hours of 8 a.m. through 8 p.m., inclusive, were calculated. Only averages computed from at least 9 hours were retained. Also, the difference (p.m. minus a.m.), the ratio (p.m./a.m.), and the average of the mixing heights were calculated for each day; both mixing heights had to be available for a given day to enter the typical day calculations. Any mixing height originally furnished as less than 100 meters was reset to 100 meters before being used.

Cluster analysis was executed for each city-season combination for three separate sets of variables: temperature, humidity, and average mixing height; temperature, humidity, and mixing height difference; and temperature, humidity, and mixing height ratio. The clustering procedure measured the distance between clusters as the average of the Euclidean distance between all possible pairs of points. Clustering was intended to find groups of days that resembled each other, but were distinct from days in other clusters.

Generally, the triplet containing the ratio of the afternoon to morning mixing heights yielded better clustering results in the sense that more clusters contained more than 30 days and the cluster sizes were more evenly distributed. In a few cases, the cluster results from either the mixing height averages or differences were used. In some cases, the bulk of the data naturally divided into only two clusters; for these, the “extra” cluster (needed to make three) consisted of a few outlying points representing relatively rare types of weather.

Once the clusters were determined, data for each typical day had to be constructed for input to the model. The model required hourly temperature and humidity numbers, a single daily atmospheric pressure value, and one morning and one afternoon mixing height. To prepare this input

data, the median temperature, humidity, and pressure were determined for each hour within each season and cluster. The medians of the averages, differences, and ratios of the mixing heights, as well as the medians of the mixing heights themselves, were also determined for each cluster within the seasons. Subsequently, the mean of the median pressures for each cluster within the seasons was calculated. These summary statistics then constituted the descriptors of the typical days, and the median hourly temperatures and humidity levels, the mean of the hourly median atmospheric pressures, and the median morning and afternoon mixing heights were supplied to the model as input. All statistical calculations were done via the SAS programming language (SAS, 1990).

Tables 6-3 and 6-4 describe the typical conditions for the clusters obtained for each city and season. The temperature and humidity values in Table 6-4 are from the middle of the day. (OZIPR is a photochemical model, so midday temperature and humidity values are of particular interest.)

**Table 6-3. Typical Conditions for Each City and Season**

---

**A. Atlanta**

<u>Season</u>	<u>Days in Cluster</u>	<u>Comments on Midday Conditions</u>
Autumn	213	Upper 70s, moderate humidity, significant mixing
	89	Mid to upper 60s, high humidity, no mixing (ht. ~ 500 m)
	37	Mid 60s, low humidity, significant mixing
Spring	225	Low 70s, low humidity, significant mixing
	76	Low 70s, moderate humidity, significant mixing
	52	Low 60s, high humidity, little mixing (ht. ~500 m)
Summer	204	Mid 80s, moderate humidity, significant mixing
	120	Low 90s, moderate to low humidity, very much mixing (max. ht. ~2200 m)
	31	Mid 70s, high humidity, mixing height contraction
Winter	137	Upper 40s to low 50s, low humidity, some mixing (max. ht. ~1000 m)
	116	Upper 40s to low 50s, moderate humidity, slight mixing between ~400 and ~700 m
	90	Upper 40s to low 50s, high humidity, no mixing (~400 m)

**Table 6-3. Continued****B. Boston**

<u>Season</u>	<u>Days in Cluster</u>	<u>Comments on Midday Conditions</u>
Autumn	210	Upper 50s to low 60s, moderate to low humidity, some mixing (max. ht. ~1000 m)
	94	Low 60s, high humidity, no mixing (~400 m)
Spring	123	Low 50s, moderate humidity, some mixing (max. ht. ~1000 m)
	120	Upper 40s, high humidity, no mixing (~300 m)
	102	Low 50s, low humidity, noticeable mixing from high morning level (~1000 to ~1800 m)
Summer	134	Upper 70s to low 80s, low humidity, significant mixing
	126	Upper 70s to low 80s, moderate humidity, noticeable mixing
	94	Low 70s, high humidity, no mixing (~500 m)
Winter	109	Upper 30s, moderate humidity, little mixing
	90	Upper 20s, low humidity, no mixing (~1000 m)
	54	Low 40s, high humidity, no mixing (~300 m)

**C. Chicago**

<u>Season</u>	<u>Days in Cluster</u>	<u>Comments on Midday Conditions</u>
Autumn	178	Low 60s, moderate humidity, significant mixing
	141	Low 50s, moderate to high humidity, no mixing (~600 m)
Spring	250	Mid 50s, moderate humidity, significant mixing
	92	Mid 40s, high humidity, no mixing (~700 m)
Summer	205	Upper 70s, moderate humidity, significant mixing
	151	Upper 70s, low to moderate humidity, much mixing (~100 to ~1700 m)
Winter	258	Low 30s, moderate to high humidity, no mixing (~500 m)
	66	Mid 20s, moderate humidity, little mixing

**D. Denver**

<u>Season</u>	<u>Days in Cluster</u>	<u>Comments on Midday Conditions</u>
Autumn	124	Upper 50s, low humidity, much mixing (~100 to ~1700 m)
	81	Upper 70s, very low humidity, very much mixing (~100 to ~3300 m)
	55	Low 40s, moderate humidity, little mixing
Spring	132	Upper 60s, very low humidity, very much mixing (~100 to ~3300 m)
	97	Upper 50s, low humidity, much mixing (~500 to ~2500 m)
	41	Mid 40s, moderate humidity, little mixing
Summer	158	Upper 70s, low humidity, much mixing (~300 to ~2300 m)
	96	Upper 80s, very low humidity, very much mixing (~100 to ~4000 m)
Winter	203	Upper 40s, low humidity, much mixing (~100 to ~1400 m)
	100	Low 30s, moderate humidity, little mixing

**Table 6-3. Continued****E. Houston**

<u>Season</u>	<u>Days in Cluster</u>	<u>Comments on Midday Conditions</u>
Autumn	174	Mid 80s, moderate humidity, significant mixing
	107	Lower 70s, low to moderate humidity, noticeable mixing
	65	Lower 70s, high humidity, little mixing
Spring	209	Mid 70s, moderate humidity, some mixing
	126	Mid 70s, moderate humidity, noticeable mixing
Summer	298	Low 90s, moderate humidity, noticeable mixing (~600 to ~1400 m)
	34	Upper 70s to low 80s, high humidity, no mixing
Winter	202	Mid 60s, moderate to high humidity, little mixing
	124	Upper 50s, moderate humidity, some mixing

**F. Los Angeles**

<u>Season</u>	<u>Days in Cluster</u>	<u>Comments on Midday Conditions</u>
Autumn	296	Low 70s, moderate humidity, no mixing (~500 m)
	63	Low 70s, low humidity, significant mixing
Spring	281	Mid 60s, moderate humidity, no mixing (~700 m)
	85	Mid 60s, moderate humidity, little mixing (~1400 m)
Summer	304	Low to mid 70s, moderate humidity, no mixing (~400 m)
	51	Low 70s, moderate humidity, no mixing (~1000 m)
Winter	152	Low 60s, moderate humidity, noticeable mixing
	131	Low 60s, moderate to high humidity, no mixing (~600 m)
	69	Upper 60s, low humidity, significant mixing

**G. Phoenix**

<u>Season</u>	<u>Days in Cluster</u>	<u>Comments on Midday Conditions</u>
Autumn	283	Upper 80s, low humidity, very much mixing (~400 to ~3000 m)
	75	Low 70s, moderate humidity, some mixing
Spring	230	Upper 70s, low humidity, much mixing (~1000 to ~3100 m)
	89	Upper 80s, very low humidity, very much mixing (~400 to ~4100 m)
	44	Mid 60s, moderate humidity, little mixing (~2000 m)
Summer	229	~100, very low humidity, very much mixing (~1200 to ~4400 m)
	114	Mid 90s, low humidity, significant mixing (~2200 to ~3400 m)
Winter	226	Mid 60s, low humidity, significant mixing
	83	Upper 50s, moderate humidity, some mixing (~1100 to ~1600 m)
	49	Upper 50s, moderate to high humidity, no mixing (~1400 m)

**Table 6-3. Continued****H. Pittsburgh**

<u>Season</u>	<u>Days in Cluster</u>	<u>Comments on Midday Conditions</u>
Autumn	126 107	Lower 60s, moderate humidity, significant mixing Upper 50s, moderate humidity, some mixing
Spring	114 90 60	Mid 60s, low humidity, significant mixing Mid 50s, moderate humidity, noticeable mixing Mid 40s, high humidity, little mixing
Summer	125 70 66	Low 80s, moderate humidity, significant mixing Low 80s, low to moderate humidity, very much mixing (~100 to 2000 m) Mid 70s, moderate humidity, some mixing
Winter	147 87	Mid 30s, moderate to high humidity, mixed layer contraction (~700 to ~500 m) Low 30s, moderate humidity, little mixing

**I. Seattle**

<u>Season</u>	<u>Days in Cluster</u>	<u>Comments on Midday Conditions</u>
Autumn	227 118	Mid 50s, high humidity, no mixing Mid 60s, moderate humidity, some mixing
Spring	238 122	Mid 50s, moderate humidity, some mixing Mid 60s, moderate humidity, significant mixing
Summer	203 133	Upper 60s, moderate humidity, noticeable mixing (~700 to ~1400 m) Mid 60s, moderate humidity, noticeable mixing (~1200 to ~1900 m)
Winter	277 49	Mid 40s, high humidity, mixed layer contraction (~600 to ~300 m) Mid 40s, moderate humidity, some mixing

**J. Washington, DC**

<u>Season</u>	<u>Days in Cluster</u>	<u>Comments on Midday Conditions</u>
Autumn	241 101	Mid 60s, moderate humidity, noticeable mixing Upper 60s, high humidity, no mixing
Spring	182 98 75	Low 60s, low to moderate humidity, significant mixing Upper 60s, moderate humidity, noticeable mixing Mid 50s, high humidity, no mixing
Summer	151 115 84	Mid 80s, moderate humidity, significant mixing Mid 80s, moderate humidity, significant mixing Upper 70s, moderate to high humidity, little mixing
Winter	203 67 62	Low 40s, moderate humidity, little mixing Mid 30s, low humidity, no mixing (~1300 m) Low 40s, high humidity, no mixing (~500 m)

**Table 6-4. Results of Cluster Analysis for Each City and Season****A. Atlanta**

<b>Season</b>	<b>No. Days</b>	<b>Temperature (°F)</b>	<b>Humidity (%)</b>	<b>Mixing Height Difference (m)</b>
Autumn	213	71	55	250–1300
	89	67	89	500–500
	37	66	32	100–1250
Spring	225	72	40	150–1800
	76	71	61	500–1450
	52	62	88	500–600
Summer	204	84	62	550–1650
	120	90	46	200–2250
	31	75	89	900–600
Winter	137	49	39	250–950
	116	49	64	400–700
	90	50	94	400–400

**B. Boston**

<b>Season</b>	<b>No. Days</b>	<b>Temperature (°F)</b>	<b>Humidity (%)</b>	<b>Mixing Height Difference (m)</b>
Autumn	210	59	45	600–1050
	94	62	82	450–400
Spring	123	52	55	500–1000
	120	48	83	350–300
	102	53	33	1000–1800
Summer	134	79	40	550–1650
	126	80	56	550–1400
	94	71	80	500–450
Winter	109	38	55	700–850
	90	27	37	950–1000
	54	41	85	300–300

**Table 6-4. Continued****C. Chicago**

<b>Season</b>	<b>No. Days</b>	<b>Temperature (°F)</b>	<b>Humidity (%)</b>	<b>Mixing Height Difference (m)</b>
Autumn	178	60	50	200–1150
	141	51	75	600–650
Spring	250	56	46	300–1500
	92	46	83	700–700
Summer	205	78	66	400–1300
	151	79	46	150–1700
Winter	258	32	75	450–500
	66	25	49	400–700

**D. Denver**

<b>Season</b>	<b>No. Days</b>	<b>Temperature (°F)</b>	<b>Humidity (%)</b>	<b>Mixing Height Difference (m)</b>
Autumn	124	59	33	150–1650
	81	79	18	100–3300
	55	40	70	700–800
Spring	132	68	20	100–3350
	97	57	38	550–2450
	41	44	72	900–800
Summer	158	78	37	350–2350
	96	88	19	100–4000
Winter	203	48	29	100–1500
	100	30	62	300–500

**Table 6-4. Continued****E. Houston**

<b>Season</b>	<b>No. Days</b>	<b>Temperature (°F)</b>	<b>Humidity (%)</b>	<b>Mixing Height Difference (m)</b>
Autumn	174	84	58	250–1250
	107	72	40	200–1050
	65	70	83	450–700
Spring	209	77	69	600–1100
	126	74	48	400–1150
Summer	298	91	55	650–1450
	34	79	87	850–850
Winter	202	63	77	350–600
	124	58	44	350–900

**F. Los Angeles**

<b>Season</b>	<b>No. Days</b>	<b>Temperature (°F)</b>	<b>Humidity (%)</b>	<b>Mixing Height Difference (m)</b>
Autumn	296	71	66	450–500
	63	72	24	100–1300
Spring	281	66	70	700–750
	85	63	65	1350–1500
Summer	304	73	68	450–450
	51	72	65	950–950
Winter	152	62	52	250–1050
	131	60	77	700–600
	69	68	21	100–1250

**Table 6-4. Continued****G. Phoenix**

<b>Season</b>	<b>No. Days</b>	<b>Temperature (°F)</b>	<b>Humidity (%)</b>	<b>Mixing Height Difference (m)</b>
Autumn	283	87	22	450–3000
	75	71	44	900–1600
Spring	230	78	25	1000–3100
	89	88	17	400–4150
	44	66	48	2050–2250
Summer	229	100	18	1250–4400
	114	95	31	2200–3450
Winter	226	64	30	300–1700
	83	59	52	1100–1650
	49	59	76	1400–1400

**H. Pittsburgh**

<b>Season</b>	<b>No. Days</b>	<b>Temperature (°F)</b>	<b>Humidity (%)</b>	<b>Mixing Height Difference (m)</b>
Autumn	126	62	48	200–1400
	107	59	69	700–1000
Spring	114	63	39	250–1900
	90	54	60	750–1450
	60	45	85	750–650
Summer	125	80	56	450–1800
	70	81	41	100–2000
	66	74	74	650–1200
Winter	147	36	77	700–550
	87	30	54	750–950

**Table 6-4. Continued****I. Seattle**

<b>Season</b>	<b>No. Days</b>	<b>Temperature (°F)</b>	<b>Humidity (%)</b>	<b>Mixing Height Difference (m)</b>
Autumn	227	54	78	800–700
	118	66	54	300–900
Spring	238	54	69	1100–1300
	122	63	48	400–1750
Summer	203	69	56	700–1350
	133	66	56	1250–1950
Winter	277	46	80	650–300
	49	45	44	250–550

**J. Washington, DC**

<b>Season</b>	<b>No. Days</b>	<b>Temperature (°F)</b>	<b>Humidity (%)</b>	<b>Mixing Height Difference (m)</b>
Autumn	241	63	49	650–1400
	101	67	81	700–750
Spring	182	62	40	800–1900
	98	67	58	550–1350
	75	54	90	700–600
Summer	151	86	59	500–1800
	115	84	46	750–1950
	84	79	74	850–1150
Winter	203	42	56	750–950
	67	35	35	1250–1350
	62	40	94	550–450

Note that the tables indicate that no single variable distinguishes one typical day from another. Furthermore, the interpretation of the clusters is not standard across seasons or across study areas.

For input into the OZIPR model, the morning and afternoon mixing heights are provided as

the variables MHINIT and MHFINAL under the DILUTION option. The pressure is converted to atmospheres and entered as the variable PRESSURE[AT]. For temperature and humidity, a series of hourly values are required—a total of 13 hourly values are needed, from 8 a.m. to 8 p.m., inclusive. (The model treats these as instantaneous measurements at the top of each hour, not hourly averages.) For the input files used in this study, the temperatures were converted to degrees Celsius. A total of 120 meteorological files were prepared (3 per season, 4 seasons, 10 study areas). In addition to establishing the typical days via clustering and preparing the meteorological data for input, SAS programming was used to automatically generate all 120 files for use in OZIPR.

## Section 7

### Running the OZIPR Model

The OZIPR model is a photochemical box model that simulates the production and removal of certain chemical species over the course of a day. To run the model, parameter settings must be defined and scenario-specific data must be supplied. Each scenario to be modeled with OZIPR requires its own input file. A line-by-line description of an example input file is provided in Appendix A, along with a discussion of file-naming conventions and batch processing.

Once the OZIPR input files are ready, the model can be run. Each run requires one DOS command (OZIPR is not a Windows program). A set of batch files were prepared, one per study area, to run all 48 scenarios for that study area and to combine the output tables into a single file. Figure 7-1 shows a complete OZIPR input file.

**Figure 7-1. Complete OZIPR input file for summertime urban Houston, day type #1, with primary emissions of carbonyls.**

```
! The mechanism for OZIPR model is updated with SAPRC97 and two species added:
1,3-butadiene (BDIE) and acrolein (ARCO).
MECH [CM] >
  CNUM=
    ALK4 = 4.5,
    ALK7 = 7.0,
    ETHE = 2.0,
    PRPE = 3.0,
    TBUT = 4.0,
    TOLU = 7.0,
    XYLE = 8.0,
    TMBZ = 9.0,
    RCHO = 3.0,
    BDIE = 4.0,
    HCHO = 1.0,
    ALD2 = 2.0,
    ACRO = 3.0,
    NRHC = 1.0;

REACTIONS =
{1} NO2          =      NO      +      O          #0.016667      /L1;
{2} O            =      O3              #1.0500E+03 @ -1282.0;
{3} O + NO2     =      NO              #6.5000E-12 @ -120;
{4} O + NO2     =      NO3             #1.1100E-13 @ -894.0;
```

```

{ 5} NO + O3 = NO2 #2.0000E-12 @ 1400.0;
{ 6} NO2 + O3 = NO3 #1.4000E-13 @ 2500.0;
{ 7} NO + NO3 = 2*NO2 #1.7000E-11 @ -150.0;
{ 8} NO + NO = 2*NO2 #8.1500E-20 @ -528.0;
{ 9} NO2 + NO3 = N2O5 #4.6200E-13 @ -273.0;
{10} N2O5 = NO2 + NO3 #1.3300E+15 @ 11379;
{11} N2O5 + H2O = 2*HNO3 #1.0000E-21;
{12} NO2 + NO3 = NO + NO2 #2.5000E-14 @ 1228.0;
{13} NO3 = NO #0.016667 /R1;
{14} NO3 = NO2 + O #0.016667 /R2;
{15} O3 = O #0.016667E-03 /R3;
{16} O3 = O1D #0.016667E-03 /R4;
{17} O1D + H2O = 2*OH #2.2000E-10;
{18} O1D = O #7.2000E+08;
{19} NO + OH = HONO #4.0300E-13 @ -833.0;
{20} HONO = NO + OH #0.016667 /R5;
{21} NO2 + H2O = HONO + -1* NO2 + HNO3 #4.0000E-24;
{22} NO2 + OH = HNO3 #9.5700E-13 @ -737.0;
{23} HNO3 + OH = NO3 #6.4500E-15 @ -818;
{24} CO + OH = HO2 #2.400E-13;
{25} OH = HCHO + RO2R + RO2 #28.3^2 @ 1280.0;
{26} O3 + OH = HO2 #1.6002E-12 @ 941.0;
{27} NO + HO2 = NO2 + OH #3.7000E-12 @ -242.0;
{28} NO2 + HO2 = HNO4 #1.0200E-13 @ -773.0;
{29} HNO4 = NO2 + HO2 #4.3500E+13 @ 10103;
{30} HNO4 + OH = NO2 #1.3000E-12 @ -380;
{31} O3 + HO2 = OH #1.1000E-14 @ 500.0;
{32} HO2 + HO2 = H2O2 # 2.200E-13 @ -619.0;
{33} HO2 + HO2 + H2O = H2O2 # 3.100E-34 @ -2818.0;
{34} NO3 + HO2 = HNO3 # 2.200E-13 @ -619.0;
{35} NO3 + HO2 + H2O = HNO3 # 3.100E-34 @ -2818.0;
{36} H2O2 = 2*OH # 0.016667E-03 /R6;
{37} H2O2 + OH = HO2 # 3.3000E-12 @ 200.0;
{37a} HO2 + OH = # 4.6000E-11 @ -230;
{38} RO2 + NO = NO # 4.2000E-12 @ -181.0;
{39} RCO3 + NO = NO # 4.2000E-12 @ -180.0;
{40} RCO3 + NO2 = NO2 # 2.8000E-12 @ -180.0;
{41} RO2 + HO2 = HO2 # 3.4000E-13 @ -800;
{42} RCO3 + HO2 = HO2 # 3.4000E-13 @ -800;
{43} RO2 + RO2 = # 1.0000E-15;
{44} RO2 + RCO3 = # 1.8600E-12 @ -530;
{45} RCO3 + RCO3 = # 2.8000E-12 @ -530;
{46} RO2R + NO = NO2 + HO2 # 4.2000E-12 @ -181.0;
{47} RO2R + HO2 = ROOH # 3.4000E-13 @ -800;
{48} RO2R + RO2 = 0.5*HO2 + RO2 # 1.0000E-15;
{49} RO2R + RCO3 = 0.5*HO2 + RCO3 # 1.8600E-12 @ -530;
{50} ROOH = HO2 + OH # 0.016667E-03 /R7;
{51} HCHO = 2*HO2 + CO # 0.016667E-03 /R8;
{52} HCHO = CO # 0.016667E-03 /R9;
{53} HCHO + OH = HO2 + CO # 1.125000E-12^2.0 @ -648;
{54} HCHO + NO3 = HNO3 + HO2 + CO #2.8000E-12 @ 2516;
{55} HCHO + HO2 = RO2R + RO2 #1.0000E-14;
{56} ALD2 = CO + HCHO + HO2 + RO2R + RO2 #0.016667E-03 /R10;
{57} ALD2 + OH = MCO3 + RCO3 #5.55000E-12 @ -311;
{58} ALD2 + NO3 = HNO3 + MCO3 + RCO3 #1.40000E-12 @ 1860;
{59} MCO3 + NO = NO2 + HCHO + RO2R + RO2 #4.2000E-12 @ -180;
{60} MCO3 + NO2 = PAN #2.8000E-12 @ -180;
{61} MCO3 + HO2 = ROOH + HCHO #3.4000E-13 @ -800;
{62} MCO3 + RO2 = 0.5*HO2 + HCHO + RO2 #1.8600E-12 @ -530;
{63} MCO3 + RCO3 = HO2 + HCHO + RCO3 #2.8000E-12 @ -530;
{64} PAN = MCO3 + NO2 + RCO3 #2.0000E+16 @ 13542;
{65} RCHO = ALD2 + HO2 + CO + RO2R + RO2 #0.016667E-03 /R11;
{66} RCHO + OH = RCO3 + PCO3 #8.5000E-12 @ -252;
{67} RCHO + NO3 = HNO3 + PCO3 + RCO3 #1.4000E-12 @ 1860;
{68} PCO3 + NO = NO2 + ALD2 + RO2R + RO2 #4.2000E-12 @ -180;
{69} PCO3 + NO2 = PPN #8.4000E-12;
{70} PCO3 + HO2 = ROOH + ALD2 #3.4000E-13 @ -800;

```

{71} PCO3 + RO2 = 0.5\*HO2 + ALD2 + RO2 #1.8600E-12 @ -530;  
 {72} PCO3 + RCO3 = HO2 + ALD2 + RCO3 #2.8000E-12 @ -530;  
 {73} PPN = PCO3 + NO2 + RCO3 #1.6000E+17 @ 14073;  
 {74} ACET = MCO3 + HCHO + RCO3 + RO2R + RO2 #0.016667E-03 /R12;  
 {75} ACET + OH = RO2R + RO2 + MCO3 + RCO3 + HCHO #4.81E-13 ^ 2.0 @ 230;  
 {76} MEK = MCO3 + ALD2 + RCO3 + RO2R + RO2 #0.016667E-03 /R13;  
 {77} MEK + OH = 1.5\*R2O2 + 1.5\*RO2 + 0.5\*MCO3 + 0.50\*ALD2  
 + 0.5\*HCHO + 0.5\*PCO3 + RCO3 #2.9200E-13^2.0@ -414;  
 {78} GLYX = 0.13\*HCHO + 1.87\*CO #0.016667E-03 /R14;  
 {79} GLYX + OH = 0.6\*HO2 + 1.2\*CO + 0.4\*GCO3 + 0.4\*RCO3 #1.1400E-11;  
 {80} GLYX + NO3 = HNO3 + 0.6\*HO2 + 1.2\*CO + 0.4\*GCO3  
 + RCO3 #1.4000E-12 @ 1860;  
 {81} GCO3 + NO2 = GPAN #2.8000E-12 @ -180.0;  
 {82} GCO3 + NO = NO2 + HO2 + CO #4.2000E-12 @ -180.0;  
 {83} GPAN = GCO3 + NO2 + RCO3 #2.00E+16 @ 13542.0;  
 {84} GCO3 + HO2 = ROOH + CO #3.40E-13 @ -800;  
 {85} GCO3 + RO2 = 0.5\*HO2 + CO + RO2 #1.8600E-12 @ -530;  
 {86} GCO3 + RCO3 = HO2 + CO + RCO3 #2.8000E-12 @ -530;  
 {87} MGLY = MCO3 + HO2 + CO + RCO3 #0.016667E-03 /R15;  
 {88} MGLY + OH = MCO3 + CO + RCO3 #1.7200E-11;  
 {89} MGLY + NO3 = HNO3 + MCO3 + CO + RCO3 #1.4200E-12 @ 1860;  
 {90} ALK4 + OH = 0.19\*HCHO + 0.31\*ALD2 + 0.170\*RCHO + 0.34\*ACET + 0.44\*MEK  
 + 0.070\*RO2N + 0.930\*RO2R + 0.600\*R2O2 + 1.600\*RO2 #1.05E-11 @ 353;  
 {91} ALK7 + OH = 0.02\*HCHO + 0.03\*ALD2 + 0.25\*RCHO + 0.36\*ACET + 0.88\*MEK  
 + 0.180\*RO2N + 0.820\*RO2R + 0.840\*R2O2 + 1.840\*RO2 #1.62E-11 @ 288;  
 {92} ALKN + OH = NO2 + 0.155\*MEK + 1.05\*RCHO + 0.48\*ALD2 + 0.16\*HCHO  
 + 1.390\*R2O2 + 1.390\*RO2 #2.19E-11 @ 708;  
 {93} RO2N + NO = ALKN #4.20E-12 @ -181;  
 {94} RO2N + HO2 = ROOH + MEK #3.4000E-13 @ -800;  
 {95} RO2N + RO2 = RO2 + 0.5\*HO2 + MEK #1.0000E-15;  
 {96} RO2N + RCO3 = RCO3 + 0.5\*HO2 + MEK #1.8600E-12 @ -530;  
 {97} R2O2 + NO = NO2 #4.2000E-12 @ -181;  
 {98} R2O2 + HO2 = ROOH #3.4000E-13 @ -800;  
 {99} R2O2 + RO2 = RO2 #1.0000E-15;  
 {100} R2O2 + RCO3 = RCO3 #1.8600E-12 @ -530;  
 {101} ETHE + OH = RO2R + RO2 + 1.56\*HCHO + 0.22\*ALD2 #1.9600E-12 @ -438;  
 {102} ETHE + O3 = HCHO + 0.12\*HO2 + 0.42\*CO #9.1400E-15 @ 2580;  
 {103} ETHE + O = HCHO + HO2 + CO + RO2R + RO2 #1.0400E-11 @ 792;  
 {104} ETHE + NO3 = NO2 + 2\*HCHO + R2O2 + RO2 #5.4300E-12 @ 3041;  
 {105} PRPE + OH = RO2R + HCHO + ALD2 + RO2 #4.8500E-12 @ -504;  
 {106} PRPE + O3 = 0.65\*HCHO + 0.5\*ALD2 + 0.285\*CO + 0.06\*OH + 0.165\*HO2  
 + 0.135\*RO2R + 0.135\*RO2 #1.32E-14 @ 2105.0;  
 {107} PRPE + O = 0.6\*ACET + 0.4\*HCHO + 0.2\*ALD2 + 0.2\*HO2  
 + 0.6\*RO2R + 0.4\*CO + 0.6\*RO2 #1.18E-11 @ 324;  
 {108} PRPE + NO3 = NO2 + HCHO + ALD2 + R2O2 + RO2 #5.00E-12 @ 1935;  
 {109} TBUT + OH = RO2R + 2\*ALD2 + RO2 #1.0100E-11 @ -549;  
 {110} TBUT + O3 = ALD2 + 0.15\*CO + 0.27\*RO2R + 0.12\*OH + 0.21\*HO2  
 + 0.270\*RO2 + 0.300\*HCHO #9.08E-15 @ 1137;  
 {111} TBUT + O = MEK + 0.4\*HO2 #2.2600E-11 @ -10;  
 {112} TBUT + NO3 = NO2 + 2\*ALD2 + R2O2 + RO2 #1.0000E-11 @ 975;  
 {113} TOLU + OH = 0.16\*CRES + 0.16\*HO2 + 0.84\*RO2R + 0.4\*DIAL  
 + 0.840\*RO2 + 0.144\*MGLY + 0.114\*GLYX #2.1E-12 @ -322.0;  
 {114} DIAL + OH = PCO3 + RCO3 #3.0000E-11;  
 {115} DIAL = HO2 + CO + MCO3 + RCO3 #0.016667E-03 /R16;  
 {116} XYLE + OH = 0.17\*CRES + 0.17\*HO2 + 0.83\*RO2R + 0.83\*RO2  
 + 0.65\*DIAL + 0.316\*MGLY + 0.095\*GLYX #1.66E-11 @ -116;  
 {117} TMBZ + OH = 0.17\*CRES + 0.17\*HO2 + 0.83\*RO2R + 0.83\*RO2  
 + 0.49\*DIAL + 0.86\*MGLY #6.2E-11;  
 {118} CRES + OH = 0.2\*MGLY + 0.15\*RO2P + 0.85\*RO2R + RO2 #4.2000E-11;  
 {119} CRES + NO3 = HNO3 + BZO #2.1000E-11;  
 {120} BZO + NO2 = NPHE #1.3000E-11 @ -300;  
 {121} BZO + HO2 = PHEN #3.4000E-13 @ -800;  
 {122} BZO = PHEN #1.0E-03;  
 {123} PHEN + OH = 0.2\*GLYX + 0.15\*RO2P + 0.85\*RO2R + RO2 #2.6300E-11;  
 {124} PHEN + NO3 = HNO3 + BZO #3.6000E-12;  
 {125} NPHE + NO3 = HNO3 + BZN2 #3.6000E-12;  
 {126} BZN2 + NO2 = #1.3000E-11 @ -300;

```

{127} BZN2 + HO2 = NPHE #3.4000E-13 @ -800;
{128} BZN2 = NPHE #1.0000E-03;
{129} RO2P + NO = NPHE #4.2000E-12 @ -181.0;
{130} RO2P + HO2 = ROOH #3.4000E-13 @ -800;
{131} RO2P + RO2 = 0.5*HO2 + RO2 #1.0000E-15;
{132} RO2P + RCO3 = 0.5*HO2 + RCO3 #1.8600E-12 @ -530;
{133} NRHC = NRHC #1.0000E+00;

{135} ACRO + OH = #1.9900E-11;
{136} ACRO + O3 = #2.8000E-18;
{137} ACRO + NO3 = #1.2000E-15;
{138} BDIE + OH = ACRO #1.4800E-11 @ 448;
{139} BDIE + O3 = ACRO #3.3000E-14 @ -2500;

```

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ZENITH>

L1 = 0.560, 0.550, 0.548, 0.520, 0.479, 0.417, 0.322,  
0.188, 0.0724, 0.00436,

R1: 2.2600, 2.2600, 2.2800, 2.3200, 2.3900, 2.5600,  
2.8300, 3.3400, 4.0600, 2.7900,  
R2: 20.4000, 20.5000, 20.7000, 21.1000, 21.8000, 23.1000,  
25.4000, 29.7000, 35.5000, 25.8000,  
R3: 55.2000, 55.3000, 55.6000, 56.1000, 57.1000, 59.9000,  
64.5000, 74.3000, 89.0000, 66.0000,  
R4: 4.5600, 4.4100, 4.0500, 3.5000, 2.7300, 1.8800,  
1.0200, 0.3500, 0.0810, 0.0230,  
R5: 0.1960, 0.1960, 0.1960, 0.1960, 0.1940, 0.1930,  
0.1900, 0.1850, 0.1810, 0.1880,  
R6: 0.9080, 0.9030, 0.8820, 0.8450, 0.7910, 0.7180,  
0.6250, 0.5120, 0.4310, 0.3830,  
R7: 0.9080, 0.9030, 0.8820, 0.8450, 0.7910, 0.7180,  
0.6250, 0.5120, 0.4310, 0.3830,  
R8: 3.6700, 3.6200, 3.4500, 3.3000, 3.0200, 2.6000,  
2.0700, 1.3300, 0.7100, 0.6500,  
R9: 4.6600, 4.6400, 4.4900, 4.4200, 4.2300, 3.8900,  
3.4700, 2.6500, 1.7700, 1.7700,  
R10: 0.5870, 0.5790, 0.5510, 0.5010, 0.4360, 0.3530,  
0.2580, 0.1630, 0.1010, 0.0598,  
R11: 1.1900, 1.1800, 1.1400, 1.0800, 0.9940, 0.8750,  
0.7260, 0.5530, 0.4270, 0.3310,  
R12: 0.1340, 0.1320, 0.1270, 0.1180, 0.1060, 0.0897,  
0.0705, 0.0498, 0.0355, 0.0249,  
R13: 0.1910, 0.1890, 0.1820, 0.1690, 0.1510, 0.1280,  
0.1010, 0.0711, 0.0507, 0.0356,  
R14: 7.7900, 7.8100, 7.8700, 7.9700, 8.1700, 8.4600,  
8.9700, 9.8800, 10.9000, 9.7300,  
R15: 17.2000, 17.2000, 17.4000, 17.6000, 18.0000, 18.7000,  
19.8000, 21.7000, 23.7000, 21.4000,  
R16: 63.8000, 63.6000, 62.9000, 61.5000, 59.5000, 56.6000,  
52.5000, 47.0000, 42.9000, 42.7000,

< (ZENI)

TITLE > Houston - Summer - Day#1 - Urban - Carbonyls <  
PLACE >

CITY = Houston;  
LAT = 29.8; LON = 95.2; TZONE = 6;  
YEAR = 1996; MONTH = 7; DAY = 15;

< (PLACE)

TIME > 0800, 2000 <

BOUNDARY >

REAC =  
ALK4, 0.2794, 0.2794, 0.2794,  
ALK7, 0.2073, 0.2073, 0.2073,  
ETHE, 0.0356, 0.0356, 0.0356,  
PRPE, 0.0191, 0.0191, 0.0191,

```

    TBUT,    0.0721,    0.0721,    0.0721,
    TOLU,    0.0511,    0.0511,    0.0511,
    XYLE,    0.0333,    0.0333,    0.0333,
    TMBZ,    0.1018,    0.1018,    0.1018,
    RCHO,    0.0090,    0.0090,    0.0090,
    BDIE,    0.0000,    0.0025,    0.0025,
    HCHO,    0.0000,    0.0200,    0.0200,
    ALD2,    0.0000,    0.0200,    0.0200,
    ACRO,    0.0000,    0.0010,    0.0010,
    NRHC,    0.1913,    0.1478,    0.1478;
IFRACTION NO2 = 0.20;
TRANSPORT =
    VOCALOFT = 0.1000,
    NOXALOFT = 0.0003,
    O3ALOFT = 0.0200,
    COALOFT = 0.2000;
INIT =
    HCHO = 0.00600,
    ALD2 = 0.00600,
    ACRO = 0.00030,
    BDIE = 0.00075,
    HONO = 0.001;
DEPO [12] =
    NO2 = 0.48,0.54,0.60,0.60,0.60,0.60,0.60,0.60,0.54,0.48,0.36,0.24,
    O3 = 0.60,0.70,0.80,0.80,0.80,0.80,0.80,0.80,0.70,0.60,0.50,0.30,
    HNO3 = 3.00,3.30,3.50,3.50,3.50,3.50,3.50,3.50,3.30,3.20,3.00,2.60,
    H2O2 = 1.80,1.90,2.00,2.00,2.00,2.00,2.00,2.00,1.90,1.80,1.70,1.70,
    PAN = 0.48,0.54,0.60,0.60,0.60,0.60,0.60,0.60,0.54,0.48,0.36,0.24;
< (BOUNDARY)
MET > {HOUSTON,SUMMER 1 }
DILUTION=
    MHINIT = 671,
    MHFINAL = 1457;
TEMPERATURE [13,C] =
    27.8, 29.4, 30.6, 31.7, 32.8, 33.3,
    33.9, 33.3, 32.8, 32.2, 31.1, 30.0, 28.9;
PRESSURE [AT] = 1.00;
RH [13] =
    82.0, 72.0, 63.0, 58.0, 54.5, 52.0,
    50.0, 51.0, 52.5, 54.0, 59.0, 65.5, 70.5;
< (MET)
MASS [12] >
    VOC = 0.3000,
    9.65,10.65,11.44,12.26,12.95,13.33,13.79,14.25,14.13,13.68,10.29, 7.33,
    NOX = 0.0300,
    4.61, 4.57, 4.69, 4.85, 4.95, 4.92, 5.00, 5.24, 5.35, 5.29, 4.62, 2.25,
    CO = 0.5000,
    31.2, 35.6, 36.9, 38.4, 39.4, 39.1, 40.0, 42.6, 43.8, 43.5, 35.9, 16.5,
    HCHO [30] = 0.0000001,
    .0466, .0478, .0487, .0499, .0505, .0503, .0510, .0529, .0538, .0535, .0468, .0230,
    ALD2 [44] = 0.0000001,
    .1594, .1725, .1789, .1870, .1918, .1902, .1953, .2089, .2161, .2139, .1797, .0972,
    ACRO [56] = 0.0000001,
    .0074, .0074, .0074, .0074, .0074, .0074, .0074, .0074, .0074, .0074, .0074, .0074,
    BDIE [54] = 0.0000001,
    .0262, .0259, .0259, .0259, .0259, .0259, .0259, .0259, .0260, .0259, .0259, .0259;
< (MASS)
CALCULATE >
    VOC = 0.3000;
    NOX = 0.0300;
    CO = 0.5000;
    PRINT [CONC] =
        NAMES [5] = CO,O3,HCHO,ALD2,ACRO,
        AVG [5] = CO,O3,HCHO,ALD2,ACRO;
< (CALCULATE)
END.

```

## 7.1 Estimation of Secondary HAP Production

The concentration of HAPs can be conceptually divided into two types: primary and secondary. Primary HAPs are the result of the direct emission into the air of the species in question, that is, the concentration that would result if there were no atmospheric chemical reactions that either form or remove the species. Secondary HAPs are the net results of chemical reactions in the atmosphere.

The method used to determine the relative amount of primary to secondary production for each target HAP was to conduct two OZIPR model runs for each scenario: one with emissions of the target HAP and the other without these emissions. For the latter run, all of the HAP production is secondary. This can then be compared to the HAP concentrations from the first run which represent the sum of both primary and secondary production.

If the target HAP concentrations were principally due to primary emissions, then this technique of eliminating the primary emissions would result in changes in the chemical equilibrium, particularly in the concentration of radicals that interact with the target HAPs as well as with many other compounds. This is not the case, however, since secondary formation generally dominates primary emissions, and test runs have shown that the radical concentrations are not greatly affected by removing primary target HAP emissions.

To eliminate primary target HAP emissions from an OZIPR run, several changes must be made to the input file. The first change is to remove the terms representing the target HAPs from the MASS option (that is, remove the HCHO, ALD2, and ACRO terms). Also, the second and third columns of data under the REAC option are modified to reflect changes in the aloft air concentrations. The assumption is made that in the absence of primary emissions, the aloft air would contain only 80% of the normal concentration of each carbonyl species. This is based on an assumed 20% primary to 80% secondary breakdown. The effect of the aloft concentrations on the surface concentrations seen later in the day is generally not that large, so uncertainties in the initial aloft concentrations should not result in large uncertainties in the final results. The final input file change needed is to set the initial carbonyl concentrations in the surface air (i.e., in the box) at the start of the run. These concentrations would not be zero, even without emissions, since there would be secondary production of carbonyls left in the atmosphere from the previous day. Similarly for the aloft concentrations, the initial surface concentrations are set to 80% of the values of the run, which includes primary emissions. This is done under the INIT option of the boundary command. In test runs, it was found that the concentrations of the target HAPs late in the day depend much more on the chemistry, the weather, and the hourly emissions than they do on the initial concentrations. Therefore, like the aloft concentrations, moderate uncertainties in the initial concentrations result in small uncertainties in the final HAP concentrations.

## 7.2 OZIPR Model Output

Each run of the OZIPR model (each scenario) produces two output files. The larger of the two has the filename extension .OUT, and it contains a log of the model run, detailing inputs, parameter settings, and certain values calculated internally by the model. For the purposes of this study, the second output file (with filename extension .TXT) is more important. This file contains a table of the concentrations of selected chemical species at the top of each hour; in particular, the three target HAPs. The concentrations are all in parts per million volume (ppmV). The times are in local standard (not daylight saving); standard time was used since all four seasons were being modeled. For presentation in the output tables in Section 9 of this report, the concentrations were converted to units of micrograms per cubic meter ( $\mu\text{g m}^{-3}$ ), using the ideal gas law applied to the model results with the appropriate temperature and pressure for each hour.

The OZIPR model was not run for the nighttime hours since it is a photochemical model and relatively little chemistry happens at night. At night, two effects will generally serve to reduce atmospheric concentrations: (1) horizontal transport away from the emission sources and (2) deposition on the ground. The OZIPR model does not account for dilution due to possible spreading of the pollutant “cloud.” Also, the model, as implemented here, does not reduce mixing height after the afternoon value has been reached. (OZIPR would allow varying nighttime mixing heights if one supplied them on an hourly basis as input.) The effect of stabilizing the nighttime air is that the upper levels become decoupled from, and no longer influence, the ground-level concentration. Also, in the relatively thin ground-level layer that is still mixed, surface deposition becomes much more important than in the daytime when the mixing box is much taller. Since these effects are not well modeled in OZIPR, a simple interpolation was used to estimate nighttime values. This was done by linearly interpolating in time between the 8 p.m. and 8 a.m. concentrations for each HAP of interest, assuming that the evening value was higher. In the relatively few cases where the morning concentrations were higher than the evening ones, the nighttime values were set equal to the evening value, under the assumption that the larger morning value was due to early morning emissions just prior to the start of the model run at 8 a.m. These interpolated nighttime values were used in the construction of seasonal and annual average concentrations.

## **Section 8**

### **Results and Discussion**

The OZIPR model was run for up to 48 scenarios for each of the 10 study areas; all runs were for the 8 a.m. to 8 p.m. time period. Within each of the four seasons, two or three typical days were used, and runs were made separately for both urban and rural areas. To estimate the relative importance of secondary production, each of these scenarios was run both with and without primary emissions of the target HAPs. The runs without target HAPs emissions provide estimates of secondary formation alone. The runs with emissions yield total concentrations. The ratio between these two gives the percentage of secondary production.

#### **8.1 Summary Tables of OZIPR Model Results**

Results for the secondary formation of the target HAPs for the 10 study areas for both urban and rural scenarios are presented in Tables 8-1, 8-2, and 8-3, corresponding to formaldehyde, acetaldehyde, and acrolein, respectively. The values are instantaneous concentrations at the top of each hour (indicated in military time), spatially averaged through the model study area and seasonally averaged across typical days. Seasons were defined as indicated in Sections 2 and 6 of this report.

All concentrations have been converted from parts per million (ppm), the OZIPR output units, to micrograms per cubic meter ( $\mu\text{g m}^{-3}$ ). Using the ideal gas law, conversions were made with the temperature and barometric pressure pertaining to each hour. For 25°C and a pressure of 1 atmosphere, the multiplicative factors for ppb units are 1.23, 1.80, and 2.29 for formaldehyde, acetaldehyde, and acrolein, respectively (i.e., 1 ppb of acetaldehyde gives 1.80  $\mu\text{g m}^{-3}$ ). Each concentration in these tables represents a seasonal average, with each typical day contributing to the weighted average according to its frequency of occurrence as listed in Table 6-3. As an example, for autumn in Atlanta (Table 6-3 A) the statistical weights were 213/339 for the first typical day, 89/339 for the second, and 37/339 for the third.

**Table 8-1. Secondary Production of Formaldehyde in  $\mu\text{g m}^{-3}$  as estimated by the OZIPR Model**

----- CITY=ATLANTA AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	3.9	4.8	5.4	5.7	5.7	5.8	5.9	5.9	6.1	6.3	6.4	6.5	6.5
SPRING	3.9	4.8	5.0	4.9	4.9	4.9	5.0	5.0	5.1	5.2	5.4	5.5	5.6
SUMMER	3.8	5.5	6.1	6.3	6.5	6.4	6.3	6.1	5.9	5.8	5.8	5.9	6.0
WINTER	4.1	4.4	5.2	6.1	6.5	6.5	6.2	6.0	6.0	6.1	6.1	6.2	6.2

----- CITY=ATLANTA AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	3.9	4.1	5.2	6.4	7.4	8.1	8.4	8.6	9.0	9.3	9.6	9.7	9.8
SPRING	3.9	4.2	5.2	6.1	6.6	6.8	6.8	6.8	7.0	7.2	7.5	7.7	7.8
SUMMER	3.8	4.8	6.2	7.3	7.9	7.9	7.8	7.6	7.5	7.5	7.7	8.0	8.1
WINTER	4.1	4.1	4.5	5.6	6.9	7.8	8.3	8.6	8.9	9.2	9.4	9.5	9.6

----- CITY=BOSTON AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.8	2.0	2.5	2.8	3.0	3.2	3.3	3.4	3.5	3.6	3.6	3.7	3.7
SPRING	0.8	2.5	2.7	2.8	2.9	3.0	3.0	3.0	3.1	3.1	3.2	3.2	3.3
SUMMER	0.8	2.6	3.0	3.3	3.4	3.5	3.5	3.5	3.6	3.8	3.9	4.0	4.1
WINTER	0.9	1.2	2.0	2.6	2.9	3.1	3.2	3.3	3.3	3.3	3.3	3.4	3.4

----- CITY=BOSTON AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	1.2	2.0	2.6	3.2	3.7	4.1	4.5	4.9	5.2	5.4	5.5	5.5	5.6
SPRING	1.2	2.5	3.1	3.6	4.0	4.3	4.7	4.9	5.2	5.5	5.7	5.8	5.8
SUMMER	1.2	2.7	3.5	4.2	5.0	5.7	6.1	6.5	6.9	7.3	7.7	7.9	8.0
WINTER	1.3	1.5	2.0	2.7	3.3	3.8	4.1	4.4	4.5	4.5	4.5	4.6	4.6

**Table 8-1. Continued**

----- CITY=CHICAGO AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	1.0	1.5	1.8	2.0	2.2	2.3	2.3	2.4	2.5	2.5	2.5	2.5	2.6
SPRING	1.0	1.8	1.8	1.9	1.9	1.9	1.8	1.8	1.8	1.8	1.8	1.9	1.9
SUMMER	1.0	1.8	1.9	2.0	2.1	2.1	2.1	2.1	2.1	2.2	2.3	2.3	2.3
WINTER	1.1	1.3	2.0	2.6	3.0	3.1	3.2	3.3	3.3	3.3	3.3	3.4	3.4

----- CITY=CHICAGO AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	2.4	2.3	3.2	4.5	5.6	6.6	7.3	8.0	8.6	9.0	9.2	9.3	9.5
SPRING	2.4	2.7	3.4	4.1	4.8	5.3	5.7	6.0	6.4	6.8	7.1	7.4	7.5
SUMMER	2.3	2.7	3.5	4.5	5.5	6.2	6.6	6.9	7.3	7.8	8.3	8.6	8.9
WINTER	2.6	2.7	3.2	4.5	6.4	8.2	9.6	10.5	11.0	11.1	11.1	11.2	11.2

----- CITY=DENVER AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	3.4	3.0	3.1	3.0	2.9	2.9	2.8	2.9	2.9	3.0	3.0	3.0	3.1
SPRING	3.4	3.4	3.2	3.0	2.8	2.7	2.6	2.6	2.6	2.6	2.7	2.7	2.7
SUMMER	3.3	3.2	2.9	2.9	2.9	3.0	3.0	3.0	3.1	3.1	3.1	3.2	3.2
WINTER	3.6	3.1	3.1	3.1	3.1	3.0	2.9	2.9	2.9	3.0	3.0	3.0	3.1

----- CITY=DENVER AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	3.4	3.0	3.7	4.6	5.4	5.8	6.1	6.4	6.7	6.8	6.9	7.0	7.1
SPRING	3.4	3.5	4.2	4.8	5.2	5.3	5.4	5.4	5.5	5.6	5.7	5.8	5.9
SUMMER	3.3	3.4	4.1	4.9	5.6	5.9	6.0	6.0	6.1	6.2	6.4	6.5	6.6
WINTER	3.6	3.0	2.9	3.5	4.4	5.2	5.8	6.2	6.5	6.6	6.6	6.7	6.7

----- CITY=HOUSTON AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	4.0	4.5	4.4	4.5	4.6	4.7	4.8	4.9	5.0	5.1	5.2	5.3	5.3
SPRING	4.0	5.7	5.9	5.9	5.9	5.8	5.8	5.7	5.6	5.6	5.7	5.8	5.9
SUMMER	3.9	6.3	7.1	7.3	7.3	7.0	6.7	6.4	6.1	6.0	6.0	6.1	6.2
WINTER	4.2	4.8	5.3	5.3	5.2	5.1	5.1	5.2	5.3	5.4	5.5	5.5	5.6

----- CITY=HOUSTON AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	6.0	6.0	6.8	7.8	8.6	8.9	9.0	9.2	9.5	9.8	10.0	10.2	10.4
SPRING	6.0	8.2	9.3	9.9	10.1	9.7	9.2	8.9	8.9	9.1	9.4	9.6	9.8
SUMMER	5.8	9.1	11.2	11.9	11.5	10.6	9.9	9.4	9.2	9.3	9.5	9.8	10.0
WINTER	6.2	6.5	7.4	8.4	9.2	9.7	10.0	10.4	10.8	11.1	11.3	11.5	11.6

**Table 8-1. Continued**

----- CITY=LOS ANGELES AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	8.4	11.5	14.0	15.0	14.8	14.0	13.4	13.2	13.2	13.4	13.6	13.8	13.9
SPRING	8.4	14.7	17.2	17.1	15.5	14.0	13.2	12.5	12.1	12.1	12.3	12.5	12.7
SUMMER	8.3	15.3	18.2	18.0	16.4	15.4	14.5	13.7	13.2	13.0	13.2	13.5	13.7
WINTER	8.6	8.0	9.1	10.3	11.0	11.2	11.1	11.1	11.2	11.3	11.4	11.5	11.5

----- CITY=LOS ANGELES AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	8.4	10.3	13.3	15.1	15.9	16.2	16.3	16.5	16.8	17.2	17.6	17.8	18.0
SPRING	8.4	13.2	16.4	17.2	17.0	16.3	15.3	14.5	14.1	14.2	14.4	14.7	14.9
SUMMER	8.3	14.0	17.8	19.2	19.2	18.5	17.5	16.5	15.9	15.9	16.3	16.7	17.1
WINTER	8.6	7.4	8.3	9.9	11.2	11.9	12.2	12.6	12.9	13.2	13.4	13.5	13.6

----- CITY=PHOENIX AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	3.8	3.9	3.9	4.0	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.7	4.8
SPRING	3.9	4.6	4.5	4.4	4.4	4.5	4.5	4.4	4.4	4.4	4.4	4.5	4.6
SUMMER	3.7	5.5	6.2	6.3	6.1	5.8	5.4	5.0	4.7	4.5	4.4	4.4	4.4
WINTER	4.0	4.0	4.1	4.2	4.2	4.2	4.2	4.3	4.5	4.6	4.6	4.7	4.7

----- CITY=PHOENIX AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	3.8	3.8	4.2	5.0	5.6	5.8	5.8	5.8	5.8	5.9	6.0	6.0	6.0
SPRING	3.9	4.5	5.1	5.5	5.7	5.7	5.4	5.2	5.1	5.0	5.1	5.1	5.2
SUMMER	3.7	5.3	6.4	7.1	7.1	6.6	6.0	5.4	5.0	4.7	4.6	4.6	4.7
WINTER	4.0	3.8	3.9	4.4	4.9	5.3	5.5	5.6	5.7	5.8	5.8	5.9	5.9

----- CITY=PITTSBURGH AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	4.0	4.7	5.4	5.7	5.8	5.7	5.6	5.7	5.8	5.9	5.9	6.0	6.0
SPRING	4.0	5.7	6.2	6.0	5.6	5.2	4.9	4.8	4.7	4.8	4.8	4.9	4.9
SUMMER	3.8	5.6	5.9	5.9	6.0	6.0	5.9	5.7	5.7	5.6	5.6	5.7	5.8
WINTER	4.2	4.5	5.6	7.1	8.1	8.5	8.6	8.5	8.4	8.5	8.5	8.6	8.6

----- CITY=PITTSBURGH AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	4.0	4.3	5.1	6.0	6.6	7.0	7.2	7.3	7.5	7.7	7.8	8.0	8.1
SPRING	4.0	5.1	6.1	6.6	6.7	6.6	6.4	6.2	6.2	6.3	6.4	6.6	6.7
SUMMER	3.8	5.1	6.0	6.7	7.0	7.0	6.8	6.7	6.7	6.7	6.9	7.1	7.2
WINTER	4.2	4.3	5.0	6.3	7.6	8.4	8.9	9.1	9.3	9.5	9.6	9.8	9.8

**Table 8-1. Continued**

----- CITY=SEATTLE AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.8	1.6	2.2	2.5	2.7	2.8	2.9	3.0	3.1	3.1	3.2	3.2	3.2
SPRING	0.8	2.1	2.4	2.4	2.4	2.4	2.3	2.2	2.2	2.2	2.3	2.3	2.3
SUMMER	0.8	2.4	2.6	2.6	2.6	2.6	2.5	2.5	2.5	2.6	2.6	2.7	2.8
WINTER	0.8	0.9	1.3	1.9	2.4	2.7	2.9	3.0	3.1	3.1	3.1	3.1	3.1

----- CITY=SEATTLE AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	1.2	1.7	2.3	2.8	3.3	3.6	3.9	4.2	4.4	4.5	4.6	4.6	4.7
SPRING	1.2	2.1	2.5	2.8	3.0	3.1	3.2	3.2	3.3	3.4	3.4	3.5	3.6
SUMMER	1.2	2.4	2.8	3.0	3.2	3.4	3.6	3.7	3.8	3.9	4.1	4.2	4.3
WINTER	1.2	1.3	1.5	2.1	2.6	3.1	3.6	3.9	4.1	4.1	4.1	4.2	4.2

----- CITY=WASHINGTON AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	1.2	1.9	2.4	2.7	2.9	3.0	3.1	3.1	3.2	3.2	3.3	3.3	3.3
SPRING	1.2	2.3	2.6	2.7	2.8	2.8	2.8	2.7	2.7	2.7	2.7	2.8	2.8
SUMMER	1.2	2.4	2.8	3.1	3.4	3.5	3.3	3.2	3.2	3.1	3.2	3.2	3.2
WINTER	1.3	1.5	2.0	2.5	2.9	3.0	3.1	3.1	3.1	3.2	3.2	3.2	3.2

----- CITY=WASHINGTON AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	3.1	3.9	5.2	6.4	7.5	8.4	9.2	10.1	10.8	11.3	11.6	11.8	11.9
SPRING	3.1	4.5	5.6	6.4	7.0	7.6	8.1	8.5	9.0	9.6	10.1	10.4	10.6
SUMMER	3.0	4.7	5.9	7.1	8.2	9.0	9.4	9.5	9.9	10.4	10.9	11.3	11.6
WINTER	3.2	3.4	4.2	5.7	7.2	8.5	9.5	10.2	10.7	10.9	11.0	11.1	11.3

**Table 8-2. Secondary Production of Acetaldehyde ( $\mu\text{g m}^{-3}$ ) Estimated by the OZIPR Model**

----- CITY=ATLANTA AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	5.8	11.4	11.0	9.6	8.7	8.2	7.7	7.4	7.3	7.3	7.5	7.6	7.7
SPRING	5.8	10.8	9.4	8.2	7.7	7.3	6.8	6.4	6.2	6.0	6.0	6.2	6.3
SUMMER	5.6	11.8	9.5	8.1	7.2	6.4	5.7	5.3	5.0	4.8	4.9	5.0	5.1
WINTER	6.0	9.0	12.8	13.2	12.0	10.7	9.8	9.4	9.3	9.3	9.4	9.5	9.6

----- CITY=ATLANTA AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	5.8	9.4	12.1	13.0	12.6	11.6	10.7	10.3	10.3	10.8	11.6	12.6	13.3
SPRING	5.8	9.8	11.2	10.7	9.4	8.1	7.1	6.6	6.4	6.5	6.9	7.4	8.0
SUMMER	5.6	11.2	11.8	10.2	8.1	6.5	5.7	5.3	5.3	5.4	5.8	6.3	6.8
WINTER	6.0	7.1	10.6	14.4	16.5	17.2	17.3	17.4	17.9	18.5	19.2	20.0	20.6

----- CITY=BOSTON AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	1.2	3.7	3.7	3.6	3.6	3.5	3.5	3.7	3.9	4.1	4.4	4.6	4.9
SPRING	1.2	3.8	3.5	3.3	3.1	3.0	2.9	3.0	3.1	3.4	3.6	3.9	4.1
SUMMER	1.2	3.5	3.1	2.6	2.2	2.1	2.1	2.2	2.5	2.7	3.0	3.3	3.5
WINTER	1.3	3.1	4.3	4.6	4.7	4.8	4.9	5.0	5.1	5.2	5.3	5.4	5.4

----- CITY=BOSTON AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	1.8	4.9	6.1	6.9	7.7	8.3	9.0	9.6	10.3	10.8	11.3	11.6	11.9
SPRING	1.8	5.8	6.6	7.3	7.9	8.5	9.1	9.7	10.5	11.3	11.9	12.4	12.8
SUMMER	1.7	5.6	6.1	6.4	6.6	6.5	6.5	6.6	7.0	7.6	8.4	9.1	10.0
WINTER	1.9	3.4	5.5	7.2	8.4	9.4	10.1	10.7	11.0	11.1	11.1	11.1	11.2

----- CITY=CHICAGO AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	1.5	3.6	3.3	3.1	2.9	2.7	2.6	2.6	2.7	2.8	3.0	3.2	3.3
SPRING	1.5	3.5	2.8	2.2	1.8	1.6	1.4	1.3	1.4	1.4	1.5	1.6	1.7
SUMMER	1.4	3.1	2.1	1.4	1.0	0.9	0.9	0.9	1.0	1.1	1.2	1.3	1.5
WINTER	1.6	3.5	5.2	5.6	5.6	5.5	5.5	5.6	5.7	5.8	5.9	6.0	6.1

----- CITY=CHICAGO AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	3.6	7.0	10.5	13.5	15.7	17.4	18.8	20.5	22.2	23.5	24.7	25.6	26.2
SPRING	3.6	8.3	10.1	11.2	12.0	12.7	13.2	13.8	14.9	16.1	17.3	18.6	19.8
SUMMER	3.4	8.3	9.4	9.3	8.8	8.0	7.4	7.1	7.5	8.3	9.4	10.6	11.9
WINTER	3.8	5.6	10.1	16.4	22.5	27.3	30.9	33.5	34.8	35.1	35.2	35.3	35.4

**Table 8-2. Continued**

----- CITY=DENVER AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	5.0	5.3	5.2	5.2	5.3	5.4	5.4	5.5	5.6	5.6	5.7	5.8	5.8
SPRING	5.0	6.1	5.5	5.4	5.3	5.3	5.2	5.1	5.2	5.2	5.2	5.3	5.3
SUMMER	4.8	5.5	4.7	4.5	4.4	4.3	4.2	4.0	4.0	3.9	3.9	4.0	4.0
WINTER	5.2	5.4	5.4	5.4	5.4	5.4	5.4	5.5	5.6	5.8	5.9	5.9	6.0

----- CITY=DENVER AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	5.0	5.2	6.7	7.7	8.0	8.1	8.1	8.4	8.7	9.0	9.4	9.7	10.0
SPRING	5.0	6.5	7.1	7.1	6.8	6.4	6.1	6.0	6.1	6.4	6.6	6.9	7.2
SUMMER	4.8	6.2	6.4	6.0	5.4	4.7	4.2	4.0	4.0	4.1	4.4	4.6	4.9
WINTER	5.2	4.6	5.2	7.0	8.9	10.1	10.9	11.5	12.0	12.3	12.4	12.4	12.5

----- CITY=HOUSTON AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	5.9	9.3	8.4	8.0	7.9	7.7	7.5	7.4	7.4	7.5	7.7	7.9	8.0
SPRING	5.9	12.1	11.0	10.0	9.1	8.4	7.7	7.2	6.9	6.9	7.0	7.1	7.3
SUMMER	5.7	12.4	11.2	9.7	8.5	7.5	6.8	6.3	6.1	6.1	6.2	6.4	6.7
WINTER	6.1	10.5	11.4	10.7	10.2	9.9	9.6	9.5	9.5	9.6	9.7	9.8	9.9

----- CITY=HOUSTON AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	8.8	12.7	13.0	12.2	10.8	9.4	8.5	8.2	8.4	8.8	9.6	10.4	10.9
SPRING	8.8	17.4	16.9	14.3	11.3	8.7	7.3	6.8	6.8	7.2	7.7	8.4	8.9
SUMMER	8.6	18.3	16.7	12.8	9.1	7.1	6.4	6.2	6.2	6.6	7.1	7.7	8.1
WINTER	9.1	12.6	16.1	17.4	17.4	16.9	16.3	16.2	16.5	17.0	17.8	18.5	19.1

----- CITY=LOS ANGELES AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	6.1	20.8	24.2	22.7	19.6	17.0	15.5	15.0	14.9	15.1	15.4	15.6	15.8
SPRING	6.1	27.2	28.9	24.9	20.1	17.7	16.1	15.0	14.4	14.3	14.5	14.7	14.8
SUMMER	6.0	28.1	28.6	23.3	19.0	16.7	15.0	13.8	13.3	13.2	13.6	14.0	14.5
WINTER	6.3	11.5	16.1	18.0	17.7	16.7	15.7	15.3	15.2	15.3	15.4	15.5	15.6

----- CITY=LOS ANGELES AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	6.1	17.9	24.5	26.1	25.6	24.6	23.7	23.4	23.8	24.6	25.7	26.5	27.2
SPRING	6.1	24.3	30.0	29.6	27.3	24.5	21.8	19.8	18.9	18.9	19.4	19.9	20.3
SUMMER	6.0	25.9	31.3	30.6	27.8	24.4	21.0	18.5	17.5	17.7	18.5	19.4	20.3
WINTER	6.3	9.3	14.4	18.2	19.8	20.2	20.2	20.4	20.8	21.2	21.9	22.4	22.9

**Table 8-2. Continued**

----- CITY=PHOENIX AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	5.6	8.3	7.4	7.1	6.9	6.7	6.3	6.1	6.0	5.9	6.0	6.0	6.1
SPRING	5.7	9.8	8.7	8.0	7.5	7.0	6.5	6.0	5.7	5.5	5.4	5.4	5.5
SUMMER	5.4	10.8	9.4	7.9	6.8	5.8	5.1	4.6	4.2	4.0	3.9	3.9	4.0
WINTER	5.9	8.1	8.9	8.6	8.4	8.4	8.2	8.2	8.2	8.3	8.4	8.4	8.5

----- CITY=PHOENIX AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	5.6	7.4	7.8	7.4	6.3	5.3	4.7	4.2	4.0	4.0	4.0	4.1	4.0
SPRING	5.7	9.3	9.0	7.8	6.3	5.0	4.1	3.6	3.4	3.2	3.2	3.3	3.3
SUMMER	5.4	10.4	9.5	7.3	5.2	4.0	3.4	3.1	2.8	2.7	2.7	2.7	2.7
WINTER	5.9	6.6	7.8	8.8	9.0	8.6	7.9	7.4	7.2	7.1	7.2	7.3	7.3

----- CITY=PITTSBURGH AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	5.8	12.7	13.0	11.8	10.5	9.6	9.0	8.7	8.6	8.7	8.8	9.0	9.1
SPRING	5.9	14.8	13.2	11.0	9.6	8.8	8.2	7.6	7.2	7.0	7.0	7.0	7.1
SUMMER	5.6	13.4	10.7	9.0	7.9	7.0	6.1	5.5	5.0	4.7	4.6	4.7	4.8
WINTER	6.1	9.5	15.8	19.0	19.1	18.0	16.8	15.9	15.7	15.8	15.9	16.1	16.2

----- CITY=PITTSBURGH AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	5.8	11.0	13.6	14.2	13.6	12.5	11.6	11.3	11.4	11.7	12.4	13.0	13.6
SPRING	5.9	13.8	14.8	13.9	12.3	10.8	9.6	8.8	8.4	8.4	8.7	9.2	9.7
SUMMER	5.6	13.2	12.8	10.6	8.4	6.8	5.9	5.4	5.2	5.1	5.4	5.7	6.2
WINTER	6.1	7.8	13.0	18.3	21.4	22.8	23.5	24.0	24.5	25.2	25.8	26.4	26.8

----- CITY=SEATTLE AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	1.2	3.4	3.5	3.4	3.2	3.1	3.0	3.0	3.1	3.2	3.3	3.5	3.7
SPRING	1.2	3.4	2.9	2.5	2.1	1.7	1.5	1.4	1.4	1.4	1.5	1.5	1.6
SUMMER	1.2	3.4	2.7	2.2	1.6	1.3	1.1	1.1	1.2	1.3	1.5	1.7	1.9
WINTER	1.2	1.8	3.2	4.1	4.4	4.5	4.6	4.7	4.8	4.9	5.0	5.0	5.1

----- CITY=SEATTLE AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	1.8	4.1	5.4	6.0	6.5	6.8	7.1	7.4	7.8	8.1	8.6	9.0	9.5
SPRING	1.8	4.8	5.0	5.0	4.8	4.5	4.3	4.2	4.2	4.4	4.6	4.9	5.2
SUMMER	1.8	5.1	5.1	4.8	4.3	3.9	3.4	3.2	3.1	3.2	3.5	3.8	4.2
WINTER	1.8	2.2	3.8	5.7	7.1	8.3	9.3	10.1	10.6	10.8	10.9	11.0	11.0

**Table 8-2. Continued**

----- CITY=WASHINGTON AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
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AUTUMN	1.8	3.8	4.1	3.9	3.6	3.3	3.1	3.0	3.0	3.1	3.2	3.2	3.3
SPRING	1.8	4.2	3.9	3.4	3.0	2.6	2.3	2.0	1.9	1.9	2.0	2.0	2.1
SUMMER	1.7	4.0	3.6	2.9	2.2	1.7	1.4	1.3	1.3	1.3	1.4	1.5	1.5
WINTER	1.9	2.8	4.1	4.7	4.8	4.7	4.6	4.5	4.5	4.6	4.6	4.6	4.6

----- CITY=WASHINGTON AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	4.5	9.1	11.8	13.5	14.7	15.5	16.3	17.4	18.6	19.8	21.2	22.4	23.2
SPRING	4.5	10.3	11.8	12.4	12.8	13.1	13.4	13.7	14.6	15.7	16.9	18.1	19.3
SUMMER	4.3	10.2	11.0	10.6	9.9	9.1	8.3	7.8	8.1	8.7	9.8	10.7	11.7
WINTER	4.7	6.4	10.2	14.4	17.6	20.1	21.9	23.4	24.5	25.0	25.1	25.2	25.4

**Table 8-3. Secondary Production of Acrolein ( $\mu\text{g m}^{-3}$ ) Estimated by the OZIPR Model**

----- CITY=ATLANTA AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.4	0.5	0.3	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
SPRING	0.4	0.4	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0
SUMMER	0.4	0.4	0.2	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WINTER	0.4	0.8	0.6	0.4	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

----- CITY=ATLANTA AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.4	0.6	0.4	0.3	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.2
SPRING	0.4	0.5	0.3	0.2	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.1	0.1
SUMMER	0.4	0.5	0.3	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WINTER	0.4	0.9	0.7	0.6	0.5	0.4	0.4	0.4	0.3	0.4	0.4	0.4	0.4

----- CITY=BOSTON AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
SPRING	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SUMMER	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WINTER	0.1	0.3	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2

----- CITY=BOSTON AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.1	0.4	0.3	0.3	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4
SPRING	0.1	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3
SUMMER	0.1	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
WINTER	0.1	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.5

----- CITY=CHICAGO AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.1	0.2	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1
SPRING	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SUMMER	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WINTER	0.1	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

----- CITY=CHICAGO AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.2	0.6	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.6
SPRING	0.2	0.6	0.4	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3
SUMMER	0.2	0.4	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
WINTER	0.2	1.0	1.0	0.9	0.9	0.9	0.9	0.9	1.0	1.1	1.1	1.1	1.1

**Table 8-3. Continued**

----- CITY=DENVER AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
SPRING	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1
SUMMER	0.3	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
WINTER	0.3	0.6	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

----- CITY=DENVER AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.3	0.4	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
SPRING	0.3	0.4	0.3	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
SUMMER	0.3	0.3	0.2	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WINTER	0.3	0.7	0.5	0.4	0.4	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4

----- CITY=HOUSTON AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.4	0.7	0.5	0.4	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2
SPRING	0.4	0.9	0.6	0.5	0.3	0.3	0.2	0.2	0.1	0.1	0.1	0.1	0.1
SUMMER	0.4	0.8	0.5	0.4	0.2	0.2	0.1	0.1	0.1	0.0	0.0	0.0	0.0
WINTER	0.4	1.3	0.9	0.6	0.6	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4

----- CITY=HOUSTON AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.6	1.2	0.7	0.5	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.2	0.2
SPRING	0.6	1.5	0.9	0.6	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1
SUMMER	0.5	1.4	0.8	0.4	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.1
WINTER	0.6	2.1	1.5	1.1	0.9	0.7	0.6	0.6	0.6	0.6	0.6	0.7	0.7

----- CITY=LOS ANGELES AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.2	2.2	1.6	1.1	0.7	0.5	0.4	0.3	0.3	0.3	0.3	0.3	0.3
SPRING	0.2	2.4	1.7	1.1	0.7	0.5	0.4	0.3	0.2	0.2	0.2	0.2	0.2
SUMMER	0.2	2.2	1.5	0.8	0.5	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.1
WINTER	0.2	2.3	1.6	1.2	0.9	0.7	0.6	0.5	0.5	0.5	0.5	0.5	0.5

----- CITY=LOS ANGELES AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.2	2.4	1.8	1.4	1.1	0.9	0.8	0.7	0.7	0.7	0.7	0.7	0.7
SPRING	0.2	2.6	2.0	1.6	1.2	0.8	0.6	0.5	0.4	0.4	0.4	0.4	0.4
SUMMER	0.2	2.5	1.9	1.4	1.0	0.6	0.4	0.3	0.2	0.2	0.2	0.2	0.3
WINTER	0.2	2.4	1.8	1.4	1.2	1.0	0.9	0.8	0.8	0.8	0.8	0.9	0.9

**Table 8-3. Continued**

----- CITY=PHOENIX AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.4	0.8	0.5	0.4	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2
SPRING	0.4	0.8	0.6	0.4	0.4	0.3	0.2	0.2	0.2	0.1	0.1	0.1	0.1
SUMMER	0.3	0.9	0.5	0.4	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1
WINTER	0.4	1.3	0.9	0.7	0.5	0.5	0.5	0.4	0.4	0.4	0.4	0.4	0.4

----- CITY=PHOENIX AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.4	0.9	0.5	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
SPRING	0.4	0.9	0.6	0.4	0.2	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0
SUMMER	0.3	0.9	0.5	0.3	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WINTER	0.4	1.4	1.0	0.7	0.5	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3

----- CITY=PITTSBURGH AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.4	0.8	0.6	0.4	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
SPRING	0.4	0.8	0.5	0.3	0.3	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1
SUMMER	0.4	0.6	0.3	0.2	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0
WINTER	0.4	1.5	1.3	1.1	0.9	0.7	0.6	0.6	0.6	0.6	0.6	0.6	0.6

----- CITY=PITTSBURGH AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.4	0.9	0.7	0.5	0.4	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2
SPRING	0.4	0.9	0.6	0.4	0.3	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.1
SUMMER	0.4	0.7	0.4	0.2	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0
WINTER	0.4	1.5	1.4	1.3	1.1	1.0	0.9	0.9	0.9	0.9	0.9	0.9	1.0

----- CITY=SEATTLE AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
SPRING	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SUMMER	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WINTER	0.1	0.3	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.2	0.2	0.2	0.2

----- CITY=SEATTLE AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.1	0.4	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
SPRING	0.1	0.3	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
SUMMER	0.1	0.3	0.2	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WINTER	0.1	0.5	0.4	0.4	0.4	0.4	0.3	0.4	0.4	0.4	0.4	0.4	0.4

**Table 8-3. Continued**

----- CITY=WASHINGTON AREA=RURAL -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.1	0.4	0.3	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
SPRING	0.1	0.4	0.2	0.2	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0
SUMMER	0.1	0.3	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WINTER	0.1	0.6	0.5	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

----- CITY=WASHINGTON AREA=URBAN -----

SEASON	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
AUTUMN	0.3	1.2	1.0	0.8	0.7	0.6	0.6	0.5	0.6	0.6	0.7	0.7	0.8
SPRING	0.3	1.1	0.8	0.6	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.5
SUMMER	0.3	0.9	0.6	0.4	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.2	0.2
WINTER	0.3	1.6	1.5	1.4	1.3	1.2	1.2	1.2	1.3	1.3	1.4	1.4	1.4

## 8.2 Discussion of OZIPR Output Tables

### 8.2.1 Variation by Pollutant

The above tables for secondary production generally show that late in the day (when levels tend to be highest) formaldehyde and acetaldehyde concentrations are comparable in summer, with somewhat more acetaldehyde than formaldehyde in winter. For most hours in most scenarios, the formaldehyde concentration was between 3 and 10  $\mu\text{g m}^{-3}$ , with extreme values ranging from 0.8 to 19.2  $\mu\text{g m}^{-3}$ . For acetaldehyde, the typical values ranged from 3 to 20  $\mu\text{g m}^{-3}$ , with extreme values varying from 1.1 to 35.4  $\mu\text{g m}^{-3}$ . The levels of acrolein were much lower than the other two HAPs at all times. For acrolein, the typical levels were 0.1 to 0.4  $\mu\text{g m}^{-3}$ , with extreme levels ranging from zero (i.e., below 0.05  $\mu\text{g m}^{-3}$ ) to 2.6  $\mu\text{g m}^{-3}$ . Concentrations of acrolein above 1  $\mu\text{g m}^{-3}$  are generally seen only early in the day, as photochemical destruction of acrolein tends to outpace formation.

### 8.2.2 Variation by Hour of Day

For most scenarios, both formaldehyde and acetaldehyde concentrations tend to increase over the course of the day, with the daily maximum occurring near (or at) the end of the simulation. Some scenarios also show a morning peak around 10 or 11 a.m., creating a bimodal profile. It should be noted that the 8 a.m. values in the above tables are determined by the initial conditions provided to the OZIPR model, which are somewhat uncertain because the chemistry of the immediately preceding hours (before 8 a.m.) was not modeled. Because the reaction rates that dominate production and removal of the target HAPs are fairly fast, values later in the day tend to reflect the chemical transformation of recent emissions, with relatively little impact from the initial conditions. For both formaldehyde and acetaldehyde, the largest concentrations occur late in the day when the initial conditions have almost no influence. On the other hand, acrolein levels, while always small,

tend to peak in the morning around 9 a.m. Therefore, the estimation of the daily maximum concentration for acrolein presumably would benefit from an improved characterization of the early morning chemistry.

### **8.2.3 *Variation by Season***

The formaldehyde concentrations in Table 8-1 show relatively little variation by season. Even the final hour of the simulations (8 p.m.), which shows more variation than other hours, is generally within 20% of the annual mean in all seasons. Acetaldehyde, particularly in urban areas, shows much more seasonal variation, with autumn and winter values sometimes at two or three times the levels seen in spring and summer. The ratio of acetaldehyde to formaldehyde is generally close to unity in the summer, but several scenarios show substantially larger ratios in winter. Observed data (see the discussion later in this section) tend to support ratios near unity, but most observations are made in the summertime.

### **8.2.4 *Urban/Rural Variation***

In every study area except Phoenix, the urban area showed higher concentrations of all three pollutants than the rural area. The size of the differences between the urban and rural results depend on the particular choice of counties in each study area. For cases including Washington, DC, and Chicago, the urban area is almost entirely built up, with a universally very high road and traffic density. The rural areas for these cities (see Table 2-1 for the counties) are largely farms or forest, with very different emissions. For several western cities, particularly Phoenix, the nominally “urban” county is extremely large, and in fact is mostly nonurbanized. In such cases, the box model as used by OZIPR effectively averages urban and rural areas within the same county, which reduces the contrast with truly rural areas. Note that for all three pollutants, the very high concentrations occurred in urban areas. The only exception to this was for Los Angeles, where Ventura County was used as the rural study area. Compared to the rest of the Los Angeles area, Ventura County is relatively unpopulated, but with 700,000 people, it is comparable to some of the urban counties in other study areas.

Another observation from these OZIPR runs is that there often appeared to be a time lag of about an hour or two for the rural areas in the development of the peak for formaldehyde and acetaldehyde. This may be a reflection of morning rush hour emissions in the urban areas and the greater importance of biogenic emissions in the rural areas.

### **8.3 Annual Averages of Target Compounds from Secondary Formation**

The results discussed above were used to estimate the secondary contribution of formaldehyde, acetaldehyde, and acrolein on an annual basis. The determination of an annual average required estimates for the 12-hour nighttime period for which the model was not run. OZIPR or any photochemical model is designed to be used during daylight hours when radical concentrations are sufficiently high to render a reasonable conversion of precursors to products. During periods when reactive conversions are minimized, advective transport plays a much bigger role. Therefore, the OZIPR model was not run at night and the nighttime formaldehyde, acetaldehyde, and acrolein concentrations were obtained by linear interpolation. This was done by interpolating between the 8 p.m. value and using the 8 a.m. value as the concentration 12 hours later. In the occasional instances where the initial value of the day was greater than the ending value, the nighttime concentrations were simply set equal to the 8 p.m. level. This procedure was consistent with the expectation of decreasing aldehyde concentrations at night.

Once nighttime values were obtained for each OZIPR scenario, annual estimates of secondary production were determined as follows. First a daily value for each pollutant under each scenario was computed by averaging across all hours. Seasonal means were constructed by weighting each daily value according to the frequency of the typical day. (The weighting technique is illustrated in the example calculation for Tables 8-1 through 8-3.) The seasonal means were then averaged to generate the final annual estimate of secondary production. Similarly, using the OZIPR runs that included HAPs emissions, annual total levels were derived for each pollutant. Annual primary levels were found by subtraction. The resulting annual numbers are tabulated in Tables 8-4, 8-5, and 8-6 for formaldehyde, acetaldehyde, and acrolein, respectively. Table 8-7 provides the percentage of secondary production on an annual basis for both urban and rural areas for each city. (Note that the percentages for acrolein are somewhat more uncertain than the others due to the low concentrations combined with model round-off error.) Figures 8-1 through 8-3 display maps of annual average secondary production estimates for the target HAPs.

**Table 8-4. Annual Averages for Formaldehyde Concentrations. All values are  $\mu\text{g m}^{-3}$ .**

City	Urban			Rural		
	Secondary	Primary	Total	Secondary	Primary	Total
Atlanta	6.8	0.7	7.5	5.3	0.5	5.8
Boston	4.0	0.5	4.5	2.6	0.2	2.8
Chicago	6.2	0.8	7.1	2.0	0.2	2.2
Denver	5.2	0.8	6.0	3.0	0.3	3.3
Houston	8.8	0.9	9.7	5.2	0.5	5.7
Los Angeles	13.4	1.1	14.5	11.8	0.8	12.7
Phoenix	5.0	0.5	5.4	4.4	0.4	4.8
Pittsburgh	6.4	0.7	7.1	5.6	0.5	6.1
Seattle	3.0	0.3	3.3	2.2	0.2	2.3
Washington, DC	7.8	1.0	8.8	2.5	0.2	2.7

**Table 8-5. Annual Averages for Acetaldehyde Concentrations. All values are  $\mu\text{g m}^{-3}$ .**

City	Urban			Rural		
	Secondary	Primary	Total	Secondary	Primary	Total
Atlanta	9.8	1.3	11.1	7.2	0.6	7.8
Boston	7.5	1.1	8.6	3.2	0.3	3.5
Chicago	14.9	1.9	16.8	2.6	0.2	2.8
Denver	7.0	1.2	8.3	5.1	0.4	5.5
Houston	10.9	1.2	12.0	7.7	0.7	8.4
Los Angeles	18.0	1.3	19.3	13.8	0.8	14.6
Phoenix	5.0	0.3	5.3	6.2	0.5	6.7
Pittsburgh	11.4	1.1	12.5	8.9	0.7	9.6
Seattle	5.2	0.6	5.9	2.4	0.2	2.7
Washington, DC	13.4	2.4	15.8	2.7	0.2	2.9

**Table 8-6. Annual Averages for Acrolein Concentrations. All values are  $\mu\text{g m}^{-3}$ .**

City	Urban			Rural		
	Secondary	Primary	Total	Secondary	Primary	Total
Atlanta	0.2	0.0	0.2	0.1	0.0	0.2
Boston	0.2	0.1	0.3	0.1	0.0	0.1
Chicago	0.4	0.1	0.5	0.1	0.0	0.1
Denver	0.2	0.1	0.3	0.2	0.0	0.2
Houston	0.4	0.1	0.4	0.3	0.0	0.3
Los Angeles	0.7	0.0	0.7	0.4	0.0	0.5
Phoenix	0.2	0.0	0.2	0.3	0.0	0.3
Pittsburgh	0.4	0.1	0.4	0.3	0.0	0.3
Seattle	0.2	0.0	0.2	0.1	0.0	0.1
Washington, DC	0.6	0.1	0.7	0.1	0.0	0.1

**Table 8-7. Annual Secondary Production as a Percentage of Total**

City	Urban			Rural		
	Formaldehyde	Acetaldehyde	Acrolein	Formaldehyde	Acetaldehyde	Acrolein
Atlanta	91%	88%	82%	91%	92%	84%
Boston	89%	87%	76%	93%	91%	76%
Chicago	87%	89%	78%	91%	93%	82%
Denver	87%	84%	78%	91%	93%	89%
Houston	91%	91%	88%	91%	92%	88%
Los Angeles	92%	93%	93%	93%	94%	94%
Phoenix	92%	94%	94%	92%	92%	94%
Pittsburgh	90%	91%	87%	92%	93%	88%
Seattle	91%	88%	83%	96%	89%	77%
Washington, DC	89%	85%	80%	92%	93%	89%

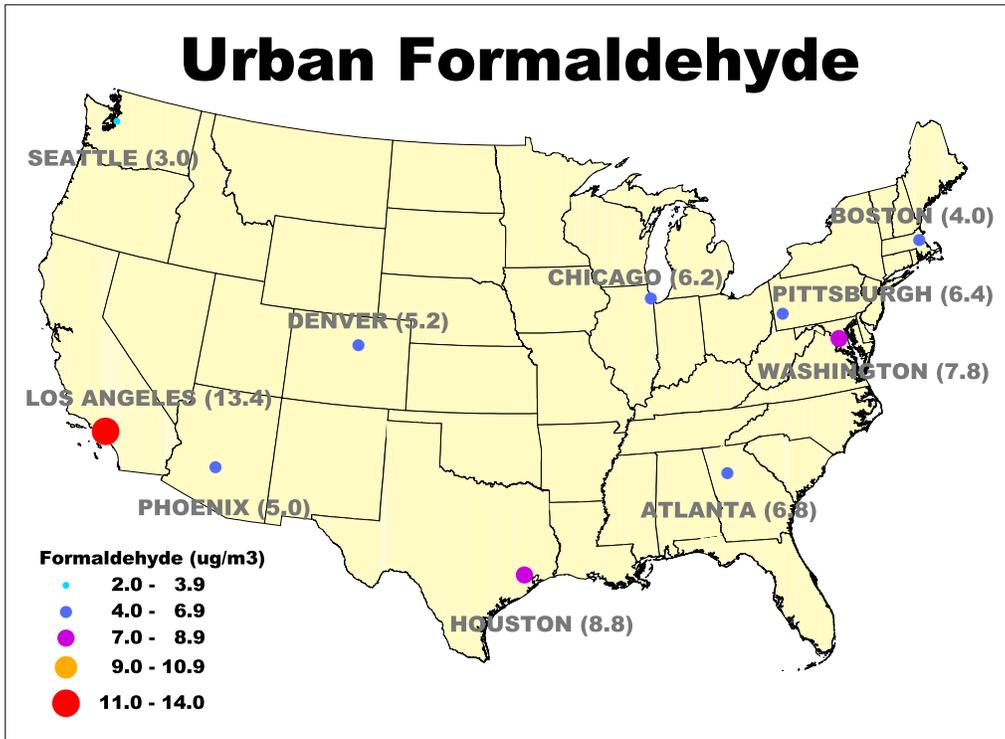


Figure 8-1a. Annual averages for secondary formaldehyde concentrations in urban areas.

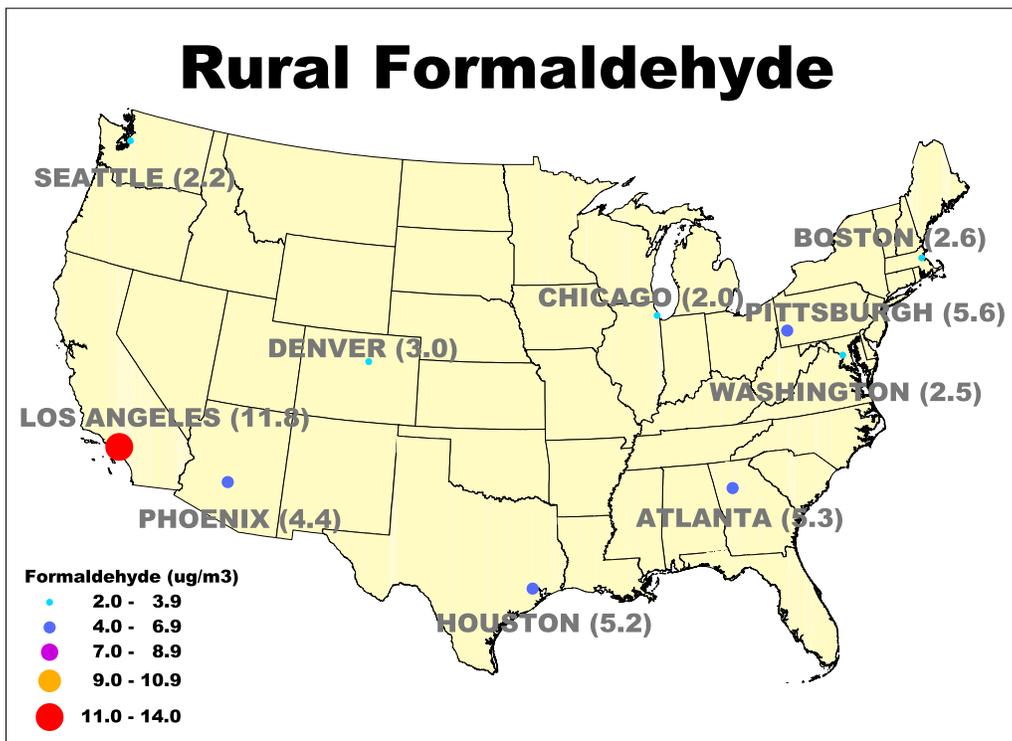


Figure 8-1b. Annual averages for secondary formaldehyde concentrations in rural areas.

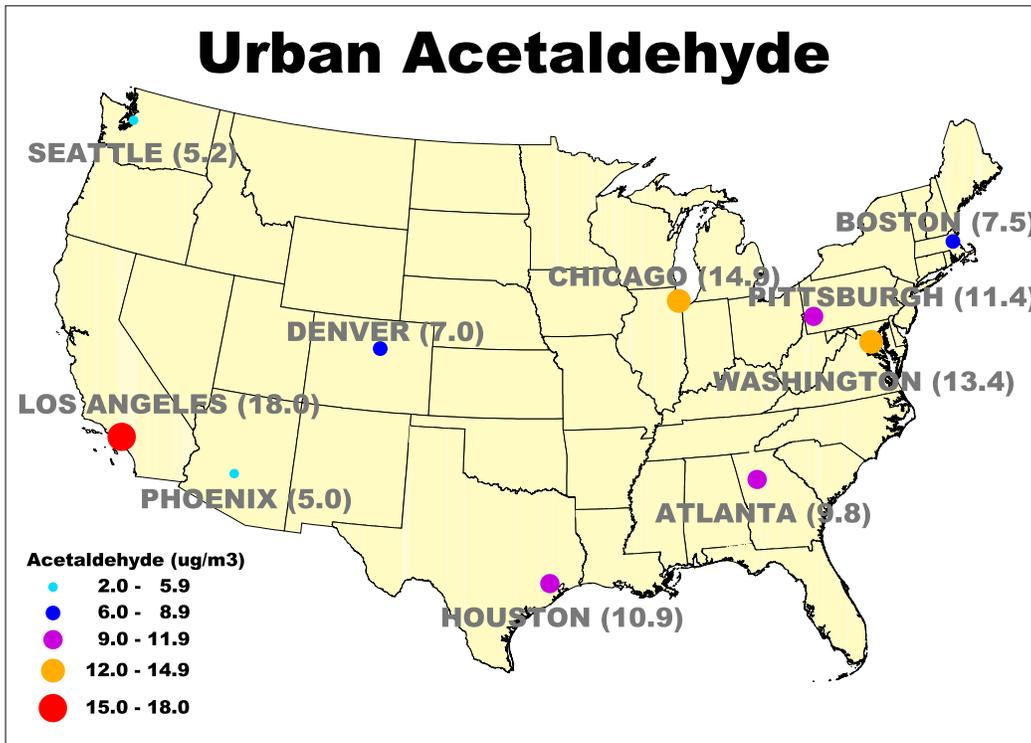


Figure 8-2a. Annual averages for secondary acetaldehyde concentrations in urban areas.

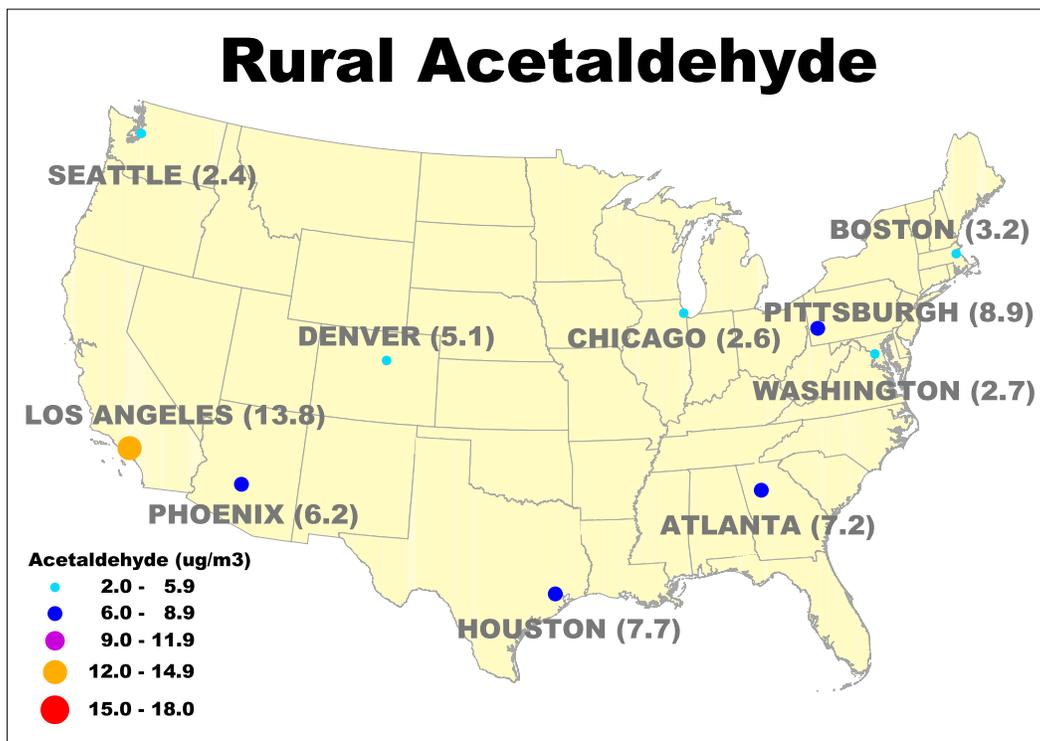


Figure 8-2b. Annual averages for secondary acetaldehyde concentrations in rural areas.

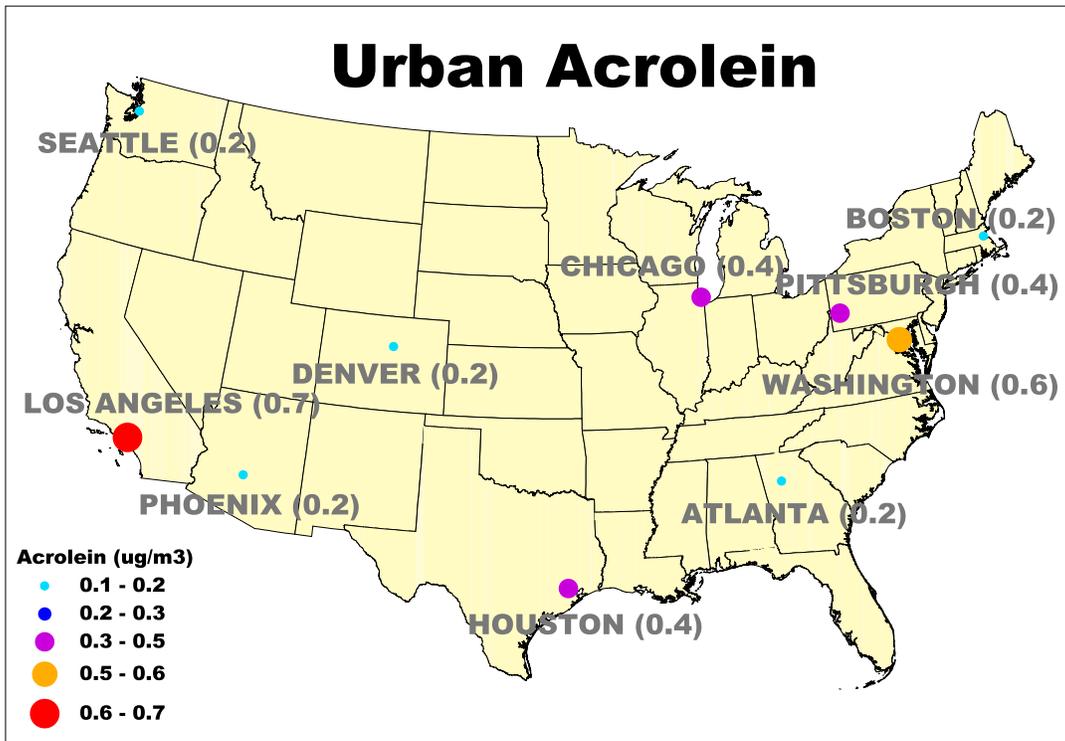


Figure 8-3a. Annual averages for secondary acrolein concentrations in urban areas.

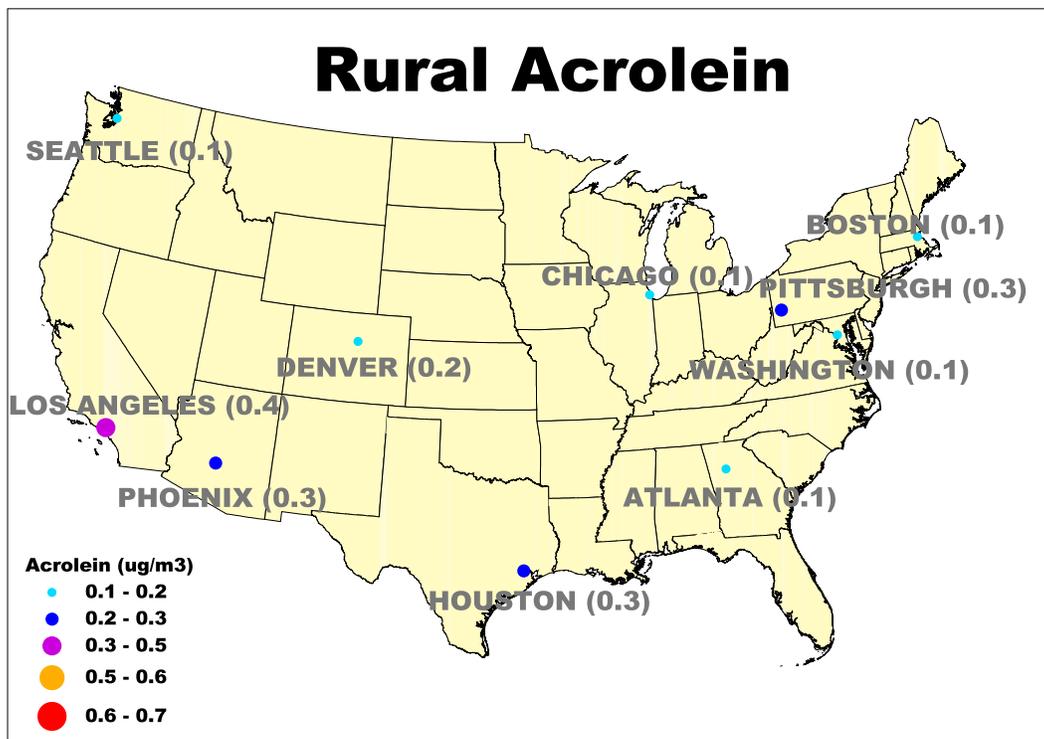


Figure 8-3b. Annual averages for secondary acrolein concentrations in rural areas.

The most striking feature of the annual estimates is that in all cases the secondary production accounts for the vast majority of the total for each pollutant. For urban formaldehyde, the percentage due to secondary formation ranged from 87% to 92%, while in rural areas the percentages were even higher, ranging from 91% to 96%. For acetaldehyde, the urban range was 84% to 94%, and the rural range was 89% to 94%. For acrolein, the percentages ranged from 76% to 94% in both urban and rural areas. These results are notable for their uniformity across the diverse set of study areas selected. Table 8-7 also indicates that the percentage of secondary formation in rural areas is generally higher than in urban areas.

For formaldehyde, in every case the rural estimate is lower than the corresponding urban estimate for primary, secondary, and total levels. The Los Angeles study area has distinctly higher formaldehyde concentrations than the other nine areas. These results also apply to acetaldehyde, except that the rural estimates for Phoenix exceed the urban estimates. These results also apply to acrolein. However, as mentioned before, the levels are quite low, so these differences are very small and possibly subject to round-off error.

Depending on the city, rural areas were estimated to have between 31% and 89% of the total formaldehyde present in urban areas. Rural acetaldehyde fell between 17% and 77% of the urban levels, except in Phoenix, where rural values exceeded urban ones.

#### **8.4 Comparison of Target Compounds with Other Models or Measurements**

The OZIPR model results were compared to monitored values from the Photochemical Assessment Monitoring Stations (PAMS) and numbers from the Regional Acid Deposition Model (RADM). The available PAMS measurements for formaldehyde, acetaldehyde, and acrolein from 1995 to 1997 are summarized in Table 8-8. Measurements of the carbonyl species in the PAMS network are typically taken using silica gel or C<sub>18</sub> cartridges coated with 2,4-dinitrophenyl-hydrazine (DNPH). Measurements of formaldehyde using the silica gel cartridge can suffer from a negative artifact due to ozone. While the use of potassium iodide scrubbers is recommended for both types of cartridges (Kleindienst et al., 1998), there is generally no consistent manner of conducting these measurements, and the possibility of systematic errors exists. Table 8-8 also contains the urban levels estimated by OZIPR.

**Table 8-8. Comparison Values for Carbonyl Compounds ( $\mu\text{g m}^{-3}$ ) from the Photochemical Assessment Monitoring Stations (PAMS) Collected During the Photochemical Pollutant Seasons for 1995–1997**

City	Pollutant	No. Observations	PAMS Mean	Standard Deviation	OZIPR Urban
Atlanta	Acetaldehyde	200	3.1	3.7	11.1
Atlanta	Formaldehyde	212	3.3	2.8	7.5
Chicago	Acetaldehyde	277	2.6	1.6	16.8
Chicago	Formaldehyde	277	8.0	7.5	7.1
Denver	Acetaldehyde	7	37.9	28.5	8.3
Denver	Acrolein	7	0.3	0.5	0.3
Denver	Formaldehyde	7	5.2	0.9	6.0
Houston	Acetaldehyde	1362	4.0	3.7	12.0
Houston	Formaldehyde	1364	6.4	4.5	9.7
Los Angeles	Acetaldehyde	604	12.4	37.5	19.3
Los Angeles	Formaldehyde	590	6.3	3.8	14.5
Washington, DC	Acetaldehyde	1461	3.1	1.7	15.8
Washington, DC	Formaldehyde	1461	7.4	4.0	8.8

For the six cities in Table 8-8, one finds that the differences between the OZIPR and PAMS mean values range from  $-0.9$  to  $8.2 \mu\text{g m}^{-3}$  for formaldehyde. Except Denver, with a difference of  $-29.6 \mu\text{g m}^{-3}$ , the differences for acetaldehyde varied from  $6.9$  to  $14.2 \mu\text{g m}^{-3}$ . The lone case of acrolein showed no difference.

Note that the PAMS values are not annual averages, and Denver only had seven measurements. Most of the PAMS observations represented in Table 8-8 are summertime measurements. Additionally, the PAMS data are collected at specific sites and may not represent areal averages. Also recall that the time periods for the PAMS data and the OZIPR modeled results do not match exactly. Despite these limitations, the data suggest that results from the model are comparable to those values measured in corresponding ambient environments. This conclusion is strongest for formaldehyde. Note from Table 8-2 that acetaldehyde is elevated in the cooler seasons, and, therefore, the annual averages from OZIPR may be expected to be larger than the PAMS measurements.

Comparisons of the results of the OZIPR model were also made with a sample output from the RADM model. RADM is a three-dimensional model that predicts (among other quantities) formaldehyde and acetaldehyde levels by combining both dispersion and chemistry. Since the model is highly complex and expensive to run, comparisons were made for an archived model run. RADM output values for the period July 11–15, 1995, are given in Table 8-9.

**Table 8-9. Comparison Values for Carbonyl Compounds ( $\mu\text{g m}^{-3}$ ) from the RADM Model Run for July 11–15, 1995, for Cities in This Study**

City	Pollutant	No. Observations	Mean Value	Standard Deviation	OZIPR Urban
Atlanta	Acetaldehyde	120	27.4	22.9	11.1
Atlanta	Formaldehyde	120	14.1	6.5	7.5
Boston	Acetaldehyde	120	7.5	3.9	8.6
Boston	Formaldehyde	120	7.3	3.5	4.5
Chicago	Acetaldehyde	120	9.5	6.5	16.8
Chicago	Formaldehyde	120	7.3	2.6	7.1
Houston	Acetaldehyde	120	20.9	18.6	12.0
Houston	Formaldehyde	120	12.1	6.6	9.7
Pittsburgh	Acetaldehyde	120	10.2	8.2	12.5
Pittsburgh	Formaldehyde	120	8.6	4.4	7.1
Washington	Acetaldehyde	120	12.6	10.7	15.8
Washington, DC	Formaldehyde	120	10.5	4.9	8.8

Generally, the OZIPR results are slightly lower than the RADM results, though there are exceptions. It should be noted that the RADM results are for a single ozone episode, whereas the OZIPR values are annual averages. The data from both OZIPR and RADM show a molar ratio of formaldehyde to acetaldehyde that is much closer to unity than seen in the PAMS data. The consistency between the values generated from OZIPR and RADM is thus quite good. This may result from a common set of assumptions, particularly regarding the photochemical mechanism.

There were four cities (Atlanta, Chicago, Houston, and Washington, DC) with both PAMS and RADM data. For Atlanta and Houston, the OZIPR estimates for both formaldehyde and

acetaldehyde were between the PAMS and RADM values. For Chicago, the OZIPR estimate of acetaldehyde exceeded both of the others, but the formaldehyde was very slightly below both the PAMS and RADM data. For Washington, DC, the acetaldehyde was above both (but close to the RADM value), while formaldehyde was between the PAMS and RADM values.

The general conclusion from the PAMS and RADM comparisons is that the simplified approach taken here is adequate for obtaining reasonable estimates for the target HAPs considered in this study. In the opinion of the authors, concentrations from this approach are probably within a factor of two of the ambient concentrations and considerably better than an order of magnitude. This level of accuracy may be sufficient to estimate risk factors.

## **8.5 Limitations of Current Study**

The use of a photochemical box model, such as OZIPR, to determine area-wide concentrations of toxic compounds involves a number of assumptions that will qualify the results. The initial concept in formulating the approach here was to use the results from a box model representing secondary formation to augment the results from a dispersion model. Ideally, the dispersion model should be intrinsically combined with the photochemical model since the physical system is highly coupled. Examples of such models include RADM and EPA's Urban Airshed Model (UAM). The present approach has rendered reasonable results because, for the HAPs considered here, a high percentage of the compound formation is due to secondary chemistry. Thus, the resultant concentrations of HAPs are due more to the area emissions of hydrocarbon precursors rather than to point source emissions of the compounds themselves.

The chemical mechanism itself has some additional limitations. First, little experimental information is available on the products from secondary reactions of first-generation reaction products. This will lead to some uncertainty in carbonyl formation from these processes. Second, the mechanism contains no chemical reactions for a wide number of oxygenated hydrocarbons, such as alcohols, ethers, and esters. (This might be significant in cities that use reformulated fuels.) In the present study, the oxygenates represent a minor fraction of the hydrocarbons and were distributed among the reactivity classes given in Section 4. Finally, for three of the cities (Pittsburgh, Seattle, and Phoenix), no reactivity data were available and were assumed based on other cities similar in geography and population. Note that the limitations described here would apply equally to a three-dimensional model.

Box models in general have some additional limitations. Perhaps the most significant of these is that the quantities being modeled are distributed homogeneously throughout the box. In this study, the finest spatial scale for emissions data was the county level. For a large county such as Los

Angeles County, which has an area of 10,515 km<sup>2</sup>, most of the emissions are concentrated over a much smaller land area; localized areas of high concentration were not identified.

Nighttime conditions can be difficult to represent in a photochemical model since the basic assumption that photochemistry is dominant is violated. Finally, some physical parameters such as wet deposition and cloud cover are not considered in the OZIPR model; these effects may lead to overestimates of HAPs when these phenomena are present.

## **8.6 Study Summary**

In this study, emissions and meteorological data were obtained as input to a one-dimensional photochemical model to estimate the contributions to formaldehyde, acetaldehyde, and acrolein from secondary processes. These data were incorporated into the model without any use of adjustable parameters or other devices to tune the output concentrations. Within the constraints of the approach, the model gave reasonable concentrations for the aldehydes of interest.

The following specific results were found:

1. In ambient air, photochemical production, on average, accounts for approximately 90% of the formaldehyde and acetaldehyde and approximately 85% of the acrolein concentrations.
2. For the cities with both PAMS and RADM data, the OZIPR results generally were between the two. The simplified approach taken here is adequate for obtaining reasonable estimates for the target HAPs considered.
3. The estimates for the rural scenarios were lower than for the corresponding urban scenarios.
4. The simplified approach used in this study (to be used to augment the results of a dispersion model) is a viable alternative to more complex and expensive methodology, such as the RADM and UAM models.

## **Section 9**

### **Practical Use of the Results from This Study**

The results from this report are designed to be of practical use to organizations that may be required to scrutinize ambient standards for formaldehyde, acetaldehyde, or acrolein. The information presented here can be used at any of three levels of application depending on the type of analysis desired. The results presented can also be extended for cities not explicitly modeled. (1) The most detailed information on secondary carbonyl formation for a specific metropolitan area can be obtained from running this model using city-specific parameters. (2) Tables 8-1 through 8-3 can be used in conjunction with a dispersion model to provide seasonal and time-specific adjustments. Table 8-4 through 8-6 and Figures 8-1 through 8-3 can be used to make annual adjustments for secondary formation to apply to a dispersion model's results. (3) When the cities examined in this study are too dissimilar from the area of interest and running the model is not feasible, the results found here can still be used to adjust predictions of aldehyde concentrations for secondary production.

#### **9.1 Use of the OZIPR Model to Estimate Secondary HAP Production**

To obtain information for a specific city regarding secondary formation of formaldehyde, acetaldehyde, or acrolein, OZIPR may be run with input tailored for that given city. The computer code for the model is available from EPA. Sample input files are given elsewhere in this report. (See Section 7 and Appendix A.) This section will describe the general principles involved in using the model and input data requirements. This will allow the user to determine whether there is sufficient information to run the model. The user may be able to obtain most of the data needed with little trouble. Mixing height and emissions inputs may be the most problematic to acquire. For example, mixing heights are collected from a relatively sparse network; a user may need to decide whether or not to utilize data from the closest sounding site or otherwise estimate mixing heights for input to the model. As another example, certain VOC species may not be available explicitly in many emissions data sets; the user may need to devise a means for supplying these. As there are myriad possibilities for scenarios that may be of interest, no attempt is made here to specify how a user should address the specific situation being modeled.

The user-supplied input file requires geographic, temporal, meteorological, and emissions

data, including the VOC composition (e.g., see Section 4). The user must also supply boundary conditions. Geographical information includes the longitude and latitude of the city being modeled; temporal information includes the date of the simulation and the starting and stopping times. The meteorological information includes the temperature, relative humidity, and barometric pressure. The model accepts mixing heights on an hourly or twice daily basis. If two values per run are supplied, the user may supply specific times or use the model defaults.

Required emissions data include the area-wide emissions of volatile organic compounds (VOCs), nitrogen oxides, and specific HAPs (if total HAPs levels are desired). The model also allows for including 1,3-butadiene, which is a hydrocarbon precursor for acrolein. As run in this study, emission rates must be provided in units of  $\text{kg km}^{-2} \text{h}^{-1}$ . For example, if total mass emission rate (kg/hr) of a chemical as a function of time of day are known for a county, these values must be divided by the area of the county to get the appropriate units.

Depending on the user's needs, the OZIPR model may be run for one or more specific days or one or more "representative" days (as was done for this report). One input file is necessary for each modeled day. Individual model scenarios run in a few seconds on a modern personal computer. Output values from the model are given in parts per million by volume (ppm). The values from secondary formation can then be used in conjunction with concentration estimates from dispersion models, as described below.

## 9.2 Use of Secondary Formation Values with Dispersion Models

The tables in Section 8 were developed to allow adjustments for secondary production to be applied to dispersion models. Here the term *dispersion model* is used to indicate a model that predicts concentration as a function of location, and possibly time, utilizing emissions from point sources as input, without considering photochemical reactions.

Concentration values output from the OZIPR model have no spatial component. The concentrations of all compounds are homogeneously distributed within the box. As explained earlier, the model was run with and without primary emissions. The run that includes primary emissions gives the total HAPs concentrations. The HAPs components due to secondary formation are obtained directly from the run without primary emissions. The difference between the two runs gives the component due to primary emissions.

The following is an example of how the entries in Tables 8-1 through 8-3 can be used. Consider the entries for urban Atlanta for formaldehyde in Table 8-1. All values in the table give  $\mu\text{g m}^{-3}$  secondary contributions as a function of season and hour of day. These represent instantaneous values from the model. Thus, if one has output from a dispersion model for Atlanta for a typical

autumn day at 12:00 noon, a value of  $7.4 \mu\text{g m}^{-3}$  would have to be added to every grid point to represent the secondary contribution. Advancing the clock by one hour to 1:00 p.m., a new value of  $8.1 \mu\text{g m}^{-3}$  would now be used to represent the secondary contribution. For other times, a linear interpolation of the tabular data could be used.

As in the case above, the formaldehyde, acetaldehyde, and acrolein values in Tables 8-4 through 8-6 are designed to be additive adjustments. These tables are to be applied on an annual time scale. Thus, they would be used with output from a dispersion model that did not have a finer time resolution. Again taking urban Atlanta as an example, Table 8-4 would be used for formaldehyde, and a value of  $6.8 \mu\text{g m}^{-3}$  would be added to the dispersion estimates in a spatially uniform manner.

If one is interested in a location not appearing in this study and running the OZIPR model is not feasible, then the area of interest should be matched as closely as possible to one of those modeled here. The cities examined in this study cover a variety of urban areas. Users will need to make the decision of suitability on a case-by-case basis. The most obvious considerations are factors such as population size, industrial base, geography, land use, and climate. Note that both urban and rural scenarios are included in this report. Generally, secondary formation in metropolitan areas should be estimated using the tabulated urban values and outlying areas should use the rural values. However, for smaller and medium-size urban areas, the rural values reported here may be more appropriate.

### **9.3 Estimation of Secondary Formation without Using Tables**

If none of the cities in this report typifies the area of interest, the secondary component of the HAPs concentrations may be estimated from values for the primary component. This can be seen by examining the percentages in Table 8-7. Note that for formaldehyde and acetaldehyde the percentage of secondary production is near 90% for all of the urban areas (and slightly higher in the rural areas). For acrolein, both the urban and rural areas averaged near 85% secondary, with somewhat more variation from city to city than for the other two HAPs. In the absence of better information, these average percentages could be used to estimate the effect of secondary formation in any study area.

It should be noted that the percentages in Table 8-7 represent the ratio of spatially averaged secondary production to spatially averaged total production for each HAP. These averages are over the entire study area (one or more counties). There is good reason to believe that the spatial distribution of secondary HAPs does not match the spatial distribution for primary HAPs. Primary HAPs will be concentrated around the large point sources in the study area. The distribution of secondary HAPs will differ for two reasons: (1) the pattern of sources for the chemical precursors that transform into the target HAPs may not match the source pattern for direct emission of the

HAPs, and (2) the reactions take some time, which means that the precursors may move some distance from the emission location before being transformed into HAPs.

As a result, it is not correct to simply amplify the distribution of primary HAPs as determined by a dispersion model by a multiplicative factor to account for secondary formation. That would lead to very high estimates of total HAPs concentrations at the localized “hot spots” seen in the primary distribution, with little evidence that such levels are accurate.

A better approach is to first calculate a spatial average for the primary HAPs concentrations, then to multiply this by a factor of 9.0 (90% secondary / 10% primary), or 5.7 (85% / 15%), as appropriate, to find the average secondary contribution. The resultant secondary contribution may then be added in a spatially uniform manner to the distribution of primary HAPs.

The method described here will preserve the character of the spatial distribution seen for the primary HAPs (in particular, the location of any hot spots in the study area), since the secondary component affects all locations equally. However, the method is more conservative than a simple multiplicative scaling of the primary distribution. There is no reason to expect the secondary HAPs concentrations at primary hot spots to be either higher or lower than elsewhere. In the absence of knowledge of the secondary spatial distribution, a uniform distribution is a reasonable choice.

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1. REPORT NO. EPA-454/R-99-054		2.	3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE A Simplified Approach for Estimating Secondary Production of Hazardous Air Pollutants (HAPs) Using the OZIPR Model  Replaces Section 2.4 in Dispersion Modeling of Toxic Pollutants in Urban Areas, EPA-454/R-99-021			5. REPORT DATE December 1999	
			6. PERFORMING ORGANIZATION CODE	
7. AUTHOR (S)			8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS ManTech Environmental Technology 2 Triangle Drive Research Triangle Park, NC 27411			10. PROGRAM ELEMENT NO.	
			11. CONTRACT/GRANT NO. EPA Contract No. 68D50049	
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Office of Air Quality Planning and Standards Emissions, Monitoring & Analysis Division Research Triangle Park, NC 27711			13. TYPE OF REPORT AND PERIOD COVERED Final Report	
			14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES EPA Work Assignment Manager: Thomas McCurdy				
16. ABSTRACT Hazardous air pollutants are found in the atmosphere as a result of primary emissions or from the transformation of organic compounds emitted into the atmosphere. Several very complex models exist that can include both dispersion and atmospheric chemistry to yield HAPs concentration estimates. However, these models are very expensive to execute, often requiring the use of supercomputers. This report describes a simplified approach for estimating total HAPs concentrations by estimating secondary HAP with a stand-alone model, run in a personal computing environment, that incorporated only non dispersive processes, such as photochemistry. The results from this model would then be coupled to those from a relatively simple dispersion model such as the EPA's Industrial Source Complex (ISC) dispersion model which uses primary emissions.				
17. KEY WORDS AND DOCUMENT ANALYSIS				
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group
Air Pollution Air Quality Dispersion Models Meteorology Air Toxics Urban Area Modeling				
18. DISTRIBUTION STATEMENT Release Unlimited		19. SECURITY CLASS (Report) Unclassified		21. NO. OF PAGES 86
		20. SECURITY CLASS (Page) Unclassified		22. PRICE