# Phoenix, Arizona Air Toxics Assessment – Final Comprehensive Report

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# ES1.0 Abstract and Executive Summary of the Phoenix Air Toxics Assessment

#### **ES1.1** Abstract

"Air toxics", a group of nearly 200 chemical compounds emitted in virtually all industrial, agricultural, and urban activities, pose risks to human health through inhalation that can be quantified through studies that incorporate special air pollutant measurement programs with subsequent air quality, exposure, and toxicity modeling. In Phoenix, Arizona the risk from air toxics has been determined by a consortium (called the Joint Air Toxics Assessment Project or "JATAP") of Arizona tribal, local, and state environmental officials, funded and supported by the U.S. Environmental Protection Agency. The extensive measurement and analysis program, which took place in 2005 and 2006, involved several different sites at which air toxics concentrations were measured. A risk assessment based on these measurements was conducted, and subsequent emissions, meteorological, and air quality modeling were carried out. The realistic and best estimate of risk to human health from both gaseous and particulate air toxics in metropolitan Phoenix, expressed as excess lifetime cancer cases per 1,000,000 population, is 300 - 700 cancer cases, from diesel exhaust (DPM), arsenic, cadmium, and nine gaseous species, depending on the monitoring site and its neighborhood. (Note that, in contrast to the more common air pollutants that have National Ambient Air Quality Standards, air toxics concentrations and their risks have neither national "standards" nor recommended "attainment" levels.) This range of risk reflects the variation of air toxics concentrations among the different neighborhoods, which included one freeway corridor site, several urban core sites, two tribal sites on the urban perimeter, and two background sites. This degree of risk places Phoenix above the national average, lower than either Houston or Los Angeles, but similar to the risk in Detroit and Seattle (see section 5.10, page 92 for details). As carbonaceous particulates consist of both elemental carbon (mostly diesel exhaust or DPM) and of organic carbon; and if this complex mixture of organic carbon particulates is assigned a toxicity similar to its elemental counterpart (and a considerable body of health effects studies suggests that it should be, although the scientific jury remains out), then the risk from air toxics would be from 600 to 1,300 lifetime cancer cases per 1,000,000 people. These higher risk estimates must be considered provisional for two reasons: (1) the U.S. EPA has yet to assign any cancer risk to DPM, although the Air Resources Board of California did so over ten years ago; and (2) the scientific communities investigating the health effects of organic carbon have yet to arrive at anything remotely resembling a consensus. In any case, the risk estimates given in this report clearly distinguish between the two types of carbonaceous particulates. In addition to the technical aspects of this project, the consortium provided the opportunity for tribal staff and managers to work cooperatively with their counterparts in local, state, and federal governmental organizations. Such cross-cultural cooperative efforts have been rare in the environmental arena. Perhaps the most important benefit of the JATAP has been the growing mutual confidence and cohesive working relationships forged between Native American and local, state, and federal environmental officials.

#### **ES1.2 Executive Summary**

Community-wide assessments of human health risk from airborne toxic species, which have been conducted in many cities worldwide, ideally consist of air toxics measurements, numerical modeling (emissions, meteorological, and air quality modeling), exposure modeling, and, lastly, risk assessment. ("Exposure modeling", based on the resident locations of various sub-populations and their average daily activity patterns, such as spending time at home, at work, or at school, and the transportation time and mode to get from place to place, is a numerical reckoning of just what air toxics concentrations a member of the population is exposed to, because air pollution levels vary widely among the diverse urban environments.) The net results of this four-part assessment answer such questions as what portion of an urban population incurs certain levels of risk, what is the mean exposure and risk of the entire urban area, and what populations are exposed to the maximum risk. Although the Joint Air Toxics Assessment Project (JATAP) planned to accomplish all four of these components, it fell somewhat short of this goal. Its accomplishments, nonetheless, were considerable: measurements of ambient concentrations of air toxics were made in 2005 and early 2006; risk assessments based on these measurements have been conducted; and emissions, meteorological, and air quality modeling were also carried out. The outcome of the air quality modeling, however, did not result in a set of simulated air toxics concentrations that matched well with the measured ones. This outcome precludes any comprehensive, community-wide risk assessment, thus limiting the assessment to the immediate neighborhoods in which the measurements were made. Furthermore, these assessments lack any exposure modeling, which was not conducted. Nevertheless, it should be noted that some risk assessments present their results based primarily on measured air toxics concentrations, and the JATAP's findings are in this category.

Measured in metropolitan Phoenix by a consortium of Arizona tribal, local, and state environmental officials and funded and supported by the U.S. Environmental Protection Agency, gaseous and particulate air toxics species pose a human health risk of 300 - 700 lifetime excess cancer cases per one million population. These estimates are based on the annual average concentrations measured at several air monitoring sites in 2005 throughout the metropolitan area. Annual averages of particulate species revealed that of the six with chronic health-based guidelines – arsenic, cadmium, diesel particulate matter (DPM), chromium VI, manganese, and nickel - the first three exceeded guideline values, but the last three were within them at all urban sites. Expressed as excess lifetime cancer cases per 1,000,000 population, the risk from particulate air toxics was dominated by DPM, with arsenic and cadmium combined contributing the remaining 10%. Among the central urban sites the various populations would be expected to develop 200 - 500 excess cancers per million people through a lifetime of exposure to these particulate air toxics. This risk increases considerably if all carbonaceous particulates, rather than just those from diesel combustion, are included. (Organic carbon particulates have been shown to have adverse human health effects, but the state of the science has not advanced to the point where a numerical "health guideline concentration" can be specified.) Depending on the particulate species, urban concentrations were enriched from three to 40 times above background, with the "background" coming from measurements made about 60

miles east of central Phoenix. Situated on the urban perimeter, the two tribal sites generally had lower concentrations than the urban core sites.

For the gaseous air toxics, the combination of nine different compounds, including benzene, formaldehyde, and others, posed a genuine human health risk, though not as severe as the particulates: excess lifetime cancer cases per 1,000,000 population ranged from about 120 to 180, depending on the urban monitoring site. Combining the risk from gaseous and particulate species gives a net excess cancer rate of about 300 – 700 cases.

The realistic and best estimate of risk to human health from both gaseous and particulate air toxics in metropolitan Phoenix, expressed as excess lifetime cancer cases per 1,000,000 population, is

300 - 700 cancer cases, from diesel exhaust, arsenic, cadmium, and nine gaseous species, depending on the monitoring site and its neighborhood; and

from 600 to 1,300 cancer cases, if organic carbon particulates are considered as toxic as elemental carbon.

This degree of risk -300 to 700 lifetime excess cancer cases per 1,000,000 population -places Phoenix above the national average, lower than either Houston or Los Angeles, but similar to the risk in Detroit and Seattle.

A wide variety of non-cancer health effects are associated with air toxics species. Particulate concentrations in 2005 were all lower than the minimum risk levels (MRLs) for non-cancer effects; only one gaseous species at one site (formaldehyde at Greenwood) exceeded an MRL. Exceeding an MRL should be interpreted as presenting the possibility, but not certainty, of being associated with adverse health effects. The concentrations of each of several air toxics species at one site, when divided by each one's MRL, are typically added together to produce a so-called "benchmark index". This measure of the cumulative non-cancer effects for all gaseous species was high enough to indicate the possibility of adverse non-cancer health effects at all the urban core sites and at one Indian Community site (Salt River).

Two independent Phoenix studies have shown that 51% of the wintertime  $PM_{2.5}$  comes from fossil fuel combustion, itself dominated by vehicular emissions (gasoline plus diesel; on-road and non-road); 21% is particulate nitrate formed both by local and regional emissions of gaseous nitric oxide; 12% is geological; 12% is particulate sulfate from regional transport; and 4% comes from wood burning.

In addition to the measurement-based risk assessment, work accomplished by the JATAP consisted of a thorough examination and discussion of air toxics emissions and three kinds of numerical modeling: emissions, meteorological, and air quality modeling. The first resulted in two inventories of air toxics emissions: an "accounting" inventory with metropolitan emissions expressed in tons per year and a "model-ready" inventory with gridded, hourly emissions. The second provided gridded "fields" of such weather

variables as wind speeds and directions and temperatures throughout the metropolitan area for each hour in calendar year 2005. With the first two as inputs, the third produced simulated, annual average concentrations of air toxics in an array of 4x4 km and 1x1 km grids throughout the Phoenix area. These simulated concentrations, however, generally under-estimated the measured ones and would be difficult (but not impossible) to employ in a metropolitan-wide risk assessment. Such an assessment would require two more analyses.

- 1. Exposure modeling, which would estimate the actual concentrations to which the various populations are exposed, based on the time spent in various indoor and outdoor environments such as offices, factories, schools, homes, automobiles and so forth.
- 2. A spatially comprehensive toxicity analysis, which would produce estimates of cancer and non-cancer risk for each segment of the metropolitan populations in each grid.

Although these additional analyses appear to be beyond the resources of the JATAP as this final report is issued, they could still be carried out should the various project members decide that this goal is worth pursuing.

The risk analysis and related work described in this report are necessarily technical. But, over and above the technical aspects of this project, the consortium provided the opportunity for tribal staff and managers to work cooperatively with their counterparts in local, state, and federal governmental organizations. Such cross-cultural cooperative efforts, rare in the environmental arena, should be recognized, nurtured, and enhanced. Perhaps the most important overall benefit of the JATAP has been the growing mutual confidence and cohesive working relationships forged between Native American and local, state, and federal environmental officials.

# **Table of Contents**

ES1.0 Abstract and Executive Summary of the Phoenix Air Toxics Assessment	1
ES1.1 Abstract	1
ES1.2 Executive Summary	2
Table of Contents	5
Figures Tables Acknowledgements 1.0 Introduction	6 7 9 10
1.1 Joint Air Toxics Assessment Project (JATAP)	10
1.2 General Introduction to Air Toxics and the JATAP	13
2.0 Emissions	16
2.1 Introduction	16
2.2 Emissions Modeling Domains	18
2.3 Air Toxics Species of Interest	19
2.4 Emission Sources of Criteria Air Pollutants	20
2.5 Ozone Precursor and $PM_{10}$ Emissions Inventories for Maricopa County	21
2.6 Air Toxic Emissions by General Source Category	27
2.7 Annual Air Toxics Emissions in Metropolitan Phoenix	37
2.8 Conclusions about Emissions	40
2.9 Emission Density Maps	41
3.0 Meteorological Modeling	45
3.1 Introduction	45
3.2 Comparisons Between MM5 and Surface-Based Measurements	46
4.0 Air Quality Modeling	48
4.1 Introduction	48
4.2 Modeling Overview	48
4.3 Modeling Domain	49
4.4 Spatial Distributions of Simulated Annual Concentrations	51
4.5 Comparisons with Measurements	54

4.5.1 Particulate Air Toxics, Simulated Annual Averages Versus Measurements
4.5.2 Gaseous air toxics simulated annual averages versus measurements
5.0 Human Health Risk, Based on Measurements Only
5.1 Monitoring Sites
5.2 Sampling and Analysis
5.3 Diesel Particulate Matter (DPM)71
5.4 Emissions
5.5 Apportionment to Source Categories
5.6 Ambient Concentrations of Particulate Air Toxics
5.7 Human Health Risk from Particulate Air Toxics
5.8 Ambient Concentrations and Human Health Risk from Gaseous Air Toxics
5.9 Human Health Risk from Both Gaseous and Particulate Air Toxics
5.10 Comparison of the Cancer Risk from Air Toxics in Phoenix with Other Cities
5.11 Conclusions on Risk, Based on Neighborhood Monitors Only
6.0 Appendix A. Meteorological Modeling
7.0 Appendix B. Averages, Non-Detects, and the Method Detection Level (MDL) 118
8.0 Appendix C. History of the Joint Air Toxics Assessment Project
9.0 References

# Figures

Eiguro 2 2-1	IATAP Modeling Domains	0
Figure 2.2-1		.9
Figure 2.5-1	Maricopa County VOC Emissions on an Annual Basis by Source Category 2	23
Figure 2.5-2	Maricopa County Oxides of Nitrogen Emissions on an Annual Basis by Source	
Category		24
Figure 2.5-3	Maricopa County PM <sub>10</sub> Emissions on an Annual Basis by Source Category	25
Figure 2.5-4	Maricopa County PM <sub>2.5</sub> Emissions on an Annual Basis by Source Category	26
Figure 2.6-1	Diesel Particulate Matter Emissions by Sub-Category - Phoenix Metropolitan Area	
		32
Figure 2.6-2	Arsenic Emissions by Sub-Category – Phoenix Metropolitan Area	33
Figure 2.6-3	Acetaldehyde Emissions by Sub-Category – Phoenix Metropolitan Area	34
Figure 2.6-4	1,3-Butadiene Emissions by Sub-Category – Phoenix Metropolitan Area	35
Figure 2.6-5	Seasonality of Air Toxics Emissions – Phoenix Metropolitan Area	36
Figure 2.9-1	Metropolitan Phoenix Emissions "roadmap" 4	12
Figure 2.9-2	Nitrogen Oxides Emission Density Map 4	13
Figure 2.9-3	Volatile Organic Compounds Emission Density Map 4	14

Figure 4.4-1 Annual Concentrations for Gaseous Pollutants	52
Figure 4.4-2 Annual Concentration for Particles	53
Figure 5.1-1 JATAP Monitoring Sites	70
Figure 5.10-1 Comparative Cancer Risk from Air Toxics in the United States, including the JA	TAP
for Phoenix, AZ	95

# **Tables**

Table 2.3-1         Air Pollutant and Air Toxics Species of Interest	. 20
Table 2.5-1         Source Category Contributions (%) to the Emissions of Four Air Pollutants	. 22
Table 2.6-1         Sources of Air Toxic Emissions	. 27
Table 2.6-2         Average Annual Gaseous Air Toxics Emissions by Sub-Category – Phoenix	
Metropolitan Area	. 30
Table 2.6-3         Average Annual Particulate Air Toxics Emissions by Sub-Category – Phoenix	
metropolitan area	. 31
Table 2.7-1         Annual Air Toxics Emissions (tons per day) in Metropolitan Phoenix	. 38
Table 2.7-2         Annual Air Toxics Emissions in Metropolitan Phoenix: Percentage Contributions.	. 39
Table 4.3-1         Projection Definition for the Modeling Grid	. 49
Table 4.3-2 Grid Definitions for CAMx	. 50
Table 4.3-3         Vertical Layer Structure	. 50
Table 4.5-1         CAMx Evaluations in Simulating Air Toxics and Ozone	. 54
Table 4.5-2         CAMx Simulated Concentrations of Air Toxics Versus Measured Concentrations for	or
Selected Sites in the MATES III Air Toxics Study of the South Coast Air Quality Management	
District	. 55
Table 4.5.1-1         Annual Fine Particulate Air Toxics Concentrations: Observations vs. the Model.	. 57
Table 4.5.1-2         Performance Statistics for Particulate Air Toxics	. 58
Table 4.5.1-3         Widely Varying Emission Estimates of Elemental Carbon in the Air Toxics (AT)	
Inventory and in the Maricopa County (MC) Inventory	. 61
Table 4.5.2-1         Annual Average Gaseous Air Toxics Concentrations in ppbV: Observations vs	
Model Simulations	. 63
Table 4.5.2-2         Performance Statistics for Gaseous Toxics	. 64
Table 4.5.2-3 Comparison of the Air Toxics (AT) and Maricopa County (MC) Emission Inventor	ries
for Ozone Precursors and Carbon Monoxide	. 65
Table 5.1-1         JATAP 2005 Monitoring Sites	. 69
Table 5.4-1         Metropolitan Phoenix PM <sub>2.5</sub> Emissions Inventory for 1995, with elemental and	
organic carbon in metric tons per year	. 74
Table 5.5-1         Wintertime Phoenix PM2.5 Apportioned to its Principal Emission Source Categories	ies
	. 76
Table 5.5-2         Wintertime Phoenix PM2.5 Apportioned to its Principal Emission Source Categor	ies
in Greater Detail	. 78
Table 5.6-1         Annual Average PM <sub>10</sub> , PM <sub>2.5</sub> , and Selected Air Toxics	. 80
Table 5.6-2         Particulate Air Toxics, Divided by their Standard or Guideline Values	. 81

Table 5.6-3         Urban Toxic Particulate Concentrations Normalized to Tonto         82
Table 5.7-1         Excess Lifetime Cancer Cases per Million Population from Fine Particulates (PM2.5)
in Metropolitan Phoenix
Table 5.7-2         Non-Cancer Benchmark Values and Annual Concentrations of Particulate Air Toxics
Table 5.8-1         Non-Cancer Benchmarks (RfC) with 2005 Annual Averages of Gaseous Air
Toxics
Table 5.8-2         Non-Cancer Benchmark Quotients and (in the last row) the Non-Cancer Benchmark
index for the 2005 Annual Average Concentrations of Gaseous Air Toxics
Table 5.8-3         Cancer Benchmarks in $\mu g/m3$ , Reference Concentrations for Chronic Inhalation
Exposure (RfC) in $\mu$ g/m3 (for non-cancer effects), and inhalation unit risks (IUR) in ( $\mu$ g/m3) <sup>-1</sup> 89
Table 5.8-4         Lifetime excess cancer risk from gaseous air toxics         89
Table 5.9-1         Total Risk of Excess Lifetime Cancer Cases per One Million Population from both
Gaseous and Particulate Air Toxics
Table 5.10-1         Cancer Risk in Metropolitan Phoenix, AZ (from the JATAP) and Other Air Toxics
Assessments throughout the United States
Table 7.0-1         Recommended Methods for Estimating Summary Statistics
Table 7.0-2         Percentage of Non-Detectable Values for Gaseous Species         119
Table 8.0-2         Joint Air Toxics Assessment Project, a Detailed History

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## **1.0 Introduction**

#### **1.1 Joint Air Toxics Assessment Project (JATAP)**

The Joint Air Toxics Assessment Project, or "JATAP", is a consortium of Arizona tribal, local, and state environmental officials, along with officials from the U.S. Environmental Protection Agency (EPA), whose goal is to assess the risk from air toxics in metropolitan Phoenix. Active from the early 2000s until the present, the JATAP's principal completed project has been a comprehensive, multi-site ambient air monitoring campaign conducted in 2005 and early 2006. Funded by grants from EPA's Office of Air Quality Planning and Standards, this air monitoring work was conducted by staff of the Gila River Indian Community, the Salt River Pima Maricopa Indian Community, and the Arizona Department of Environmental Quality, with generous cooperation from the Maricopa County Air Quality Department, who made available several of their permanent monitoring sites for this more specialized, temporary air toxics monitoring. In contrast to most of the monitoring of the better know air pollutants such as carbon monoxide, ozone, and particulate matter – which to a large extent is accomplished by continuously operated instruments – quantifying the concentrations of air toxics usually requires the collection of discreet samples that are later analyzed by environmental chemistry laboratories. Most of the funding for this field campaign paid for these chemical analyses.

As is the case in all such risk assessment projects, collecting and analyzing the samples, while by no means easy and straightforward, is but the first step in assessing the risk these substances pose to human health. To accomplish a metropolitan-wide risk assessment, as opposed to one based only on the measured concentrations whose representativeness is necessarily limited to the immediate neighborhoods in which they were taken, it is necessary to employ numerical air quality models. These models estimate concentrations of air pollutants, including the air toxics group, throughout the metropolitan area. These simulated concentrations are verified by comparing them with the measured ones. For assessment of chronic, or lifetime risk, the annual average concentrations of air pollutants throughout an urban area are employed. These measured and simulated concentrations are in the outside air, but people spend considerable time each day in various environments: inside homes, schools, offices, and cars, as well as outside. Therefore, another kind of numerical model estimates the actual exposure of the population to air pollutants throughout the day and year, based on both the outside simulated concentrations and on their relationship to indoor concentrations. Such relationships are determined through national and international research efforts. Finally, these "exposure" concentrations, averaged for a calendar year, are translated into actual human risk by comparing them (1) with toxicologically based concentrations associated with excess lifetime cancer risk, expressed as excess cancer cases per 1,000,000 population and (2) with concentrations associated with various non-cancer diseases, usually of a respiratory or cardiovascular nature (This non-cancer risk is typically expressed as a "hazard quotient", which is the ambient concentration divided by the minimum-risk-level concentration.) Thus, an urban-wide risk assessment begins with the monitoring of air toxics for one year and culminates with estimates of how much risk these air pollutants pose to the human populations.

In the collective efforts of the JATAP, however, not all of these steps have been accomplished. What the JATAP has done, and what this report describes, are the following:

- 1. Annual average air toxics concentrations that were monitored at several sites throughout metropolitan Phoenix in 2005 and early 2006;
- 2. An inventory of the air toxics emissions, from all sources: vehicles, industry, commercial operations, and so forth;
- 3. Meteorological modeling, which provides a quantitative description of such "weather" variables as wind speed and direction in the surface layer (the lowest 20 meters of the atmosphere, next to the ground surface);
- 4. Air quality modeling that results in simulated concentrations of air toxics throughout the region; and
- 5. Assessment of the risk to the human populations in the several neighborhoods that were monitored.

From the discussions above the missing steps of the JATAP, compared with an ideal, full-scale risk assessment, are the urban-wide exposure modeling and the subsequent human risk assessment. These region-wide analyses were not conducted for two reasons: the emissions inventory was marred by some fatal flaws in its estimates of the most deleterious air toxic, so-called "diesel particulate matter (DPM)"; and, even if the inventory had been perfect, full funding was not available for the urban-wide exposure and risk assessment modeling.

To clarify the discussion above, it's worth noting in greater detail exactly what the JATAP did and did not accomplish, and what, therefore, this report will and will not contain. First, a brief description of the principal JATAP products is in order, followed by, secondly, those elements of ideal community-wide risk assessments that the project did not conduct.

# JATAP products

- Twelve months of extensive air toxics monitoring at several sites in metropolitan Phoenix in 2005 and early 2006: collected samples were analyzed by environmental chemistry laboratories for both gaseous and particulate species.
- Air toxics emissions were quantified in two kinds of emission inventories: a socalled "accounting" inventory that provides annual emissions of air toxics in a report format; and a so-called "model-ready" inventory whose format is hourly emissions of multiple air toxics species in geographically defined square grids

that cover the metropolitan study area. This model-ready inventory served as one of the principal inputs for the air quality modeling.

- Hourly meteorological fields in layered geographical grids from the surface layer (the layer from ground surface to 20 meters above) to about four kilometers above ground. These meteorological fields, with variables such as wind speed and direction, served as the second principal input for the air quality modeling.
- Simulated concentrations of air toxics for each hour in 2005, also in a gridded format. These numerically estimated concentrations, however, under-estimated the measured concentrations to such a degree that they could not be used in a metropolitan-region wide risk assessment.
- Assessment of both cancer and non-cancer risk, based on the measured concentrations in the several neighborhoods that were monitored for air toxics.
- A comparison of Phoenix urban air toxics concentrations with those at a "background" site about 60 miles to the east.
- A comparison of the risk to human health from air toxics among Phoenix and several other urban areas of the U.S.

# JATAP'S MISSING ELEMENTS AND QUESTIONS THAT CANNOT BE ANSWERED

- Exposure modeling was not conducted. This modeling would have estimated the actual air toxics concentrations to which the various populations in metropolitan Phoenix are actually exposed. (Note that concentrations vary widely among subregions of the urban area, between indoor and outdoor environments, and with distance from major transportation routes and industrial facilities. Different populations have different activity patterns that result in their net annual exposure to air toxics concentrations being markedly dissimilar from ambient concentrations measured at fixed monitoring sites.)
- Without a set of sufficiently accurate simulated concentrations encompassing the entire metropolitan area, the risk assessments are limited to the neighborhoods in which the monitoring took place. Ideally this assessment would have been made for all populations of the Phoenix area.
- Questions that the JATAP cannot or did not answer:
  - What percentage of the population is incurring high, moderate, or low risks from air toxics?
  - How are sensitive sub-populations, such as the very young, very old, or respiratorily compromised being affected by air toxics?
  - How do the concentrations of air toxics to which different populations are actually exposed differ from the measured ones?
  - What emission reduction strategies would decrease air toxics concentrations and to what degree?
  - What is the overall risk to the health of Phoenix area residents from both air toxics and the more "conventional" air pollutants such as ozone and particulate matter?
  - How does the risk from air toxics on non-cancer health outcomes differ among Phoenix and other U.S. cities?

Nonetheless, the knowledge of air toxics emissions, air toxics concentrations, and of the latter's consequent risk to human health, albeit limited to the monitored neighborhoods, still must be regarded as a welcome and fundamental addition to the general understanding of air pollution in metropolitan Phoenix. On a more positive note, even though the JATAP fell short of all of its technical goals, this project has proven to be a lasting success through the collaboration of tribal and non-tribal staff and managers.

#### **1.2 General Introduction to Air Toxics and the JATAP**

Measured by a consortium of Arizona tribal, local, state, and federal environmental officials (called the Joint Air Toxics Assessment Project, or "JATAP") in metropolitan Phoenix in 2005, gaseous and particulate air toxics species pose a genuine human health risk (300 – 700 lifetime excess cancer cases per one million population, plus demonstrable non-cancer health effects, as well) (1,2). As a term, "air toxics" refers to a group of some 200 different chemical compounds that are emitted into the ambient air through diverse human activities as well as through natural emissions. While the general populace may not be familiar with most of these compounds, some have become, if not household words, at least better known, including, for example, particulate arsenic from the suspension of topsoil; diesel particulate matter from heavy-duty trucks, buses, and earthmoving equipment; and gaseous benzene from filling a vehicle's tank at a gasoline station. If their concentrations are high enough, which many are in most large urban areas around the world, these air toxics, along with the more familiar air pollutants such as ozone and particulate matter, constitute genuine threats to both the short-term and long-term health of the general citizenry, but more particularly, to the more sensitive elements of the population, such as the very young, the very old, and those with preexisting respiratory or cardiovascular conditions.

In the work conducted by the JATAP, however, this human health risk is based solely on the measured concentrations of air toxics near a number of urban air monitoring sites. This report describes these localized risk assessments, as well as the emissions calculations, meteorological modeling, and air quality modeling whose goal was to produce a metropolitan-wide assessment of risk to human health for all the populations of the metropolitan (and peripheral rural) areas. For reasons given above, this region-wide risk assessment was not completed. Instead, the risk assessment presented in this report is limited to discrete, small neighborhoods encompassing the urban monitoring sites. Nonetheless, the numerically generated concentrations -- calculated for each square 1km or 4km grid in the inner and outer modeling domains that cover the entire Phoenix area – are described in this report. What's missing in this report is the exposure modeling. Such "exposure" models account for the time spent in various environments that a mobile populace encounters: outside air, commuting on streets and freeways, and inside homes, offices, factories, and schools. This type of locational accounting is necessitated by the substantially different air pollutant concentrations that prevail inside the structures of the built environment versus the outside ambient air in which the concentrations are measured and for which they are simulated. The work reported on here, while concentrating on the numerical modeling producing the gridded, spatial concentration fields of air toxics concentrations, also includes as Chapter 5 the full discussion of the measurements and their risk already presented in reference (2).

Annual averages of those gaseous and particulate species with demonstrable health effects (both cancer and non-cancer) from references (1) and (2) are the focus of this modeling effort, as chronic health effects are typically estimated from such annual or multi-year averages. Many types of air pollution, including but not limited to so-called "air toxics", are arguably the most persistent and most deleterious environmental antagonist to which most people are exposed.

At this point a description of the general methods of air quality modeling analyses is called for. Estimating air pollutant concentrations through numerical modeling generally proceeds in the following steps:

1. Emissions modeling: determine the locations, sources, and hourly rates of the air pollutant emissions;

2. Meteorological modeling: determine how the air in the boundary layer and above moves throughout the area of interest, both horizontally and vertically; and

3. Air quality modeling: determine the hourly air pollutant concentrations which are a consequence of the emissions, of the physics of air flow (e.g. wind speeds and directions), of the atmospheric chemistry that transforms some of the emitted species into others, and of the deposition of these species onto the ground, building surfaces, or foliage.

All of this work is necessarily anchored to measurements, for numerical modeling of an environmental nature (or any other, for that matter), has to be empirically grounded. Emission rates, determined through national and international research in laboratories, in vehicular emissions testing facilities, or in factories with smokestacks, are then applied to the various activities in the environmental setting of interest. Numerical models produce fields of meteorological variables such as air temperature, winds, relative humidity, and mixing height (a measure of how readily and to what height emissions at the ground move upwards). The results from such meteorological models are generally compared with measurements from ground-based networks (National Weather Service stations, for example) and from upper air measurements, either from weather balloons, aircraft, or ground-based instruments that measure vertical profiles of atmospheric variables. The air quality models then take the hourly emissions and weather variables and calculate the hourly air pollutant concentrations, accounting for all the pertinent chemistry and physics of the lower atmosphere. These simulated pollutant concentrations are then compared with air pollution measurements from various monitoring networks until satisfactory agreement has been obtained. (Often such agreement entails redoing parts of the emissions modeling or meteorological modeling, or both). At this point one has produced hourly air pollutant concentrations throughout a large area: in the present work, for metropolitan Phoenix, Arizona, for calendar year 2005, in arrays of 1km and 4km square grids, each grid representing the breathing zone of each demarcated part of the land surface. The grids are in three dimensions, with the thickness of the ground-based layer usually about seven meters, although in this work the ground-based layer extends to 20 meters. Above this lowest layer are numerous others of varying thickness that extend

to heights of several kilometers. In summary, these simulated air pollutant concentrations then enable subsequent analyses, such as (a) comparison with air quality standards and guidelines, (b) what-if emission reduction scenarios, in which future air quality is predicted as a function of how emissions are expected to change, (c) population exposure, which is done in concert with so-called "exposure" models, and, ultimately (d) the effects of air pollution on human health.

# 2.0 Emissions

#### **2.1 Introduction**

The modeling tools employed to estimate air pollutant emissions in the present work are now briefly described, with references to the original sources for the technically inclined. The principal software used is the Emissions Processing System, version 3, "EPS3" (3, 4). As described in (3), however, this system had to be augmented by a number of socalled "speciation" algorithms, because EPS3 yields annual emissions of "criteria" air pollutants (carbon monoxide, sulfur dioxide, nitrogen oxides, volatile organic compounds (VOC), and particulate matter (10 microns and smaller, PM<sub>10</sub>, and 2.5 microns and smaller,  $PM_{2.5}$ ), but not the individual components of the VOC and PM groups, which consist of dozens to hundreds of air toxic species. EPS3 produced the net annual emissions of these pollutants or pollutant groups; speciation routines were employed to divide the groups into emissions of their various constituents; and then EPS3 algorithms converted the net annual emissions into seasonal, hourly, and spatially allocated emissions. The end result is a "model-ready" inventory of hourly, gridded emissions suitable for an air quality model. EPS3 contains or extracts information from numerous emission sub-models, each one designed to calculate emissions from the five major source sectors: point, area, on-road, non-road, and biogenic emissions. Details can be found in reference (3); following immediately below are general discussions of the five emission source sectors. These brief summaries are followed by a somewhat lengthy discussion of the results of this emissions modeling, namely, for certain important air toxics, the nature of their sources, their seasonality, and their spatial distributions throughout the metropolitan area.

*Point source emissions* These emissions from fairly large, stationary sources such as electronics facilities or power plants, all of which are permitted and regulated by county, state, tribal, or federal agencies, are divided into two categories. The larger facilities with taller smokestacks, called "elevated point sources", not only have their emissions tabulated but also include the dimensions and operating parameters of their stacks, such as stack height, diameter, exit gas temperature, velocity, and so forth. This detailed information is necessary so that the release points of the emissions (the top of the stacks) and the subsequent dispersion of the plumes into the atmosphere can be described and quantified for the air quality model. The smaller, permitted facilities, and all those that lack tall stacks, are treated as "low-level" point sources, with their emissions treated as being either ground-level, or near ground-level ambient-temperature releases. All elevated point sources are precisely geo-located for the air quality model. There were about 6,000 air pollution permits for point sources under the jurisdiction of the Maricopa County Department of Air Quality in 2010.

*Area source emissions* This source sector includes about 100 sub-categories of emissions, most of which are not permitted or explicitly accounted for, as are the permitted, point-source emissions. The interested reader may consult Maricopa County's two most recent periodic emission inventories for details (5, 6). An illustrative example is the case of natural gas fired, residential water heaters, of which there are tens or hundreds of

thousands throughout the metropolitan area. The emissions from these water heaters, which would be unrealistic to locate, count, and calculate individually, are treated through a combination of what are called "spatial surrogates", average natural gas consumption rates for this type of appliance, and emission factors. For these appliances the spatial surrogate is residential housing: those grids on the metropolitan land surface occupied by homes and small apartments are assigned a certain average natural gas consumption rate for these appliances per household. Emission factors (the mass of emissions of a pollutant per unit of natural gas burned) are determined experimentally at the national level. These emission factors are applied to the consumption rates to yield the emissions, which themselves are temporally allocated from annual to hourly values. Similar methods -- starting with the activity producing the emissions, proceeding next to apply the appropriate emission factor to this activity, invoking a surrogate to allocate the emissions spatially throughout the appropriate grids in the metropolitan area, and finally choosing a logical temporal adjustment scheme to convert annual to hourly and seasonal emissions – are employed for the other area source subcategories. To mention but a few of these, there are emissions from dry cleaners, from cooking in restaurants, from commercial bakeries, from large boilers for heating and cooling in office buildings, and from a myriad of other "area source" activities that cannot be efficiently accounted for on an individual basis.

*On-road mobile emissions* This source sector, which consists of those emissions from licensed vehicles on public roadways, has its emissions estimated through a combination of transportation and emissions modeling. Various levels of rigor are possible here, with the simplest being the product of a single representative emission factor (usually in grams per mile for each pollutant) with the total vehicle miles traveled in one day in an urban area. In the most sophisticated approach transportation modeling can provide geo-located link-based traffic volumes and speeds by day and then by hour. Vehicle registration data, sometimes supplemented with automated videos of the passing traffic, can then divide this traffic into vehicle types, such as heavy-duty diesel trucks, motorcycles, pick-up trucks, and gasoline-powered passenger vehicles. Separate emissions models, such as the MOBILE series or its successor the MOVES series, produce tailpipe emission factors based on vehicle type, age, speed, ambient temperature, humidity, and other variables. These emission factors are multiplied by the link-based traffic volume by vehicle type to yield a definitive accounting of vehicular emissions.

In the present work the EPA's 2005 National Emission Inventory for Maricopa County, which includes on-road mobile emissions, was used as a starting point and then spatially and temporally allocated to produce model-ready emission files of criteria pollutants. The two pollutant groups of volatile organic compounds and particulate matter were then divided into their component air toxics species with EPA's software called "SPECIATE4.0".

*Non-road mobile emissions* The non-road source sector has emissions from vehicles such as bulldozers and earthmoving scrapers *not* licensed for travel on public roadways, as well as from "mobile" equipment such as gasoline- or propane-powered generators, lawn and garden equipment, recreational vehicles, and so forth. Also included are emissions from railroads and aircraft. Non-road mobile emissions from the 2005 National Emission

Inventory were treated similarly to the on-road emissions, i.e. spatial allocation, temporal allocation, and speciation were all carried out.

*Biogenic emissions* All photosynthetic plants emit certain volatile organic compounds such as isoprene and terpenes and small amounts of carbon monoxide through their daytime metabolic conversion of sunlight and carbon dioxide into nutrients for their growth. In addition, nitrogen-fixing bacteria in the topsoil release nitric oxide, although the quantity tends to be dwarfed by combustion emissions in large urban areas. VOCs from photosynthetic plants, however, constitute an important and fairly large share of total VOC emissions in most urban areas, including metropolitan Phoenix. These biogenic emissions are estimated with numerical models that start with the degree to which the land surface is vegetated with trees, grass, desert shrub, or agricultural fields on a grid by grid basis (including the species or genera of these plants). These numerical models then calculate the VOC and nitric oxide emissions through plant- and topsoilspecific emission factors derived from laboratory and field work. These emission factors depend on soil moisture, cloud cover, and ambient temperature, and therefore vary throughout the day, approach or reach zero at night for the VOCs, and naturally vary by the season of the year. A series of specialized biogenic emission models has been developed nationally and locally, including BEIS, MAGBEIS, and so forth. In the present work the MAGBEIS model was employed to calculate these biogenic emissions.

## 2.2 Emissions Modeling Domains

By "modeling domain" is meant that geographical area which is being studied, in this case, for air toxics emissions and their resultant concentrations. Figure 2.2-1 depicts the inner and middle domains of the study region, centered in metropolitan Phoenix.

Those even somewhat familiar with the Phoenix, Arizona area will note that this modeling domain covers a much larger area than just the urbanized portions. Near the northwest corner, at the junction of highways 60 and 93, is the town of Wickenburg; the southwest-most portion extends nearly to Gila Bend; the south-central portion lies just north of the town of Casa Grande; the southeast corner approaches the town of Florence; and the northeast part nearly reaches to the town of Payson. The two large water bodies shown are Lake Pleasant in the north-central and Roosevelt Lake in the east-central areas. Mountain ranges such as the Estrellas and South Mountains (south-central) and the Mazatzals (east-central) are clearly shown. Altogether, the more urbanized land comprises about one sixth of the entire modeling domain.



**Figure 2.2-1** JATAP Modeling Domains (The complete map (excluding the central white square) is the 4km domain; the white inset is the 1km domain. Approximate areas of Gila River and Salt River Pima Maricopa Indian Communities are denoted by solid black lines.)

#### 2.3 Air Toxics Species of Interest

Air toxics, also known as Hazardous Air Pollutants (HAPs), are a large group of gaseous, semi-volatile, and particulate species with known adverse human health effects; altogether they number about 200 different elements or compounds. Of the various air pollutants and air toxics species, the following ones were chosen for study in this work, either because they are of inherent interest because of their status as criteria air pollutants (defined below), because they are precursors of ozone, or because they have demonstrable health effects (Table 2.3-1).

Species	Symbol	G or P*	Rationale for inclusion
Nitrogen oxides	NO <sub>x</sub>	0	
Volatile organic compounds	VOC	G	Ozone precursors
Nitrogen dioxide	NO <sub>2</sub>		
Carbon monoxide	СО	G	Criteria air pollutants
Sulfur dioxide	SO <sub>2</sub>		
Isoprene + terpenes	ISOP +	G	Biogenic emissions
	TERP		
Acetaldehyde	ACET_P	-	Gaseous air toxics whose 2005
Benzene	BENZENE	-	concentrations have been shown to have
1,3-butadiene	BUTA	G	important health affects in metropolitan
Chloroform	CHCL3		Phoenix as documented in Chapter 5
Formaldehyde	FORM_P		Thoema, as documented in Chapter 5
Arsenic (fine**)	As		Particulate air toxics whose 2005
Cadmium (fine)	Cd	D	concentrations have been shown to have
Diesel Particulate Matter	DPM	1	important health effects in metropolitan
(total)			Phoenix (Chapter 5)
Chromium III (fine)	Cr III		Particulate species with chronic health
Manganese (fine)	Mn	P	effects (although their concentrations in
Nickel (fine)	Ni		metropolitan Phoenix were within health guideline values in 2005)

#### Table 2.3-1 Air Pollutant and Air Toxics Species of Interest

\* G or P: G is gaseous; P is particulate.

\*\*"fine" means the emissions in the fine fraction of particulate matter ( $PM_{2.5}$ ). "Total", for DPM only, is the sum of the fine fraction (0 – 2.5 microns) and the coarse fraction (2.5 – 10 microns) to give the "total" emissions for particles 10 microns and smaller ( $PM_{10}$ ).

### 2.4 Emission Sources of Criteria Air Pollutants

As is the case in many U.S. cities, air pollutant emissions in metropolitan Phoenix are dominated by the combustion of fuel in transportation (on an average weekday more than 90 million miles are driven throughout the metropolitan area). In any rapidly growing and expanding urban area such as Phoenix, moreover, emissions from heavy equipment used in earthmoving and construction of roads and buildings also play an important role. Many other sources come into play, as well, such as agriculture, manufacturing, wood burning, forest fires, evaporation of volatile liquids such as gasoline and solvents, household cleaning and painting products, and so forth. Because of its warm, arid climate, however, Phoenix has another important source of air pollutant emissions but lacks one present in colder climates: the former being dust resuspended by vehicles on paved roads (and, to a lesser extent, from unpaved roads); the latter, extensive wintertime heating emissions. Phoenix can be considered somewhat unusual in its lack of any coal combustion emissions.

Emissions need to be considered in light of the ambient pollutant concentrations they produce. The U.S. EPA has designated the following air pollutants as "criteria pollutants", meaning that they have National Ambient Air Quality Standards (NAAQS),

are found commonly throughout most of the United States, and cause adverse health effects at concentrations that were typically found in the 1970s and 1980s when these standards were first being established. These criteria air pollutants are carbon monoxide, nitrogen dioxide, sulfur dioxide, ozone, lead, particulate matter 10 microns and smaller  $(PM_{10})$ , and particulate matter 2.5 microns and smaller  $(PM_{2.5})$ . Because metropolitan Phoenix has yet to achieve national air quality standards for  $PM_{10}$  and ozone, the Maricopa County Department of Air Quality assembles inventories of emissions for  $PM_{10}$  and for the precursors of ozone, which are volatile organic compounds (VOC) and nitrogen oxides  $(NO_x)$ . This department does not build emission inventories for air toxics. Although the serious reader may obtain these inventories at <u>http://www.maricopa.gov/AQ/</u>, they are briefly described in a following section. Their importance in understanding air toxics emissions comes about for the following reasons:

- VOCs include acetaldehyde, benzene, 1,3-butadiene, and formaldehyde four gaseous hydrocarbons with quantifiable health effects at their present concentrations in Phoenix.
- The category of non-road emissions includes most of the diesel particulate matter and a healthy share of the human-caused VOC and NO<sub>x</sub> emissions.
- The elements of arsenic and cadmium also contribute slightly to human risk; and, as their source in Phoenix is mostly from suspended topsoil, the PM<sub>10</sub> and PM<sub>2.5</sub> emissions distribution by source type can shed light on their origin. (Those especially interested in air pollutant emissions can learn more at the EPA's <a href="http://www.epa.gov/oaqps001/emissns.html">http://www.epa.gov/oaqps001/emissns.html</a> or in the monograph by Sjaak Slanina (Lead Author); Wayne Davis (Topic Editor) "Air pollution emissions". In: Encyclopedia of Earth. Eds. Cutler J. Cleveland (Washington, D.C.: Environmental Information Coalition, National Council for Science and the Environment). [First published in the Encyclopedia of Earth August 21, 2008; Last revised Date July 14, 2011; Retrieved October 3, 2011 < <a href="http://www.eoearth.org/article/Air\_pollution\_emissions">http://www.eoearth.org/article/Air\_pollution\_emissions</a> )

The following section discusses these inventories in light of which air toxics cause adverse health effects in Phoenix.

#### 2.5 Ozone Precursor and PM<sub>10</sub> Emissions Inventories for Maricopa County

Although the two Maricopa County emission inventories – one for ozone precursors; the other for  $PM_{10}$  – include all known sources of air pollution, the following discussion omits certain source categories which may not be important on a consistent year-to-year basis (for example, wildfire emissions in 2005 for ozone precursors were unusually high) or may not be so important for long-term chronic health effects (windblown dust). Biogenic emissions of ozone precursors, on the other hand, are included, mainly to show just how predominant they are for VOCs over human-caused emissions. Table 2.5-1 and Figures 2.5-1 through 2.5-4, which depict the category-by-category percentage contributions to the emissions of four air pollutants (VOC, NO<sub>x</sub>, PM<sub>10</sub>, and PM<sub>2.5</sub>), show variable source category distributions for the different pollutants. Because the air toxics inventory does not contain either PM<sub>10</sub> or PM<sub>2.5</sub>, this will be their only examination in this work. The particulate air toxics of arsenic and cadmium are likely to have similar

source distributions as PM, depending on the size fraction of the emitted particles. (This similarity of source distributions can be attributed to the general lack of industrial emissions of arsenic and cadmium in the Phoenix area, combined with the fact that most airborne arsenic and cadmium particulates comes from their natural presence in the topsoil. Those activities that disturb, suspend, and re-suspend top soil result in airborne particulates that include such chemical constituents as heavy metals such as arsenic and cadmium.) Diesel particulate matter emissions mostly come from heavy equipment in the non-road category and to a lesser extent from heavy-duty diesel vehicles in the on-road category. (A numerical breakdown of these two sources, from G. Mansell et al 2008, "Development of CAMx Gridded Emissions Input Data for the JATAP Study", memorandum, from ENVIRON to L. Montenegro, Arizona Department of Environmental Quality, page 31, for wintertime diesel particulate exhaust, is that of the sum of emissions from the non-road and on-road emission source sectors, 51% is from construction and earthmoving equipment, 35% from heavy-duty diesel vehicles on roadways, with the remaining 14% from commercial and industrial equipment, railroads, lawn & garden equipment, aviation, and light-duty diesel vehicles.) With the exception of the biogenic emissions (isoprene and terpenes), the individual VOCs (from Table 2.3-1) would be distributed among solvent use, storage and transport of volatiles, and exhaust from onroad and non-road vehicles, among other less important contributing sources.

Source category	PM <sub>10</sub>	PM <sub>2.5</sub>	VOC	NO <sub>x</sub>
miscellaneous*	29.4	18.7	0.0	0.0
paved road dust	24.5	4.3	0.0	0.0
industrial processes**	22.2	34.0	0.5	0.5
unpaved road/alley dust	16.5	8.8	0.0	0.0
non-road exhaust & dust***	2.7	13.8	7.1	26.0
on-road exhaust	2.2	7.2	15.7	61.6
fuel combustion	1.8	9.2	0.9	6.2
point	0.8	4.0	1.7	2.6
waste/disposal	0.3	1.5	0.3	0.0
biogenic	0.0	0.0	57.8	3.0
solvent use	0.0	0.0	14.9	0.0
storage/transport of volatiles	0.0	0.0	1.0	0.0

**Table 2.5-1** Source Category Contributions (%) to the Emissions of Four Air Pollutants (shaded values indicate the more important contributions (greater than 10%))

\* "miscellaneous": Four categories contribute most of the PM: dust from off-road recreational vehicles, travel on unpaved parking lots, agricultural tilling, and travel on unpaved farm roads, which, together, account for 91% of the miscellaneous  $PM_{10}$  emissions and 71% of the  $PM_{2.5}$  emissions. Left out of the miscellaneous category are wildfires and windblown dust.

\*\*Industrial processes for PM are dominated by construction dust (73% of  $PM_{10}$ ; 15% of  $PM_{2.5}$ ) and commercial cooking (25% of  $PM_{10}$ ; 50% of  $PM_{2.5}$ ).

\*\*\*Non-road VOC emissions are dominated by lawn & garden activities (40%); non-road NOx emissions, by construction and mining equipment (56%).



Figure 2.5-1 Maricopa County VOC Emissions on an Annual Basis by Source Category



**Figure 2.5-2** Maricopa County Oxides of Nitrogen Emissions on an Annual Basis by Source Category



Figure 2.5-3 Maricopa County PM<sub>10</sub> Emissions on an Annual Basis by Source Category



Figure 2.5-4 Maricopa County PM<sub>2.5</sub> Emissions on an Annual Basis by Source Category

While the discussion above concerns source category contributions to four air pollutant groups based on their Maricopa County inventories, the next section presents category contributions in a general sense for the air toxic species of interest in the emissions modeling domain of the present work.

## 2.6 Air Toxic Emissions by General Source Category

The inventory of air toxic emissions on which this report is based was commissioned by the Arizona Department of Environmental Quality (ADEQ) on behalf of the Joint Air Toxics Assessment Project, a consortium of tribal and governmental officials active in greater Phoenix since the early 2000s. The inventory is described to some extent in (3), but annual emission totals were not provided and the emission density maps were too coarse and too small to provide the more detailed information sought by certain interested parties. Table 2.6-1 describes the various sources of air toxic emissions in metropolitan Phoenix.

Species	Emission Sources	Comments
nitrogen oxides	Fuel combustion: gasoline, diesel, natural gas, wood	"nitrogen oxides" is the sum of nitric oxide and nitrogen dioxide, of which 95% are nitric oxide.
volatile organic compounds	This group of gaseous hydrocarbons comes from fuel combustion, solvent evaporation, various industrial processes, and includes emissions from trees, grass, and other plants ("biogenic emissions").	Volatile organic compounds react with oxides of nitrogen in sunlight to produce the criteria air pollutant ozone.
nitrogen dioxide <sup>1</sup>	Fuel combustion	
carbon monoxide <sup>1</sup>	Fuel combustion	
sulfur dioxide <sup>1</sup>	Very little emitted in metropolitan Phoenix. Gasoline, diesel fuel, and natural gas have trace quantities of sulfur compounds. When these fuels are burned, small quantities of sulfur dioxide are emitted.	Criteria air pollutants
isoprene + terpenes	Trees, grass, plants	Biogenic emissions
acetaldehyde	Key photochemical reaction product, i.e. it is produced in the lower atmosphere through chemical reactions. Also this compound is emitted directly in fuel combustion. Used as a fruit and fish preservative and flavoring agent.	Secondary source from degradation of other volatile organic compounds (VOCs); most likely to correlate with formaldehyde.
benzene	Constituent in motor fuels. Also present in fuel combustion, refining, and solvents. Pumping gasoline exposes one to all its volatile components, including benzene.	Tracer for vehicle exhaust
1,3-butadiene	Motor vehicle exhaust, production of plastics. Also from forest fires and cigarette smoke.	Likely to correlate with benzene and other mobile source tracer species.

**Table 2.6-1** Sources of Air Toxic Emissions

Species	Emission Sources	Comments
chloroform	Solvent for adhesives, pesticides, fats, oils, and rubbers. By-product of chlorination from drinking water plants and from swimming pools. In Phoenix the largest source is swimming pools.	
formaldehyde	Key photochemical reaction product, i.e. it is produced in the lower atmosphere through chemical reactions and is emitted directly from power plants, manufacturing facilities, incinerators, and automobile exhaust emissions. Used as a chemical intermediate, analytical reagent, concrete and plaster additives, cosmetics, disinfectants, fumigants, photography, and wood preservation; Also in resins and particle board products.	Secondary source from degradation of other VOCs; most likely to correlate with acetaldehyde.
hexachlorobutadiene	Found in transformer and hydraulic fluids, heat transfer liquids, solvents, laboratory reagents, and as a wash liquor for removing hydrocarbons with four or more carbon atoms.	Not manufactured in the U.S Not detected in PHX in 2005
arsenic	Component of soil, resuspended dust from paved (and unpaved) roads, semiconductor manufacturing, nonferrous metals	Mostly "crustal" or "geological" in Phoenix
cadmium	Component of soil, resuspended dust from paved (and unpaved) roads, nickel-cadmium batteries, ceramics, glasses, paints and enamels, cadmium alloys; Also present in non-ferrous metals and alloys of zinc, lead and copper, in cement, and in phosphate fertilizer.	Mostly "crustal" or "geological" in Phoenix
diesel particulate matter	Diesel exhaust from cars, trucks, heavy equipment, generators, etc.	Also known as "black carbon", "elemental carbon", or soot. In metropolitan Phoenix 90% of the ambient elemental carbon is from diesel exhaust.

Species	Emission Sources	Comments
chromium III*	Component of soil, resuspended dust from paved (and unpaved) roads; chrome plating shops, road dust from catalytic converter erosion and asbestos brakes, tobacco smoke, and cement dust; cooling towers	Mostly "crustal" or "geological" in Phoenix
manganese	Component of soil; resuspended dust from paved (and unpaved) roads; present in dry-cell batteries, matches, fireworks, porcelain and glass-bonding materials; in animal feed, fertilizers, and as a livestock supplement; widely applied to edible crops as a fungicide; Potassium permanganate is used as an oxidizing agent; as a disinfectant; as an anti-algal agent; for metal cleaning, tanning, and bleaching; as a purifier in water and waste treatment plants; and as a preservative for fresh flowers and fruits.	Mostly "crustal" or "geological" in Phoenix
nickel	Component of soil, resuspended dust from paved (and unpaved) roads, nickel plating operations, nickel- cadmium batteries	Mostly "crustal" or "geological" in Phoenix

1. Nitrogen dioxide, carbon monoxide, and sulfur dioxide are grouped together because they are designated by EPA as "criteria pollutants".

\* "Chromium III" stands for the trivalent form of chromium, which is present in the atmosphere as insoluble chromium salts. U.S. EPA does not consider this form of chromium to be carcinogenic nor does the agency assign it any non-carcinogenic health effects (4). Chromium VI, the hexavalent form, does have adverse health effects, both for cancer and non-cancer. About 3.5 percent of ambient chromium concentrations in Phoenix are of the chromium VI type, from unpublished work by P. Hyde (July 2009), based on 31 monitor-years in California at 10 different sites (average -3.4%) and two years at the Phoenix Supersite (3.3% in 2006; 3.4% in 2007. In 2005 the chromium VI concentrations were within the health guideline values set by EPA. The emissions inventory on which the present work is based has chromium III but not chromium VI.

The more generalized discussion above is now supplemented with the sub-category information from reference (3), which did not report, but did calculate, emissions for stationary point sources or biogenic sources, leaving just the three emission source sectors of non-road mobile (seven sub-categories), on-road mobile (four), and stationary area sources (nine) for the following discussion. The emissions, reported for the four seasons separately, have been combined to provide annual values (although their seasonality is briefly discussed). As can be seen in Table 2.6-2 for six gaseous air toxics, and in Table 2.6-3 for six particulate air toxics, different species have different groups of sub-categories that produce emissions. All species have emissions from the non-road and

on-road sectors, with most sub-categories contributing for most species. Stationary area source sub-categories contribute zero emissions for 1,3-butadiene and all six particulate species. Hexachlorobutadiene has reported emissions of essentially zero for all sub-categories of every sector; suggesting that it is not found in the ambient air. Although reference (1) reported demonstrable health effects from this compound, this finding turns out to be an artifact of setting non-detectable concentrations to one half of the method detection level (MDL). Further examination shows that this compound was not detected in any of the 60 samples at any of the monitoring sites in 2005. Benzene, acetaldehyde, and formaldehyde have the highest number of contributing sub-categories. The distributions of air toxics emissions by sub-category for selected species are also given in the bar graphs of Figures 2.6-1 through 2-9.

acetaidenyde, BEN, benzene, CHCLS, chiorofolonii, FORM, formaidenyde, Ciobuta, nexachiorobutadiene)							
Sector	Sub-category	1,3-BUTA	ACET	BEN	CHCL3	FORM	Cl6buta
	agricultural equipment	0.10	0.10	0.23	0.00	0.09	0.00
non-road	aviation	0.10	0.03	0.12	0.00	0.10	0.00
mobile	commercial & indus. equipment	0.23	0.24	0.63	0.00	0.35	0.00
	construction/mining equipment	0.22	0.23	0.64	0.00	0.25	0.00
	lawn & garden equipment	0.30	0.43	0.34	0.00	0.34	0.00
	railroads	0.03	0.03	0.04	0.00	0.05	0.00
	recreational equipment	0.09	0.08	0.11	0.00	0.15	0.00
	heavy-duty diesel vehicles	0.06	0.09	0.13	0.00	0.11	0.00
on-road	heavy-duty gasoline vehicles	0.13	0.13	0.14	0.00	0.06	0.00
mobile	light-duty diesel vehicles	0.23	0.27	0.27	0.00	0.19	0.00
	light-duty gasoline vehicles	0.49	0.49	0.48	0.00	0.49	0.00
	industrial processes	0.00	0.03	0.06	0.00	0.06	0.00
	miscellaneous area sources	0.00	0.00	0.00	0.19	0.01	0.00
	petroleum & solvent extraction	0.00	0.00	0.00	0.00	0.00	0.00
	prescribed forest burns	0.00	0.00	0.00	0.00	0.00	0.00
stationary	solvent use	0.00	0.00	0.25	0.00	0.01	0.00
area	stationary source fuel combust.	0.00	0.01	0.10	0.00	0.07	0.00
	storage & transport	0.00	0.00	0.12	0.00	0.00	0.00
	waste disposal and handling	0.00	0.00	0.03	0.00	0.00	0.00
	waste handling	0.00	0.00	0.02	0.02	0.00	0.00
	grand total	1.99	2.16	3.69	0.21	2.33	0.00*

**Table 2.6-2** Average Annual Gaseous Air Toxics Emissions by Sub-Category – Phoenix Metropolitan Area (units are pounds per day; abbreviations: 1,3-BUTA, 1,3-butadiene; ACET, acetaldebyde: BEN\_benzene: CHCL3\_chloroform: FORM\_formaldebyde: Cl6buta\_beyachlorobutadiene)

\*The grand total in the emissions inventory for hexachlorobutadiene is 0.00000015 tons per day, all in the stationary area source sector.

Sector	Sub-category	As	Cd	Cr	Mn	Ni	DPM
off-road mobile	agricultural equipment	0.21	0.18	0.12	0.16	0.16	0.10
	Aviation	0.08	0.09	0.01	0.01	0.05	0.04
	commercial & indus. equipment	0.33	0.41	0.56	0.45	0.43	0.54
	construction/mining equipment	0.57	0.56	0.36	0.42	0.40	3.54
	lawn & garden equipment	0.34	0.41	0.31	0.33	0.05	0.07
	Railroads	0.02	0.04	0.00	0.00	0.02	0.16
	recreational equipment	0.12	0.11	0.09	0.09	0.02	0.00
on-road mobile	heavy-duty diesel vehicles	0.12	0.15	0.10	0.10	0.14	2.59
	heavy-duty gasoline vehicles	0.20	0.12	0.13	0.09	0.09	0.00
	light-duty diesel vehicles	0.26	0.25	0.22	0.20	0.25	0.04
	light-duty gasoline vehicles	0.44	0.42	0.43	0.47	0.48	0.00
stationary area	industrial processes	0.00	0.00	0.00	0.00	0.00	0.00
	miscellaneous area sources	0.00	0.00	0.00	0.00	0.00	0.00
	petroleum & solvent extraction	0.00	0.00	0.00	0.00	0.00	0.00
	prescribed forest burns	0.00	0.00	0.00	0.00	0.00	0.00
	solvent use	0.00	0.00	0.00	0.00	0.00	0.00
	stationary source fuel combustion	0.00	0.00	0.00	0.00	0.00	0.00
	storage & transport	0.00	0.00	0.00	0.00	0.00	0.00
	waste disposal and handling	0.00	0.00	0.00	0.00	0.00	0.00
	waste handling	0.00	0.00	0.00	0.00	0.00	0.00
	grand total	2.60	2.71	2.33	2.32	2.09	7.07

**Table 2.6-3** Average Annual Particulate Air Toxics Emissions by Sub-Category –Phoenix metropolitan area (units are pounds per day; abbreviations: As, arsenic; Cd, cadmium, Cr,chromium III, Mn, manganese; Ni, nickel; DPM, diesel particulate matter)



**Figure 2.6-1** Diesel Particulate Matter Emissions by Sub-Category - Phoenix Metropolitan Area



### Figure 2.6-2 Arsenic Emissions by Sub-Category – Phoenix Metropolitan Area

(The inventory of (1) does not have resuspended road dust from either paved or unpaved roads as separate sub-categories, so this graph is somewhat misleading, because these two sub-categories contribute 16% of the non-windblown PM10 in the county inventory)



Figure 2.6-3 Acetaldehyde Emissions by Sub-Category – Phoenix Metropolitan Area



Figure 2.6-4 1,3-Butadiene Emissions by Sub-Category – Phoenix Metropolitan Area
Most air pollutant emissions vary by season; air toxics are no exception. For the four gaseous species of acetaldehyde, benzene, 1,3-butadiene, and formaldehyde, the summer emissions are from 23 to 34% higher than winter, with spring and autumn in between. Chloroform emissions are constant year-round, at least according to the inventory from (3), as are the emissions of diesel particulate matter. The other particulate species of arsenic, cadmium, chromium, manganese, and nickel have summer emissions from 29 to 48% higher than winter (with spring and autumn in between). Figure 2.6-5 presents a summary of this seasonality.



Figure 2.6-5 Seasonality of Air Toxics Emissions – Phoenix Metropolitan Area

In the following section annual air toxics emissions are tabulated and emission density maps presented for metropolitan Phoenix as a whole.

# 2.7 Annual Air Toxics Emissions in Metropolitan Phoenix

This section presents the annual air toxics emissions for all of metropolitan Phoenix for calendar year 2005 (Tables 2.7-1 and 2.7-2). The emissions are in units of tons per day (Table 2.7-1) and in percentages (Table 2.7-2). The annual emissions presented are the average of the four seasonal emission totals of reference (3) for the four source sectors of low point, area, on-road, and off-road. Because their importance lies in summertime ozone formation, biogenic emissions are reported for a typically hot, sunny day (25 June 2005). Species definitions are as follows:

NOx	nitrogen oxides (the sum of nitric oxide (NO) and nitrogen dioxide (NO <sub>2</sub> ))
VOC	volatile organic compounds
$NO_2$	nitrogen dioxide
CO	carbon monoxide
$SO_2$	sulfur dioxide
ISOP+TERP	isoprene and terpenes, which are biogenic emissions
ACET_P	acetaldehyde
BENZENE	benzene
BUTA	1,3-butadiene
CrIII	chromium (trivalent form)
FORM_P	formaldehyde
BTDCL6	hexachlorobutadiene
CHCL3	chloroform
As	arsenic
Cd	cadmium
DPM	diesel particulate matter
Mn	manganese
Ni	nickel

The emissions for different air toxics species differ by several orders of magnitude, Also shown as zero emissions (0.0) are certain species whose non-zero total was nine significant figures or more (for example, nickel (Ni) in Table 2-6, and a few others).

Species	Area Sources (t/d)	Off-road Sources (t/d)	On-road Sources (t/d)	Low Point Sources (t/d)	Biogenic Sources (t/d)	All five Source sectors (t/d)
NO <sub>X</sub>	12.13	37.82	75.34	0.807	0.0	126.10
VOC	80.14	27.01	16.77	5.08	148.10	277.10
NO <sub>2</sub>	1.77	5.51	10.97	0.118	0.0	18.37
CO	16.25	502.49	929.98	0.878	21.32	1470.92
SO <sub>2</sub>	1.39	1.49	1.49	0.254	0.0	4.62
ISOP+TERP	0.011	9.61	0.000094	0.027	91.98	101.63
ACET_P	0.036	0.809	0.264	0.008	0.0	1.12
BENZENE	0.357	1.46	2.28	0.038	0.0	4.14
BUTA	0.00005	0.747	0.279	0.014	0.0	1.04
CrIII	0.0006857	1.07	0.0023	0.001	0.0	1.07
FORM_P	0.106	0.900	0.751	0.075	0.0	1.83
BTDCL6	0.0000015	0.0	0.0	0.0	0.0	0.0000015
CHCL3	0.173	0.0	0.0	0.000023	0.0	0.173
As	0.000914	1.14	0.0015	0.00000002	0.0	1.14
Cd	0.000688	1.26	0.0019	0.00000002	0.0	1.26
DPM	0.0	0.0	0.030	0.0	0.0	0.030
Mn	0.00137	1.04	0.002	0.00000630	0.0	1.04
Ni	0.000686	0.808	0.002	0.00100000	0.0	0.812

**Table 2.7-1**Annual Air Toxics Emissions (tons per day) in Metropolitan Phoenix

Craning	Area	Off-road	On-road		Biogenic
Species	Sources	Sources	Sources	Low Point	Sources
NO <sub>X</sub>	9.62	29.99	59.75	0.64	0
VOC	28.92	9.75	6.05	1.83	53.45
NO <sub>2</sub>	9.64	29.99	59.72	0.65	0
СО	1.1	34.16	63.22	0.07	1.45
SO <sub>2</sub>	30	32.25	32.25	5.5	0
ISOP+TERP	0.01	9.46	0	0.03	90.5
ACET_P	3.21	72.51	23.57	0.71	0
BENZENE	8.62	35.39	55.07	0.92	0
BUTA	0	71.82	26.83	1.35	0
CrIII	0.06	99.64	0.21	0.09	0
FORM_P	5.79	49.07	41.04	4.1	0
BTDCL6	100	0	0	0	0
CHCL3	99.99	0	0	0.01	0
As	0.08	99.79	0.13	0	0
Cd	0.05	99.8	0.15	0	0
DPM	0	0	100	0	0
Mn	0.13	99.68	0.19	0	0
Ni	0.08	99.55	0.25	0.12	0

**Table 2.7-2**Annual Air Toxics Emissions in Metropolitan Phoenix: PercentageContributions

## 2.8 Conclusions about Emissions

- Metropolitan Phoenix, with its population exceeding four million, is a large enough area with enough 21<sup>st</sup> century transportation, agricultural, and industrial activities to generate copious air pollutant emissions -- both the so-called "criteria" air pollutants such as nitrogen dioxide, carbon monoxide, and particulate matter, as well as the more specific (and exotic) air toxics such as benzene, 1,3-butadiene, and diesel particulate matter.
- These emissions lead to unhealthful concentrations of ambient air pollution to which virtually all residents are exposed at various times throughout the year, albeit with considerable seasonal and hourly variability, and with substantial variation depending on location. In this vein consider how far a home is from a major roadway, agricultural field, or industrial source; and an entire neighborhood's or community's distance and direction from the bulk of urban emissions, which are generally highest in the central urban area.
- In this respect the exposure of Phoenix residents to criteria and air toxic pollutants differs little from similar exposures in other large cities of this country, as is evident from recent air toxics studies in Los Angeles, California, Portland, Oregon, and Detroit, Michigan.
- Through the accomplishments and continuing activities of the Joint Air Toxics Assessment Project, the risk to human health from the pantheon of air toxics, lead by diesel particulate matter as the prime antagonist, is now understood in the neighborhoods of the 2005 air toxics monitoring sites. This understanding would be woefully incomplete without knowledge of the emission sources that produce them.

#### 2.9 Emission Density Maps

Now presented is a sample of emission density maps. These maps show the spatial distribution of air toxics emissions for the Phoenix metropolitan area. To pick just one example, that of nitrogen oxides in metropolitan Phoenix, the central urban area has emissions in the 1-5 tons per day range, while immediately outside the values decrease ten-fold to the 0.5 - 1.0 range. The yellow, more or less linear areas, emanating from the central city, with emission values of 0.05 to 0.1 ton per day, are coincidental with major highways and freeways. The smaller, more localized hot spots - one west of Phoenix, a second in the southeast region, a third in the northeast, and the fourth (and last) in the far east-central area - may reflect nitrogen oxides emissions either from power plants or from large tracts under active development with such activities as land clearance, earthmoving, and construction. Such activities generate nitrogen oxides emissions because of the diesel-powered, heavy equipment employed in disturbing and moving earth, as well as emissions from such ancillary activities as gasoline-powered generators and the additional vehicle miles traveled by construction workers. As for the power plants, even though such point sources account for only about 3% of the nitrogen oxides emissions in metropolitan Phoenix (see Figure 2.5-2 or Table 2.5-1), if their location is in a single 1or 4-km grid, the emission value can be quite elevated.

#### Phoenix Metropolitan

Road map – Phoenix Metropolitan



Figure 2.9-1 Metropolitan Phoenix Emissions "roadmap"

Legend for stations: 1- Greenwood; 2 – West Phoenix; 3 – Vehicle Emissions Inspection; 4 – Supersite; 5 – South Phoenix; 6 – Salt River Senior Center; 7 – Gila River St. Johns; 8 – Queen Valley; 9 – Tonto National Monument

## **Ozone precursors**



#### Figure 2.9-2 Nitrogen Oxides Emission Density Map

Legend for stations: 1- Greenwood; 2 – West Phoenix; 3 – Vehicle Emissions Inspection; 4 – Supersite; 5 – South Phoenix; 6 – Salt River Senior Center; 7 – Gila River St. Johns; 8 – Queen Valley; 9 – Tonto National Monument



# Volatile organic compounds emission density map (tons per day)

Figure 2.9-3 Volatile Organic Compounds Emission Density Map

Legend for stations: 1- Greenwood; 2 – West Phoenix; 3 – Vehicle Emissions Inspection; 4 — Supersite; 5 – South Phoenix; 6 – Salt River Senior Center; 7 – Gila River St. Johns; 8 – Queen Valley; 9 – Tonto National Monument

# 3.0 Meteorological Modeling

#### **3.1 Introduction**

The details of the meteorological modeling in the present work are described in (7), included as Appendix A of this report. To supplement this more technical description, the following discussion describes how such models are generally employed and how they were applied in the present work. First, two different meteorological models were used: **MM5** and **CALMET**.

The model called MM5 is the Pennsylvania State University / National Center for Atmospheric Research mesoscale prognostic model -- a limited-area, non-hydrostatic, terrain-following, sigma-coordinate model designed to simulate or predict mesoscale atmospheric circulation. The model is supported by several pre- and post-processing programs, which are referred to collectively as the MM5 modeling system. This system, developed as a community model, has benefitted from contributions from users worldwide. Second, although this model has been for the most part supplanted by a successor (called the Weather Research and Forecasting Model, WRF for short), it was the weather model of choice throughout the 1990s and 2000s for both weather forecasting and air quality modeling. (MM5 and WRF are comparable in their abilities to simulate meteorological variables important in air pollution studies, so the choice of the older model has no bearing on the quality of this project.) Third, for air quality studies such as the present work, the model is used retrospectively: for past years or episodes, the model is run to produce broad geographical "fields" of meteorological variables, from the land surface to high in the atmosphere, with multiple layers above the ground, and with an array of grids (e.g. 12km) throughout a continent, region, or sub-region. Fourth, the model is initialized with output from a global National Weather Service model; is usually run for about five to seven days (when it is then re-initialized and rerun); and is regarded as a reliable tool either for predicting future conditions or for reproducing historical weather patterns. Fifth, through research both "pure" and "applied", in which various modular algorithms that describe different phenomena of atmospheric physics (cloud formation, precipitation, boundary-layer wind speeds, etc.) have been developed and tested, this model has proven quite capable of simulating the meteorological variables of the greatest importance in air quality modeling.

Furthermore, considerable attention has been paid by researchers, including those simulating conditions in Phoenix, Arizona, to determining how well the results of this numerical model match up with both ground-based and upper air measurements. These fields consist of gridded, layered, hourly-averaged variables such as wind speed, wind direction, relative humidity, and the like, from the surface on up. They provide the information necessary for the air quality model to "move" air parcels from place to place, both horizontally and vertically, a process called "advection." In summary, MM5 is considered a reliable model to generate the meteorological fields that grid-based air quality models require.

In the present work, however, MM5 fields of meteorological variables were not used directly in the subsequent air quality modeling; instead, these fields were extracted and formatted for another meteorological model called CALMET. In contrast with MM5, which is characterized as a full-physics, prognostic model, CALMET is a diagnostic flow model that treats the effects of complex terrain on the winds, including parameterizations for slope flows, blocking and channeling of the wind. This two-model arrangement combines the strengths of both kinds of models and has been in common use in air quality modeling for many years. The following statements are from page 15 of Appendix A, and serve to summarize the work.

- MM5 fields without nudging from surface observations, also known as "MM5-only", proved to be superior to those that were, and have been used in the present work. ("Nudging" refers to adjusting the MM5 fields with observational data.)
- MM5 fields were developed in 12 km grids.
- The MM5-only runs generated consistent wind and temperature fields for CALMET, which then interpolated the 12km information to 4km grids, including stability-dependent-terrain adjustments important in complex terrain.

# 3.2 Comparisons Between MM5 and Surface-Based Measurements

Most surface-based meteorological measurements are made at 10 meters above ground, and most air quality measurements at 3 - 5 meters. Although many meteorological modelers prefer that the lowest layer be set from ground level to 7 meters, to better account for turbulence-inducing elements such as houses, buildings, and trees; the present MM5/CALMET meteorological fields have a lowest layer of 20 meters. This higher surface layer may confound the agreement between both the simulated meteorological and air pollutant concentrations and their respective ground-based measurements, especially for particulates, which have rather steep concentration gradients in the surface layer. Although Appendix A includes an eleven page section entitled "Evaluation of CALMET Output", and even though the contractors examined various meteorological fields in considerable detail for specific dates, they did not carry out a statistically-based performance evaluation in which the CALMET variables were compared with surface observations. The contractors offer two conclusions (p. 15 of Appendix A):

- (1) "The MM5-only run has generated consistent wind and temperature fields in which the CALMET diagnostic routines are used to interpolate 12-km MM5 data to the 4km CAMx grid..."; and
- (2) "The MM5 only run[s]...are self-consistent and remove the 'bullseyes' and related artificial spatio-temporal gradients brought about by mixing in observational data that can falsely impact transport patterns."

As such an evaluation is beyond the scope of the present work, the authors have no choice but to accept that the meteorological fields produced by the contractors are adequate and proceed with the air quality modeling, described in the following section.

# 4.0 Air Quality Modeling

#### 4.1 Introduction

This work is an integral, if somewhat late, part of the Joint Air Toxics Assessment Project (JATAP), whose stated goal is to determine the risk from airborne gaseous and particulate air toxics to the various populations of metropolitan Phoenix, Arizona. Among these populations are the community of South Phoenix and the Salt River Pima Maricopa and Gila River Indian Communities. Specialized air quality monitoring was conducted by county, state, and tribal staff in calendar year 2005 to provide measurements of air toxics concentrations. These measurements form the foundation against which simulated spatially and temporally resolved concentrations throughout the entire metropolitan area can be compared. These simulated concentrations enable a metropolitan-wide human risk assessment, work yet to take place. The simulated concentrations are in three arrays: the inner-most with 1km grids, the middle, with 4km grids, and the outermost, with 36km grids, the third of which only provides initial and boundary conditions for the inner and middle domains. The inner domain covers most of metropolitan Phoenix; the middle extends this coverage to further outlying areas, while the outer domain extends far into the surrounding region. For this project the air quality model of choice is the Comprehensive Air quality Model with extensions (CAMx), which incorporates the more important air toxics species and their chemical reactions.

#### 4.2 Modeling Overview

The Comprehensive Air quality Model with extensions (CAMx) is an Eulerian photochemical dispersion model that allows for an integrated "one-atmosphere" assessment of gaseous and particulate air pollution (ozone, PM<sub>2.5</sub>, PM<sub>10</sub>, air toxics, mercury, and so forth) over many scales ranging from sub-urban to continental. ("Eulerian" refers to the numerical approach to atmospheric dispersion in which the velocities of particles (or gases) are referenced to a rigid coordinate system, such as grids imposed on the ground surface with variable layers above. Thus, an array of cubes or rectangular cells then represent the lower atmosphere, with the concentration statistics dependent on the particle velocities relative to the demarcated cells. In contrast, the other numerical approach is termed "Lagrangian", which describes concentration statistics related to the flow of particles released within the atmosphere.) CAMx is designed to unify all of the technical features required of "state-ofthe-science" air quality models into a single system that is computationally efficient, easy to use, and publicly available. It has been widely used by regulatory agencies for ozone and PM State Implementation Plan modeling studies, as well as by regional planning organizations for multi-state regional haze modeling. The CAMx model embodies all of the key atmospheric processes for trace species, including emissions, advection, dispersion, photochemical transformation, aerosol thermodynamics, phase transfer, aqueous chemistry, and wet and dry deposition. In particular, the modeling system consists of a number of related "routines", "computational schemes", or "algorithms", with:

• Gas-phase chemistry represented by the CB05 or SAPRC99 photochemical mechanisms,

- Aqueous-phase chemistry represented by the RADM mechanism,
- Inorganic aerosol composition represented by the ISORROPIA algorithm,
- Secondary organic aerosol thermodynamics represented by a semi-volatile partitioning scheme,
- Fine particulates (PM<sub>2.5</sub>) and coarse particulates (PM<sub>2.5-10</sub>) represented by their discreet size fractions, and
- An interface to the output of the meteorological model called "MM5".

Version 5.2 of CAMx (aka "CAMx v5.2") was used in this study (<u>www.camx.com</u>), the three key attributes of which are

- Two-way gridded nesting that supports multiple levels of fully interactive grid nests,
- Flexi-nesting algorithms that automatically derive information for a nested grid from its immediate parent if the data are not provided as model inputs, and
- The ability to optionally simulate any number of user-defined, chemically reactive tracers using a probing tool called "RTRAC".

RTRAC provides a flexible approach for tracking the emission, dispersion, chemistry, and deposition of multiple gas and particle tracers. The tracers operate in parallel to the CAMx host model. Gas-phase chemistry can be defined as a simple decay rate for each species (photolysis and reactions with radicals), or as a complex non-linear system defined by the user through RTRAC's Chemical Mechanism Compiler. RTRAC can also output locally specific tracer decay rates for input to a separate Gaussian or puff dispersion model for sub-grid scale or "fence line" dispersion calculations. Potential RTRAC applications include simulating gaseous and particulate air toxic concentrations from specific emission source sectors.

# 4.3 Modeling Domain

See Figure 2-1 and the accompanying discussion for details. The projection information, the grid definitions for the 4-km and 1-km modeling domains, and the vertical layer structure are given in Tables 4.3-1 through 4.3-3.

(2140 Tone Color to Sur, Consistent for an above and Braphs in this section)					
<b>Grid Projection Parameter</b>	Value				
Projection	Universal Transverse Mercator (UTM)				
UTM zone	12				
UTM hemisphere	North				

**Table 4.3-1** Projection Definition for the Modeling Grid

 (Blue font color to stay consistent for all tables and graphs in this section)

Grid size	SW grid cell X	SW grid cell Y	n, E-W grid cells	n, N-S grid cells	n, vertical layers
4 km	297 km	3652 km	50	29	24
1 km	369 km	3676 km	80	72	24
1 km, cell number relative to the 4km grid	18th	6th			

**Table 4.3-2** Grid Definitions for CAMx ("n" stands for number of)

<b>Table 4.3-3</b>	Vertical La	yer Structure
--------------------	-------------	---------------

Index	Height (m)	Thickness (m)
24	4210	570
23	3640	530
22	3110	510
21	2600	390
20	2210	280
19	1930	270
18	1660	180
17	1480	180
16	1300	170
15	1130	170
14	960	170
13	790	80
12	710	80
11	630	80
10	550	80
9	470	80
8	390	80
7	310	80
6	230	70
5	160	40
4	120	40
3	80	40
2	40	20
1	20	20
0	0	Surface

One of several different ways to map the earth's surface, the Universal Transverse Mercator (UTM) method is widely employed in geophysical numerical modeling. Perhaps more familiar to many readers is the latitude and longitude system of navigation, or the township,

section, range system of North American land surveys. As for the two arrays of grids covering metropolitan Phoenix (see Figure 2.2-1), the central portion consists of 80x72 1km grids; the outer portion, of 50x29 4km grids. The coordinates of the southwest corner of the 4km array ( 297, 3652) are related to the origin of the third, outermost array of 36km girds (not shown); while the southwest corner of the 1km array is expressed relative to the southwest corner of the 4km array (namely 18 grids east and 6 grids north). The lowest 4 kilometers of the atmosphere has been divided into 24 layers of variable "thickness" or depth, ranging from 20 to 570 meters. Thus, for this Eulerian modeling approach, the land surface of the Phoenix region has been divided into 24 discreet layers. The net result is a three-dimensional array of (fairly thin) rectangular cells that encompasses the entire land surface of the region and which extend to about 4 kilometers above the ground surface. For example, these rectangular cells have dimensions of 4,000 x 4,000 x 20 meters at the surface in the outer domain, 1,000 x 1,000 x 20 meters at the surface of the inner domain; and, at their upper limit, have the same surface areas but become as thick as 570m.

#### 4.4 Spatial Distributions of Simulated Annual Concentrations

To estimate the risk from air toxics to chronic health conditions, annual averages are generally employed, even though by definition "chronic" toxicity is based on a 70-year lifetime. Shown in Figures 4.4-1 and 4.4-2, these spatial distributions of gaseous and particulate air toxics generally conform to their emission distributions and the prevailing meteorological conditions. As explained in Section 4.5, however, these simulated annual averages do not agree well with the measured ones for most of the species. Nonetheless, with the exception of diesel particulate matter, whose non-road emissions were somehow set at zero in the model-ready emissions inventory, these distributions faithfully reproduce the patterns established by the ambient monitoring in 2005. In other words, except for diesel particulate matter, and despite the general under-estimates of these simulated concentrations compared with the measurements, the overall spatial distributions of these air toxics species are accurately depicted in these figures.



**Figure 4.4-1** Annual Concentrations for Gaseous Pollutants [ppb]: Acetaldehyde (ACET); Formaldehyde (FORM); Benzene (BENZ); 1,3 butadiene (BUTA)



**Figure 4.4-2** Annual Concentration for Particles [ng/m3,  $\mu$ g/m3 for DPMT only]: Diesel Particulate Matter - total (DPMT); Cadmium - fine (Cd); Manganese - fine (Mn); Nickel - fine (Ni)

# 4.5 Comparisons with Measurements

While a complete, thorough, and definitive evaluation of the simulated concentrations lies beyond the scope of this work; the authors offer a number of comparisons to explore the fidelity of the CAMx model in its ability to produce concentrations that correspond with the measured air pollutant and air toxics concentrations. In section 4.5.1, the every-sixth day, annual average concentrations of particulate air toxics, e.g. diesel particulate matter and arsenic in the fine fraction (PM<sub>2.5</sub>), are compared with measurements at all sites. In section 4.5.2, annual averages of gaseous air toxics are compared with the measured concentrations.

Comprised of emissions, meteorological, and air quality modeling modules, this modeling system has been applied to other urban areas; the reported performance of CAMx in simulating air toxics and ozone concentrations provides some context to its performance in the present work. Table 4.5-1 presents some of these CAMx evaluation studies.

Authors	Affiliation	Title	Reference
R.E. Morris et al	ENVIRON International Corporation	Development And Application Of An Advanced Air Toxics Hybrid Photochemical Grid Modeling System Paper # 69437	8
J. Cassmassi et al	South Coast Air Quality Management District	APPENDIX IX, MATES III DRAFT FINAL REPORT Regional Modeling Analyses	9
Assessment and Standards Division; Office of Transportation and Air Quality	U.S. Environmental Protection Agency	Regulatory Impact Analysis: Renewable Fuel Standard Program; Chapter 5 Air Quality Impacts EPA420-R-07-004 April 2007	10
S. Tanrikulu et al	Bay Area Air Quality Management District	Toxics Modeling to Support the Community Air Risk Evaluation (CARE) Program; June 2009	11
S. Tanrikulu et al	Bay Area Air Quality Management District	Fine Particulate Matter Data Analysis and Modeling in the Bay Area; October 2009	12

### Table 4.5-1 CAMx Evaluations in Simulating Air Toxics and Ozone

Generally air quality model evaluations include numerical comparisons between the simulated concentrations either at a specified receptor or within a grid and the measured concentrations from a monitoring site at the receptor or within the grid. For example, reference (9) on pp. 39 - 44 has five different tables of these comparisons, of which, just one table is given below as Table 4.5-2. In this table the measured and simulated annual average air toxics concentrations are given, along with a measure of their difference called "PA", which stands for prediction accuracy. PA in this table is defined as the absolute value of the

percentage difference between the measured and simulated values, with the measured value serving as the basis:

 $PA = absolute value \{([obs] - [sim])/[obs]\} \times 100\%.$ 

A prediction accuracy of 0 represents perfect agreement between the two values of measured and simulated concentrations. In this table the PAs range from 0 to 363%, or, in other words, from perfect agreement to one being 3.6 times more (or less) than the other. Closer examination reveals that the PAs reflect concentrations that have not been rounded off to the two decimal places shown in the table. Of the 80 simulated concentrations (4 sites for 20 species), 67 were within 100%.

**Table 4.5-2** CAMx Simulated Concentrations of Air Toxics Versus Measured Concentrations for Selected Sites in the MATES III Air Toxics Study of the South Coast Air Quality Management District (Table IX-6, first part, from (9)) (PA = prediction accuracy =absolute value of {([obs] – [pred])/[obs]}x 100%} Abbreviations: As, arsenic; TSP, total suspended particulates; 2.5, size fraction comprised of particles 2.5 microns and smaller; Cd, cadmium; Cr6, hexavalent chromium; EC10, elemental carbon 10 microns and smaller' EC2.5, Elemental carbon 2.5 microns and smaller' Ni, nickel; Pb, lead)

-													
Compound	Units		Anaheim			Burbank		(	Compton		Inlar	id Valley S	S.B.
		Obs	Model	PA	Obs	Model	PA	Obs	Model	PA	Obs	Model	PA
1,3Butadiene	ppb	0.09	0.09	9	0.15	0.07	56	0.19	0.15	19	0.07	0.07	11
Acetaldehyde	ppb	1.28	1.04	19	1.94	1.02	47	1.57	1.04	34	1.90	1.10	42
As (TSP)	ηg/m <sup>3</sup>	0.44	1.91	333	0.74	1.49	102	0.66	3.41	417	0.75	2.94	294
As (2.5)	ηg/m <sup>3</sup>	0.50	0.76	52	0.52	0.51	2	0.46	2.14	363	0.54	1.15	115
Benzene	ppb	0.44	0.50	15	0.71	0.47	34	0.80	0.57	29	0.49	0.44	11
Cd (TSP)	ηg/m <sup>3</sup>	1.58	0.59	63	1.49	0.38	74	1.42	0.98	31	1.67	1.32	21
Cd (2.5)	$\eta g/m^3$	1.63	0.32	80	1.30	0.21	84	1.70	0.71	58	1.73	0.87	50
Cr6 (TSP)	ηg/m <sup>3</sup>	0.16	0.17	2	0.18	0.11	35	0.31	0.19	38	0.20	0.41	104
EC10	$\mu g/m^3$	1.60	1.82	13	2.35	1.35	42	1.84	2.34	27	2.40	2.30	4
EC2.5	µg/m <sup>3</sup>	1.41	1.35	4	2.04	1.03	50	1.76	1.88	7	2.18	1.77	19
Formaldehyde	ppb	2.96	2.97	0	3.84	2.85	26	3.14	3.18	1	3.70	3.08	17
Methylene Chloride	ppb	0.24	0.36	54	0.34	0.27	20	0.29	0.39	33	0.18	0.18	2
Naphthalene	ppb												
Ni (TSP)	ηg/m <sup>3</sup>	3.93	3.13	20	3.75	2.05	45	6.02	7.97	32	3.72	11.87	219
Ni (2.5)	$\eta g/m^3$	4.31	1.71	60	3.72	1.12	70	4.50	5.87	30	3.50	7.89	126
Pb (TSP)	ηg/m <sup>3</sup>	3.06	8.80	188	3.12	5.49	76	3.06	8.14	166	3.11	12.71	308
Pb (2.5)	$\eta g/m^3$	3.57	1.96	45	4.66	1.17	75	5.84	2.40	59	8.67	6.16	29
p-Dichlorobenzene	ppb	0.03	0.09	174	0.04	0.07	95	0.07	0.11	62	0.03	0.05	96
Perchloroethylene	ppb	0.06	0.10	60	0.10	0.10	1	0.12	0.13	11	0.05	0.07	34
Trichloroethylene	ppb	0.03	0.03	17	0.05	0.02	53	0.03	0.06	87	0.03	0.04	44

2005 Station Observed and CAMx Simulated MATES III Annual Average Concentrations

#### 4.5.1 Particulate Air Toxics, Simulated Annual Averages Versus Measurements

Annual averages of particulate air toxics were generally under-estimated by the CAMx modeling system, and tended to be so by a wide margin. This under-estimation, prevalent at all sites and for most species, was not reported for the South Coast simulations, as shown in Table 4.5-2. Photochemistry plays a minor, negligible role in the ambient concentrations of most particulate species (organic carbon is the only important exception), which leaves uncertainties in the emissions inventory and, to a lesser extent, in the advection/transport mechanisms, to explain this more-or-less consistent difference. Table 4.5.1-1 presents first the annual average concentrations of five important particulate species, from the measurements and from the model simulations, as well as the number of samples (24-hour average concentrations) for each species. In the lowest panel the table gives the quantity (in percent) of the model prediction divided by the observation. Method detection levels (MDLs) come into play for the four elements, and their annual averages required statistical measures to compensate for the moderate to high percentages of reported non-detectable concentrations. In contrast, all measured elemental carbon (EC) concentrations were well above the MDL, eliminating this aspect of the analysis for this species. Why the modeling system could account for no more than 14% of the measured EC is discussed below.

The elemental carbon concentrations in Tables 4.5.1-1 and 4.5.1-2 have *not* been corrected for the roughly 20% difference between the two different analytical methods employed, as discussed in the section on diesel particulate matter (pages 71 - 72). Consequently, they are lower than the annual average concentrations presented in Table 5.6-1 on page 76. While this correction is critical for consistency among the JATAP sites and for consistency within historical trends, it became a moot point in the comparison of simulated versus measured EC concentrations because, as noted above and discussed below, the two sets of concentrations were so far apart anyway.

# **Table 4.5.1-1** Annual Fine Particulate Air Toxics Concentrations: Observations vs. the Model

Abbreviations:  $\mu$ g/m3, micrograms per cubic meter; n, number of 24-hour average observations; EC, elemental carbon; As, arsenic; Cd, cadmium; Ni, nickel; Mn, manganese – all in the fine fraction (0 – 2.5 microns)

	Concentrations in $\mu g/m^3$										
		Supersit	e		West Phoe	enix	VEI				
	n	obs	model	n	obs	model	n	obs	model		
EC	119	0.8856	0.0861	59	1.3178	0.0883	59	0.8731	0.1198		
As	118	0.0013	0.0006	59	0.0015	0.0003	59	0.0012	0.0008		
Cd	118	0.0064	0.0007	59	0.0056	0.0009	59	0.0073	0.0009		
Mn	118	0.0036	0.0005	58	0.0051	0.0009	59	0.0047	0.0008		
Ni	118	0.0012	0.0005	59	0.0014	0.0008	59	0.0011	0.0007		

	Concentrations in $\mu g/m^3$										
	Gil	a River St.	Johns	Salt River Senior Center							
	n	obs	model	n	obs	model					
EC	53	0.4134	0.0202	56	0.4906	0.0501					
As	52	0.0010	0.0003	56	0.0012	0.0002					
Cd	52	0.0065	0.0003	56	0.0067	0.0005					
Mn	52	0.0033	0.0008	56	0.0043	0.0005					
Ni	52	0.0009	0.0002	56	0.0011	0.0004					

	([model]/[obs]) x 100%										
	Supersite	West	VEI	Gila	Salt						
		Phoenix		River	River						
EC	9.7	6.7	13.7	4.9	10.2						
As	45.1	22.1	62.4	28.1	16.7						
Cd	11.4	16.8	12.5	5.0	8.2						
Mn	13.8	16.8	16.4	24.8	11.0						
Ni	41.1	52.8	59.5	25.7	32.4						

#### Table 4.5.1-2 Performance Statistics for Particulate Air Toxics

Abbreviations: SS – Supersite; WPHX - West Phoenix; VEI - Vehicle Emissions Inspection; GR-SJ - Gila River St. Johns; SR-SC - Salt River Senior Center; n, number of samples; PA, percentage agreement; MB, mean bias; MAE, mean absolute error; NMB, normalized mean bias; NME, normalized mean error; RMSE, root mean square error

Location         n         Observed         Predicted         PA         MB         MAE         NMB         NME         RM:           SS         119         0.8856         0.0861         90         0.7990         0.8010         0.9030         0.9040         0.23           WPHX         59         1.3178         0.0883         93         1.2290         1.2310         0.9330         0.9340         1.89           VEI         59         0.8731         0.1198         86         0.7530         0.7540         0.8630         0.8640         0.99           GR-SJ         53         0.4910         0.0170         95         0.3930         0.9510         0.50           SR-SC         56         0.4130         0.0070         90         0.4400         0.4400         0.8980         0.8980         0.05           Performance statistics for Arsenic [ng/m3]         Incation         n         Observed         Predicted         PA         MB         MAE         NMB         NME         RMS           SS         118         0.0013         0.0006         55         0.6445         0.8000         0.5088         0.6472         0.00           WPHX         59         0.0012							-									
SS         119         0.8856         0.0861         90         0.7990         0.8010         0.9030         0.9040         0.23           WPHX         59         1.3178         0.0883         93         1.2290         1.2310         0.9330         0.9340         1.89           VEI         59         0.8731         0.1198         86         0.7530         0.7540         0.8630         0.8640         0.99           GR-SJ         53         0.4910         0.0170         95         0.3930         0.9510         0.50           SR-SC         56         0.4130         0.0070         90         0.4400         0.4000         0.8980         0.8980         0.05           Performance statistics for Arsenic [ng/m3]         Ing/m3]         Incation         NME         RMS         0.6470         0.00           SS         118         0.0013         0.0006         55         0.6445         0.8000         0.5088         0.6316         0.00           WPHX         59         0.0012         0.0003         78         0.7003         0.7117         0.4595         0.4670         0.00           GR-SJ         52         0.0010         0.0002         83         0.5166	Location	n	Observed	Predicted	I PA	4	M	B	MA	E	NM	IB	NN	ſΕ	RM	SE
WPHX         59         1.3178         0.0883         93         1.2290         1.2310         0.9330         0.9340         1.89           VEI         59         0.8731         0.1198         86         0.7530         0.7540         0.8630         0.8640         0.99           GR-SJ         53         0.4910         0.0170         95         0.3930         0.3930         0.9510         0.9510         0.50           SR-SC         56         0.4130         0.0070         90         0.4400         0.8980         0.8980         0.05           Performance statistics for Arsenic [ng/m3]         Incoation         n         Observed         Predicted         PA         MB         MAE         NMB         NME         RMS           SS         118         0.0013         0.0006         55         0.6445         0.8000         0.5088         0.6316         0.00           WPHX         59         0.0015         0.0003         78         0.7013         0.7117         0.4595         0.4670         0.00           WPHX         59         0.0012         0.0008         38         0.4627         0.7970         0.3758         0.6472         0.00           GR-SJ	SS	119	0.8856	0.0861	. 9	0	0.799	-0	0.801	0	0.903	- 30	0.90	40	0.23	850
VEI         59         0.8731         0.1198         86         0.7530         0.7540         0.8630         0.8640         0.99           GR-SJ         53         0.4910         0.0170         95         0.3930         0.9510         0.9510         0.50           SR-SC         56         0.4130         0.0070         90         0.4400         0.4400         0.8980         0.8980         0.050           Performance statistics for Arsenic [ng/m3]         Image: Construct the image	WPHX	59	1.3178	0.0883	<b>3</b> 9:	3	1.229	0	1.231	.0	0.933	- 30	0.93	40	1.89	000
GR-SJ       53 $0.4910$ $0.0170$ 95 $0.3930$ $0.3930$ $0.9510$ $0.9510$ $0.50$ SR-SC       56 $0.4130$ $0.0070$ 90 $0.4400$ $0.4400$ $0.8980$ $0.8980$ $0.050$ Performance statistics for Arsenic [ng/m3]       Image: Constraint of the image: Constraint of	VEI	59	0.8731	0.1198	8 8	6	0.753	0	0.754	0	0.863	- 30	0.86	40	0.99	000
SR-SC       56 $0.4130$ $0.0070$ 90 $0.4400$ $0.4400$ $0.8980$ $0.8980$ $0.059$ Performance statistics for Arsenic [ng/m3]       Image: constraint of the statistics of	GR-SJ	53	0.4910	0.0170	) 9	5	0.393	0	0.393	30	0.95	- 10	0.95	10	0.50	)10
Performance statistics for Arsenic [ng/m3]           Location         n         Observed         Predicted         PA         MB         MAE         NMB         NME         RM:           SS         118         0.0013         0.0006         55         0.6445         0.8000         0.5088         0.6316         0.00           WPHX         59         0.0015         0.0003         78         0.7003         0.7117         0.4595         0.4670         0.00           VEI         59         0.0012         0.0008         38         0.4627         0.7970         0.3758         0.6472         0.00           GR-SJ         52         0.0010         0.0003         72         0.7412         0.8083         0.7190         0.7842         0.00           SR-SC         56         0.0012         0.0002         83         0.5166         0.5393         0.4485         0.4681         0.00           Performance statistics for Cadmium [ng/m3]         Location         n         Observed         Predicted         PA         MB         MAE         NMB         NME         RMSE           SS         118         6.3608         0.7239         89         5.6370         5.6543         0.8862 </td <td>SR-SC</td> <td>56</td> <td>0.4130</td> <td>0.0070</td> <td>) 9</td> <td>0</td> <td>0.440</td> <td>-0</td> <td>0.440</td> <td>00</td> <td>0.898</td> <td>- 80</td> <td>0.89</td> <td>80</td> <td>0.05</td> <td>520</td>	SR-SC	56	0.4130	0.0070	) 9	0	0.440	-0	0.440	00	0.898	- 80	0.89	80	0.05	520
LocationnObservedPredictedPAMBMAENMBNMERM:SS1180.00130.0006550.64450.80000.50880.63160.00WPHX590.00150.0003780.70030.71170.45950.46700.00VEI590.00120.0008380.46270.79700.37580.64720.00GR-SJ520.00100.0003720.74120.80830.71900.78420.00SR-SC560.00120.0002830.51660.53930.44850.46810.00Performance statistics for Cadmium [ng/m3]LocationnObservedPredictedPAMBMAENMBNMERMSESS1186.36080.7239895.63705.65430.88620.88890.0066WPHX595.58760.9363831.58291.58290.28330.28330.0033VEI597.34220.9144882.25022.25020.30650.30650.0050GR-SJ526.51440.3287956.18576.18570.94950.94950.0076	Performanc	e statis	tics for Arse	nic [ng/m3	1											
SS       118       0.0013       0.0006       55       0.6445       0.8000       0.5088       0.6316       0.00         WPHX       59       0.0015       0.0003       78       0.7003       0.7117       0.4595       0.4670       0.00         VEI       59       0.0012       0.0008       38       0.4627       0.7970       0.3758       0.6472       0.00         GR-SJ       52       0.0010       0.0003       72       0.7412       0.8083       0.7190       0.7842       0.00         SR-SC       56       0.0012       0.0002       83       0.5166       0.5393       0.4485       0.4681       0.00         Performance statistics for Cadmium [ng/m3]       Incation       n       Observed       Predicted       PA       MB       MAE       NMB       NME       RMSE         SS       118       6.3608       0.7239       89       5.6370       5.6543       0.8862       0.8889       0.0066         WPHX       59       5.5876       0.9363       83       1.5829       1.5829       0.2833       0.2833       0.0033         VEI       59       7.3422       0.9144       88       2.2502       2.2502	Location	n	Observed	Predicted	I PA	4	M	В	MA	E	NM	B	NN	Æ	RM	SE
WPHX         59         0.0015         0.0003         78         0.7003         0.7117         0.4595         0.4670         0.00           VEI         59         0.0012         0.0008         38         0.4627         0.7970         0.3758         0.6472         0.00           GR-SJ         52         0.0010         0.0003         72         0.7412         0.8083         0.7190         0.7842         0.00           SR-SC         56         0.0012         0.0002         83         0.5166         0.5393         0.4485         0.4681         0.00           Performance statistics for Cadmium [ng/m3]         Ing/m3]         Indextore         Inde	SS	118	0.0013	0.0006	5 5	5	0.644	-5	0.800	00	0.508	- 88	0.63	16	0.00	)12
VEI         59         0.0012         0.0008         38         0.4627         0.7970         0.3758         0.6472         0.00           GR-SJ         52         0.0010         0.0003         72         0.7412         0.8083         0.7190         0.7842         0.00           SR-SC         56         0.0012         0.0002         83         0.5166         0.5393         0.4485         0.4681         0.00           Performance statistics for Cadmium [ng/m3]         Icoation         n         Observed         Predicted         PA         MB         MAE         NME         RMSE           SS         118         6.3608         0.7239         89         5.6370         5.6543         0.8862         0.8889         0.0066           WPHX         59         5.5876         0.9363         83         1.5829         1.5829         0.2833         0.2833         0.0033           VEI         59         7.3422         0.9144         88         2.2502         2.2502         0.3065         0.0076           GR-SJ         52         6.5144         0.3287         95         6.1857         6.1857         0.9495         0.9495         0.0076	WPHX	59	0.0015	0.0003	3 7	8	0.700	- 13	0.711	7	0.459	- 95	0.46	70	0.00	)12
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	VEI	59	0.0012	0.0008	3 3	8	0.462	7	0.797	0'0	0.375	58	0.64	72	0.00	)11
SR-SC       56       0.0012       0.0002       83       0.5166       0.5393       0.4485       0.4681       0.00         Performance statistics for Cadmium [ng/m3]         Location       n       Observed       Predicted       PA       MB       MAE       NMB       NME       RMSE         SS       118       6.3608       0.7239       89       5.6370       5.6543       0.8862       0.8889       0.0066         WPHX       59       5.5876       0.9363       83       1.5829       1.5829       0.2833       0.2833       0.0033         VEI       59       7.3422       0.9144       88       2.2502       2.2502       0.3065       0.3065       0.0076         GR-SJ       52       6.5144       0.3287       95       6.1857       6.1857       0.9495       0.9495       0.0076	GR-SJ	52	0.0010	0.0003	3 7	2	0.741	2	0.808	33	0.719	- 90	0.78	42	0.00	)11
Performance statistics for Cadmium [ng/m3]           Location         n         Observed         Predicted         PA         MB         MAE         NMB         NME         RMSE           SS         118         6.3608         0.7239         89         5.6370         5.6543         0.8862         0.8889         0.0066           WPHX         59         5.5876         0.9363         83         1.5829         1.5829         0.2833         0.2833         0.0033           VEI         59         7.3422         0.9144         88         2.2502         2.2502         0.3065         0.3065         0.0050           GR-SJ         52         6.5144         0.3287         95         6.1857         6.1857         0.9495         0.9495         0.0076	SR-SC	56	0.0012	0.0002	2 8	3	0.516	-	0.539	93	0.448	- 85	0.46	81	0.00	)09
Location         n         Observed         Predicted         PA         MB         MAE         NMB         NME         RMSE           SS         118         6.3608         0.7239         89         5.6370         5.6543         0.8862         0.8889         0.0066           WPHX         59         5.5876         0.9363         83         1.5829         1.5829         0.2833         0.2833         0.0033           VEI         59         7.3422         0.9144         88         2.2502         2.2502         0.3065         0.3065         0.0050           GR-SJ         52         6.5144         0.3287         95         6.1857         6.1857         0.9495         0.9495         0.0076	Performanc	e statis	tics for Cadr	nium [ng/n	13]											
SS       118       6.3608       0.7239       89       5.6370       5.6543       0.8862       0.8889       0.0066         WPHX       59       5.5876       0.9363       83       1.5829       1.5829       0.2833       0.2833       0.0033         VEI       59       7.3422       0.9144       88       2.2502       2.2502       0.3065       0.3065       0.0050         GR-SJ       52       6.5144       0.3287       95       6.1857       6.1857       0.9495       0.9495       0.0076	Location	n	Observed	Predicted	PA		MB		MAE	]	NMB	l	NME	RI	MSE	
WPHX         59         5.5876         0.9363         83         1.5829         1.5829         0.2833         0.2833         0.0033           VEI         59         7.3422         0.9144         88         2.2502         2.2502         0.3065         0.3065         0.0050           GR-SJ         52         6.5144         0.3287         95         6.1857         6.1857         0.9495         0.9495         0.0076	SS	118	6.3608	0.7239	89	5	- 5.6370	5	5.6543	0.	- 8862	0.	8889	0.0	)066	
VEI         59         7.3422         0.9144         88         2.2502         2.2502         0.3065         0.3065         0.0050           GR-SJ         52         6.5144         0.3287         95         6.1857         6.1857         0.9495         0.9495         0.0076	WPHX	59	5.5876	0.9363	83	1	- 1.5829	1	.5829	0.	- 2833	0.	2833	0.0	)033	
GR-SJ         52         6.5144         0.3287         95         6.1857         6.1857         0.9495         0.9495         0.0076           -	VEI	59	7.3422	0.9144	88	2	- 2.2502	2	2.2502	0.	- 3065	0.	3065	0.0	)050	
	GR-SJ	52	6.5144	0.3287	95	6	- 5.1857	6	5.1857	0.	- 9495	0.	9495	0.0	)076	
SR-SC         56         6.7275         0.5491         92         2.0759         2.0930         0.3086         0.3111         0.0039	SR-SC	56	6.7275	0.5491	92	2	- 2.0759	2	2.0930	0.	3086	0.	3111	0.0	)039	

Performance statistics for Elemental Carbon [µg/m<sup>3</sup>]

Location	n	Observed	Predicted	PA	MB	MAE	NMB	NME	RMSE
66	110	2 (172	0.5000	96	-	2 0017	-	0.0200	0.0040
	118	3.01/3	0.5006	80	2.9005	3.0017	0.8201	0.8298	0.0040
WPHX	59	5.1383	0.8618	83	- 4.2765	4.1129	0.8323	0.8004	0.0069
VEI	59	4.7154	0.7733	84	- 3.9422	3.9801	- 0.8360	0.8441	0.0058
					-		-		
GR-SJ	52	3.2577	0.8075	75	2.4502	2.5018	0.7521	0.7680	0.0034
					-		-		
SR-SC	56	4.3345	0.4778	89	3.8567	3.8567	0.8898	0.8898	0.0049
Performance	ce statist	ics for Nicl	kel [ng/m3]						
Location	n	Observed	Predicted	PA	MB	MAE	NMB	NME	RMSE
C C	110	1 2005	0 4070	50	-	0.9141	-	0 6721	0.0014
	110	1.2093	0.4970	39	0.7123	0.8141	0.3891	0.0751	0.0014
WPHX	59	1.4324	0.7559	47	- 0.6765	0.8420	0.4723	0.5878	0.0016
					-		-		
VEI	59	1.1280	0.6716	40	0.4563	0.6955	0.4046	0.6166	0.0012
CD GI	50	0.0.000	0 0007	74	-	0 7170	-	0.0252	0.0010
GR-SJ	52	0.8688	0.2237	74	0.6452	0.7170	0.7426	0.8253	0.0013
SR-SC	56	1.1157	0.3613	68	- 0.7544	0.2712	- 0.6761	0.2431	0.0006

Performance statistics for Manganese [ng/m3]

In statistics, the bias (or bias function) of an estimator is the difference between this estimator's expected value  $f_i$  and the true value  $y_i$  of the parameter being estimated. The **mean bias (MB)** is

$$MB = \frac{1}{N} \sum_{i=1}^{N} (f_i - y_i)$$

The **mean absolute error (MAE)** is a quantity used to measure how close forecasts or predictions are to the eventual outcomes. The mean absolute error (MAE) is given by

$$MAE = \frac{1}{N} \sum_{i=1}^{N} \left| f_i - y_i \right|$$

As the name suggests, the mean absolute error is an average of the absolute errors  $e_i = f_i - y_i$ , where  $f_i$  is the prediction and  $y_i$  the true value.

**Normalized mean bias (NMB)** is used as a normalization to facilitate a range of concentration magnitudes. This statistic averages the difference (model - observed) over the sum of observed values. NMB is a useful model performance indicator because it avoids over inflating the observed range of values, especially at low concentrations. Normalized mean bias is defined as:

$$NMB = \frac{\sum_{i=1}^{N} (f_i - y_i)}{\sum_{i=1}^{N} y_i}.100\%$$

**Normalized mean error (NME)** is also similar to NMB, where the performance statistic is used as a normalization of the mean error. NME calculates the absolute value of the difference (model - observed) over the sum of observed values. Normalized mean error is defined as:

$$NME = \frac{\sum_{i=1}^{N} |f_i - y_i|}{\sum_{i=1}^{N} y_i}.100\%$$

**The root mean square error (RMSE)** is a frequently-used measure of the differences between values predicted by a model or an estimator and the values actually observed from the thing being modeled or estimated. RMSE is a good measure of precision. The RMSE is more sensitive than other measures to the *occasional large error*: the squaring process gives disproportionate weight to very large errors.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N} (f_i - y_i)^2}{N}}$$

Of these five particulate species by far the most important is elemental carbon because it serves as a surrogate for diesel particulate matter (DPM), which by itself accounts for most of the human health effects. Maricopa County's 2008 periodic PM emissions inventory, coupled with a 1995 PM<sub>2.5</sub> emissions inventory that includes both elemental and organic carbon as separate species, provides an independent review of the elemental carbon total in the 2005 air toxics inventory of the present work. The 1995 emissions inventory, included in this report as Table 5.4-1, was built by staff of the Air Quality Division of the Arizona Department of Environmental Quality (P. Hyde, unpublished paper, 2004). The percentage of PM<sub>2.5</sub> that is elemental carbon in this inventory is 14%. Applying this percentage to the PM<sub>2.5</sub> total in the 2008 Maricopa County inventory yields a total for elemental carbon of about 3,500 tons per year, similar to the 1995 total of about 2,900 tons. Likewise, the reported 2005 air toxics inventory (see (3), p. 31) has a DPM total of 2495 tons per year, equivalent to 2772 tons per year of EC (90% of EC emissions can be attributed to diesel exhaust), with 1605 tons in the non-road sector and 889 tons in the on-road sector. In general diesel exhaust in national and urban settings comes more from the non-road emission sector than the on-road, with important non-road contributions from construction equipment, railroads, and, above all, heavy, diesel-fueled vehicles used in earthmoving. Examination of the electronic emissions files that were input to CAMx in the present work reveals that the non-road DPM emissions were actually zero. Thus, only the on-road DPM emissions (36% of the total) went into the model. Perhaps some of the under-estimates of the EC

concentrations by the CAMx modeling system in the present work are the result of an emissions inventory that itself accounts for but 36% of the DPM emissions (Table 4.5.1-3).

		То	ns per year		Fraction
			2005 AT		
	2008 MC	1995 EI	reported	actual	Actual/reported
<b>PM</b> <sub>10</sub>	187,850				
PM <sub>2.5</sub>	25,758	20,931			
NOx	91,702				
EC	3,575	2,905	2,495	889	36%

Table 4.5.1-3	Widely Varying Emission Estimates of Elemental Carbon in the Air Toxics
(AT) Inventory	y and in the Maricopa County (MC) Inventory

While similar emissions comparisons for the four elements (arsenic, cadmium, nickel, and manganese) are not readily available, one could reasonably at least suspect that similar systematic under-estimates may plague the air toxics inventory for these species.

#### 4.5.2 Gaseous air toxics simulated annual averages versus measurements

Simulations with the CAMx modeling system for gaseous air toxics, as was the case for the particulate species, generally under-estimated the measured concentrations, although the degree of under-estimation was less, at least for some species. For example, for the compounds of benzene and 1,3-butadiene, both of which have demonstrable health effects at their 2005 Phoenix concentrations, the model produced annual average concentrations that ranged from about 50% below to about 2% above the measured values. Chloroform was under-estimated at all five sites, from about 70 to 80% below the measured values. Simulated trichloroethene estimates were low by 95%. Acetaldehyde simulations accounted for about half of the measured values; formaldehyde simulations were lower still, from 80 to 90% below the measured annual average values. As is the case with the simulated particulate species concentrations, this systematic under-estimation was not encountered in the South Coast air toxics modeling work (see Table 4.5-2). These widespread under-estimations are shown in Table 4.5.2-1, whose lowest panel has the modeled value divided by the observed, expressed as a percent. Subtracting these percentages from 100% gives the degree of underestimation presented in the narrative immediately above (for example, if the quotient of the model divided by the observation, expressed as a percent, is about five percent, which it is for trichloroethylene, then this compound is being under-estimated by about 95%).

Reasons for these under-estimates likely vary from compound to compound. For formaldehyde and acetaldehyde, whose ambient concentrations result from both primary emissions and from photochemically produced ones, the under-estimates may be the result of either insufficiently active photochemistry or under-estimates of the primary emissions. For those gaseous compounds that are photochemically unreactive, and which arise solely from primary emissions, e.g. chloroform and trichloroethene, the wide underestimates would appear to be a consequence of their being under-estimated in the emissions inventory. As with the case of the elemental particulate species, calculating annual average measured concentrations of some of these gaseous compounds can be difficult whenever these data have one or the other of the following two aspects:

- 1. too many samples are reported by the laboratories as below the method detection level (MDL); or
- 2. the average is dominated by a single high value.

The case of trichlorethene at West Phoenix serves as an example. Its measured annual average can be calculated in at least three ways: first, by setting all nondetects to zero (0.043 ppbV); second, by setting them to one half of the MDL (0.073 ppbV); and third, by setting them to zero and eliminating the maximum value of 2.127 ppbV (0.007 ppbV). This compound was reported as below the MDL in 85% of the 60 samples analyzed. Of the nine values reported above the MDL, eight were below 0.1 ppbV, but the ninth was the annual maximum of 2.127, more than 20 times higher than any of the other samples. Let's suppose that this maximum actually did occur, and it certainly could have through a sudden, nearby release. No emissions inventory could ever account for this one-time (on one day) release. As a closing note, it may not be ironic that the annual simulated average for trichloroethene at this site is 0.007 ppbV, the same as the third scenario above.

**Table 4.5.2-1** Annual Average Gaseous Air Toxics Concentrations in ppbV:
 Observations

 vs Model Simulations
 Vs
 Vs</t

	WPHX SPHX						SS		
	n	obs	model	n	obs	model	n	obs	model
1,3-butadiene	60	0.1847	0.1629	60	0.2579	0.1785	55	0.2073	0.1343
Benzene	55	0.9326	0.5618	56	0.7848	0.5480	53	0.7172	0.4682
Chloroform				62	0.0666	0.0166	55	0.1167	0.0332
Acetaldehyde				52	1.6946	0.7128	50	1.5696	0.9746
Formaldehyde				52	3.3099	0.6467	46	4.4391	0.4688
Trichloroethene				60	0.0392	0.0035	46	0.0369	0.0013

Abbreviations: SS – Supersite; WPHX - West Phoenix; VEI - Vehicle Emissions Inspection; GR-SJ - Gila River St. Johns; SR-SC - Salt River Senior Center; n, number of samples.

	GR SR-SC GF					GR-SJ			
	n	obs	model	n	obs	model	n	obs	model
1,3-butadiene	58	0.2747	0.1715	60	0.0687	0.0697	53	0.0592	0.0381
Benzene	58	0.8471	0.6474	60	0.5044	0.2807	53	0.1865	0.1506
Chloroform	57	0.0660	0.0218	60	0.0711	0.0120	53	0.0207	0.0051
Acetaldehyde	47	5.4666	1.0216						
Formaldehyde	60	9.4827	0.7090						
Trichloroethene	52	0.0484	0.0015				53	0.0330	0.0009

			([model]/[o	obs]) x 100%					
	WPHX SPHX SS GR SR-SC								
1,3-butadiene	88.2	69.2	64.8	62.4	101.5	64.3			
Benzene	60.2	69.8	65.3	76.4	55.7	80.8			
Chloroform		25.0	28.4	33.1	16.8	24.7			
Acetaldehyde		42.1	62.1	18.7					
Formaldehyde		19.5	10.6	7.5					
Trichloroethene		8.8	3.5	3.0		2.9			

#### Table 4.5.2-2 Performance Statistics for Gaseous Toxics

Abbreviations: SS – Supersite; WPHX - West Phoenix; VEI - Vehicle Emissions Inspection; GR-SJ - Gila River St. Johns; SR-SC - Salt River Senior Center; n, number of samples; PA, percentage agreement; MB, mean bias; MAE, mean absolute error; NMB, normalized mean bias; NME, normalized mean error; RMSE, root mean square error

Site	n	Observed	Predicted	PA	MB	MAE	NMB	NME	RMSE
SS	55	0.2073	0.1343	35	-0.0730	0.0999	-0.3521	0.4817	0.1535
SPHX	60	0.2579	0.1785	31	0.0147	0.2296	0.0570	0.8901	0.3336
WPHX	60	0.1847	0.1629	12	-0.0217	0.0898	-0.1176	0.4866	0.1336
GR	58	0.2747	0.1715	38	-0.1032	0.1172	-0.3758	0.4268	0.1678
SR-SC	60	0.0687	0.0697	1	-0.0031	0.0132	-0.0454	0.1922	0.0316
GR-SJ	53	0.0592	0.0381	36	-0.0212	0.0370	-0.3572	0.6248	0.0611

Performance statistics for 1,3-butadiene [ppbV]

Performance statistics for benzene [ppbV]

Site	n	Observed	Predicted	PA	MB	MAE	NMB	NME	RMSE
SS	53	0.7172	0.4682	35	-0.2490	0.3189	-0.3471	0.4446	0.4461
SPHX	56	0.7848	0.5480	30	-0.6627	0.8229	-0.8444	1.0486	2.4541
WPHX	55	0.9326	0.5618	40	-0.3708	0.5124	-0.3976	0.5494	0.7561
GR	58	0.8471	0.6474	19	-0.1998	0.2873	-0.2358	0.3392	0.4108
SR-SC	60	0.5044	0.2807	24	-0.2237	0.4165	-0.4435	0.8258	1.2090
GR-SJ	53	0.1865	0.1506	44	-0.0359	0.1290	-0.1923	0.6919	0.1609

### Performance statistics for chloroform [ppbV]

Site	n	Observed	Predicted	PA	MB	MAE	NMB	NME	RMSE
SS	55	0.1167	0.0332	72	-0.0835	0.0836	-0.7155	0.7169	0.1079
SPHX	62	0.0666	0.0166	75	-0.0525	0.0539	-0.7501	0.7710	0.1333
WPHX									
GR	57	0.0660	0.0218	75	-0.0441	0.0443	-0.6693	0.6721	0.0528
SR-SC	60	0.0711	0.0120	67	-0.0591	0.0584	-0.8318	0.8222	0.0713
GR-SJ	53	0.0207	0.0051	83	-0.0156	0.0089	-0.7533	0.4302	0.0163

Performance statistics for acetaldehyde [ppbV]

Site	n	Observed	Predicted	PA	MB	MAE	NMB	NME	RMSE
SS	50	1.5696	0.9746	38	-0.6115	0.8363	-0.3896	0.5328	1.0492
SPHX	52	1.6946	0.7128	58	-0.9818	1.1170	-0.5794	0.6591	1.5757
WPHX									
GR	47	5.4666	1.0216	81	-4.4450	4.4675	-0.8131	0.8172	5.4921
SR-SC									
GR-SJ									

Site	n	Observed	Predicted	PA	MB	MAE	NMB	NME	RMSE
SS	46	4.4391	0.4688	89	-3.9703	3.9703	-0.8944	0.8944	4.1354
SPHX	52	3.3099	0.6467	80	-5.9729	5.9729	-1.8045	1.8045	23.8639
WPHX									
GR	60	9.4827	0.7090	93	-8.7737	8.8129	-0.9252	0.9294	10.0632
SR-SC									
GR-SJ									

Performance statistics for formaldehyde [ppbV]

Performance statistics for trichloroethene [ppbV]

Site	n	Observed	Predicted	PA	MB	MAE	NMB	NME	RMSE
SS	46	0.0369	0.0013	97	-0.0356	0.0356	-0.9652	0.9652	0.0395
SPHX	60	0.0392	0.0035	91	-0.0358	0.0361	-0.9130	0.9205	0.0822
WPHX									
GR	52	0.0484	0.0015	97	-0.0469	0.0470	-0.9696	0.9701	0.0516
SR-SC									
GR-SJ	53	0.0330	0.0009	97	-0.0321	0.0321	-0.9714	0.9714	0.0448

At this point, a comparison of emissions inventories is in order. If the air toxics emission inventory totals for the two gaseous pollutant groups of volatile organic compounds (VOC) and nitrogen oxides (NOx) and the gaseous compound carbon monoxide are consistent with the 2005 Maricopa County Periodic ozone precursor inventory; then, at least for the gaseous air toxics, we have considerable confidence in the air toxics totals. In fact, even though the geographical areas covered in the two inventories differ somewhat, their emissions are dominated by the heart of metropolitan Phoenix. The air toxics inventory includes a portion of Pinal County, north of Casa Grande, which is excluded from the Maricopa County inventory; while the latter inventory includes some territory in its southwestern corner omitted from the former. Nonetheless, the two cover similar areas. As Table 4.5.2-3 demonstrates, the two inventories do differ in their totals, with the air toxics version having about 40% of the emissions in the Maricopa County inventory. This difference may account for some of the under-estimates of ambient gaseous air toxics concentrations by the CAMx modeling system.

**Table 4.5.2-3** Comparison of the Air Toxics (AT) and Maricopa County (MC) EmissionInventories for Ozone Precursors and Carbon Monoxide

	Tons pe	Fraction	
pollutant	MC	AT	AT/MC
VOC	263,549	101,105	0.38
NOx	125,699	45,990	0.37
CO	1,319,397	536,915	0.41

In any case, these simulated concentrations would still prove useful in any metropolitan-wide risk assessment, for they could be easily increased on a compound-by-compound basis to reach closer agreement with the measured concentrations. What is not uncertain are the measured concentrations of air toxics, and their consequent health effects. These concentrations and their health effects are necessarily limited to the immediate neighborhoods of the air monitoring sites and are discussed in the following section.

# 5.0 Human Health Risk, Based on Measurements Only

## 5.1 Monitoring Sites

In preparation for the year-long air toxics monitoring field campaign in 2005, Joint Air Toxic Assessment Project (JATAP) staff realized the need to quantify particulate, as well as gaseous, air toxics. In balancing the project resources with the number of sites and types of air pollutant information to collect, the consensus was to conduct particulate matter (PM) monitoring at four JATAP sites, to utilize the ongoing PM measurements at the Arizona Department of Environmental Quality's (ADEQ) Supersite, and, as a background site, to use ambient concentrations from the Interagency Monitoring of Protected Visual Environments (IMPROVE) site at the Tonto National Monument. All of this speciated PM monitoring was limited to the fine fraction of airborne particulates, namely, particles 2.5 microns and smaller, termed " $PM_{2.5}$ ". The various sites, chosen mostly to match those with gaseous air toxics measurements, included three central Phoenix sites, the ADEQ Supersite, two tribal sites, and the background sites. Monitoring for gaseous air toxics took place at two additional urban sites and at the background site of Queen Valley (Table 5.1-1 and Figure 5.1-1). Of the five central city sites four can generally be characterized as "neighborhood", although the Vehicle Emissions Inspection (VEI) site, with neighborhoods to its immediate east, is on a large parcel of mostly vacant land, with the 202 freeway (179,000 vehicles per day) 550 meters north and with 40<sup>th</sup> Street (14,000 vpd) 100 m east of the actual monitoring site. Supersite, West Phoenix, and South Phoenix, on the other hand, lie in the centers of established neighborhoods and are at considerably greater distances from major roads. While subject to vehicular emissions from freeways, arterials, and local streets, none of these four sites has heavy "industrial" emissions close by. The West Phoenix site is situated closest to such stationary source emissions, with a number of light industrial, commercial, and warehousing facilities, but also including the Union Pacific railroad tracks, along Grand Avenue, at distances from one half to two or more miles from the site.

The odd man out in the central city sites is Greenwood. This monitoring site is considered a freeway corridor site, because it lies just 120 meters south of Interstate 10 (250,000 vpd) and five meters from 27<sup>th</sup> Avenue (18,000 vpd). Only gaseous species were measured here in JATAP.

On the Indian community lands, the Salt River Pima Maricopa Indian Community's Senior Center site is in the southwest part of the community, immediately east of densely developed Scottsdale; the monitoring site lies 2,100 meters east of the N.S. Loop 101 freeway (165,000); 2,200 m NW of the Beeline Highway (19,000); and 3,400 m NW of the 202 freeway (113,000). Most of this tribal land is agricultural, with scattered single-family homes mixed in. These tribal lands are east of the bulk of the Phoenix metropolitan area; and because of prevailing winds from the west and southwest in the daytime, are downwind of most daytime metropolitan emissions.

The Gila River St. John's site is on the south-central perimeter of greater Phoenix and is situated close to the confluence of the Salt and Gila Rivers. From this site the South Mountains lie to the northeast and the Estrella Mountains are south and west. Part of the interest in this site stemmed from potential urban transport, in spite of its southward

displacement from the principal west-east axis of urban emissions and daytime wind patterns. In contrast to the Salt River Senior Center, the Gila River St. John's site is better insulated from nearby traffic: 51<sup>st</sup> Avenue, 850 m to the west, carries 15,000 vpd, while the nearest freeway is I-10, 13.5 km to the east, which carries 102,000 vpd. Land use in the vicinity of the site is mostly open Sonoran desert, the riparian canopy of the Salt and Gila River bottoms, and single-family residential.

Finally, two background sites were used in the JATAP monitoring: Tonto National Monument for particulates and Queen Valley for gaseous species. The former lies 57 miles east-northeast (ENE) of the heart of the central city; about 25 miles ENE or NE of the eastern-most developed parts of metropolitan Phoenix; and decidedly downwind in the daytime from the entire Phoenix metropolitan area. The latter lies an equal distance from central Phoenix, although to the east-southeast; Queen Valley is 25 miles SSE of Tonto. Although this location jeopardizes the purity of its "background" designation, investigators have demonstrated through specialized ambient monitoring at Tonto and through trajectory analyses that while metropolitan Phoenix emissions are transported to the site, their overall influence is dampened by transport from both El Paso, Texas and Tucson, Arizona, as well as from numerous prescribed fires and wildfires in the surrounding national forests (13, 14). In any case, a suitable background site west or northwest of Phoenix is not reached until Sycamore Canyon or the Grand Canyon, 110 miles north and 175 miles north-northwest of the city, respectively.

Name	Abbre- viation	G or PM*	Address	Major Cross Streets	Agency**	Remarks
Greenwood	GR	G	957 N. 27 <sup>th</sup> Ave.	I-10/27 <sup>th</sup> Ave ADEQ		Central city (CC <sup>1</sup> ), freeway corridor
West Phoenix	WPXH	G, PM	3847 W. Earll Dr., Phoenix	Thomas/ Rd.39 <sup>th</sup> Ave.	ADEQ	CC, neighborhood
Vehicle Emissions Inspection	VEI	PM	600 N. 40 <sup>th</sup> St., Phoenix	McDowell Rd/.40 <sup>th</sup> Street	ADEQ	CC, near 202 freeway
South Phoenix	SP	G	53 W. Tamerisk, Phoenix	Broadway Rd. Central Ave.	ADEQ	CC, neighborhood
Supersite	SS	G, PM	4530 N. 17thAve., Phoenix	Camelback Rd./15 <sup>th</sup> Ave.	ADEQ	CC, neighborhood
Salt River Senior Center	SR-SC	G, PM	10,005 E. Osborn Rd., Scottsdale	Osborne Rd./Alma School Rd.	SRPMIC <sup>2</sup>	Urban perimeter (east), agricultural
Gila River St. Johns	GR-SJ	G, PM	4208 W. Pecos Rd., Laveen	Pecos Rd. alignment/51 <sup>st</sup> Ave.	GRIC <sup>3</sup>	Urban perimeter (south-central), village, desert
Queen Valley	QV	G	10 S. Queen Anne Dr.,Queen V. Valley	N of SR 60/ 30 mi E of Apache Jct.	PCAQCD <sup>4</sup>	Background, 57 mi ESE of CC
Tonto National Monument	TON	PM	None	SR 88/turn- off to monument	National Park Service	Background, 57 mi ENE of CC

<b>Table 5.1-1</b>	JATAP	2005	Monitoring	Sites
1 ant 5.1-1	J/ 1 I / 11	2005	Montoring	DICO

\* G and PM mean measurements of gaseous (G) and/or particulate (PM) air toxics were made.

\*\*Agency: Except GR, WPHX, SP, and QV staff operating the samplers were from the agency in charge of the site. GR, WPHX, and SP are permanent Maricopa County Air Quality Department sites made available to ADEQ staff for JATAP. QV, a permanent Pinal County site, was likewise made available to ADEQ staff.

- 1. CC has two meanings: either the intersection of Van Buren Street, 7<sup>th</sup> Avenue, and Grand Avenue in downtown Phoenix, for distances to the background sites, or "central city", for the monitoring sites in the urban core.
- 2. SRPMIC: Salt River Pima Maricopa Indian Community
- 3. GRIC: Gila River Indian Community
- 4. Pinal County Air Quality Control District



**Figure 5.1-1** JATAP Monitoring Sites: Arrowed Sites Have PM, Colored Sites have Gaseous Measurements

## 5.2 Sampling and Analysis

Gaseous and particulate air toxics sampling was conducted every sixth day in 2005, with midnight-to-midnight, 24-hour, integrated samples at most sites (Exceptions were (1) two 12-hour samples were taken at the Gila River St. John's site on alternate sampling days for gaseous analysis; (2) Queen Valley gaseous samples were taken every 12<sup>th</sup> day; and (3) speciated particulates were taken every third day at the Phoenix Supersite and at Tonto National Monument). The samples collected were then analyzed for various air toxics species by analytical chemistry laboratories. For gaseous species the samplers were of two kinds: stainless steel canisters and dinitro-phenyl hydrazine (DNPH) cartridges. Canister samples were used to collect a variety of hydrocarbons and halocarbon compounds; these canisters were analyzed by Environmental Analytical Services, Inc. (San Luis Obispo, CA) or the San Diego Air Pollution Control District, depending on the site. A subset of canister samples was also analyzed by the EPA Region 9 laboratory for quality assurance (QA) purposes. Cartridges were used to collect a set of oxygenated hydrocarbons known as carbonyl compounds (e.g., formaldehyde and acetaldehyde) at South Phoenix, JLG Supersite, and Greenwood.

For particulates, the sampler was the MetOne SASS for the "urban" sites and the "IMPROVE" sampling system for Tonto National Monument, but with two samplers in place at each urban site to collect PM on both Teflon and quartz filters, the former for elemental

analysis by X-ray fluorescence (XRF) spectroscopy; the latter, for carbon and ion analysis by various analytical methods. The chemical analyses for all samples except at the IMPROVE sites were conducted by the Eastern Research Group, Inc's Austin, Texas laboratory, an EPA contract laboratory. IMPROVE samples were analyzed by the Crocker National Laboratory in Davis, California. At the Phoenix Supersite and at the IMPROVE site of Tonto National Monument, sampling took place every third day, again with 24-hour samples. As with many environmental analyses, method detection levels (MDLs) in this project assumed a pivotal role in determining the actual annual average concentrations of several toxic metals in the PM. For several air toxic species the detection levels provided by the various laboratories were generally too high to quantify the fairly low concentrations. Therefore, MDLs for both the urban and background toxic species resulted in high percentages of non-detects for some, requiring that their annual concentrations be reported as a range. A better alternative would have been to calculate these averages as proscribed in (15) and discussed in Appendix B, but this was beyond the scope of the present work.

To describe but one example of this non-detect conundrum, hexachlorobutadiene concentrations for all sites and all samples were reported by the laboratory as zero, with the MDL for each analysis given as well. This compound was never found in the ambient air in concentrations above the MDL. Nonetheless, in the usual and traditional way, the contractor doing the QC/QA and numerical analyses expressed and reported these zero concentrations as one half of the MDL, leading to spurious non-zero annual averages with demonstrable health effects (1). Considering that this compound is found in transformer and hydraulic fluids, heat transfer liquids, solvents, laboratory reagents, and wash liquors for removing hydrocarbons with four or more carbon atoms; and considering that its emissions in the Phoenix area are virtually zero, a more prudent course of action, rather than setting all the zeros to one half of the MDL, was to forego attempts to calculate measures of central tendency such as means or medians, instead expressing these concentrations as the proportion of data below the MDL. The other complication in analytical methods concerns diesel particulate matter and is discussed next.

#### **5.3 Diesel Particulate Matter (DPM)**

Recent studies in Los Angeles (16), Portland (17), and elsewhere have shown that the risk to human health from the pantheon of gaseous and particulate air toxics is dominated by diesel particulate matter (DPM). Because the health threat from all carbonaceous components of PM far transcends DPM (18) – also know as "soot", "black carbon", or "elemental carbon from diesel exhaust" – this JATAP monitoring review and risk assessment consider both ambient elemental carbon, its diesel fraction, and organic carbon. It should be noted that the numerical methods to estimate DPM from elemental carbon concentrations remain somewhat fluid. Furthermore, because elemental carbon concentrations are quantified in the laboratory by two principal methods giving significantly different concentrations (19, 20), calculating the DPM concentrations from the JATAP monitoring required careful consideration. For example, the five urban sites in JATAP had the elemental carbon portion of their PM analyzed by one method; the IMPROVE Tonto site, by the other. The Phoenix Supersite had and still does have both IMPROVE and Speciation Trends Network (STN) PM samplers. Although these paired samplers from the two different networks would prove quite useful in relating the elemental carbon concentrations from the two methods; for consistency with
most of the other JATAP sites, the STN concentrations from Supersite have been relied upon for this comparative PM analysis.

Numerous investigations in the last two decades have been conducted into the chemical composition of airborne particulates, including elemental carbon (EC) and organic carbon (OC) concentrations, as well as their primary and secondary emissions. (21, 22, 23, 24, 25). Several different methods to estimate DPM from carbonaceous aerosol concentrations have been employed with no clear consensus emerging. At least for carbon the MDLs are much lower than the lowest ambient concentrations, simplifying the calculation of the annual averages. For the JATAP 2005 monitoring results and risk assessment, the DPM concentrations are calculated in five steps (brackets around an ambient species such as EC denote concentrations; subscripts after the brackets denote the size fraction of PM):

- 1. Calculate the annual averages of [EC]<sub>2.5</sub>. For all sites except Tonto, these concentrations came from the thermal optical transmittance (TOT) analytical method.
- 2. Determine the relationship between  $[EC]_{2.5}$  quantified by TOT, the method in the STN network, and  $[EC]_{2.5}$  quantified by thermal optical reflectance (TOR), the method in the IMPROVE network, based on the paired Phoenix Supersite records for speciated PM<sub>2.5</sub> in 2005 2006.
- 3. Convert the [EC]<sub>2.5</sub> by TOT to [EC]<sub>2.5</sub> by TOR at all the sites except Tonto.
- 4. Calculate the [EC]<sub>10</sub> by applying the reported ratio of fine particulate elemental carbon ([EC]<sub>2.5</sub>)to coarse particulate EC ([EC]<sub>2.5-10</sub>), keeping in mind that

 $[\mathbf{PM}_{10}] = [\mathbf{PM}_{2.5}] + [\mathbf{PM}_{2.5}].$ 

5. The resultant [EC]<sub>10</sub> are then decreased to the estimated [DPM]<sub>10</sub> using the fraction of total EC emissions attributable to metropolitan diesel combustion from such sources as on-road traffic, off-road construction equipment, and point-source emergency generators. Different sources, such as vegetative burning and gasoline combustion, also produce EC emissions and these must be accounted for in the final reckoning of [DPM]<sub>10</sub>.

# 5.4 Emissions

The fifth step of the DPM calculations depends on an inventory of the speciated  $PM_{25}$ emissions, presented and discussed in this section. The JATAP air toxics monitoring of 2005 took place before the advent of the most recent federally mandated cleaner diesel engines, and before the widespread use of low-sulfur diesel fuel. The most recent PM<sub>2.5</sub> emissions inventory for metropolitan Phoenix is for 1995 from the Maricopa Association of Governments (27), although it was speciated in 1999 with vehicular emission test results from the mid to late 1990s (Table 5.4-1). A few points about the inventory are worth noting. First, its exclusion of windblown dust means that its source category totals and percentages apply best to periods of light to moderate winds with hourly average speeds below the dust resuspension threshold of 15 to 25 miles per hour. Second, the largest single source category, paved road dust in the geological category, has a high degree of uncertainty and could be considered somewhat controversial. In addition, it has been demonstrated that crustal particles monitored within the freeway corridor "plume" often have elemental carbon or "soot" agglomerations adhering to the mineral portion, an admixture that may confound the separation of crustal from carbonaceous reentrained road dust (28). Third, the method to calculate the PM emissions from paved-road reentrainment has traditionally depended on measurements of the silt loading on the pavement; but recent work has determined with a new direct-measurement technique that, at least for  $PM_{10}$  emissions, the emissions based on silt loading may be quite different from those directly measured. Fourth, the geological component comprises three fourths of the total PM<sub>2.5</sub> emissions, even though ambient measurements show that the crustal content of  $PM_{2.5}$  is about 20%, not the 75% from the inventory. Even when accounting for the sulfates and nitrates -- formed secondarily from local emissions of sulfur dioxide and oxides of nitrogen and transported into region from power generation and copper smelting elsewhere – this wide disagreement would suggest that the inventory over-estimates the geological emissions. Fifth, and last, 13% of the organic carbon and 4% of the elemental carbon in the inventory come from the combustion of (mostly) natural gas from stationary industrial, commercial, and residential equipment. Urban source apportionment studies tend to identify and quantify contributing categories such as "gasoline", "diesel", or "motor vehicle", based to a large degree on the carbonaceous components of the aerosol; but cannot treat the stationary source combustion contribution separately. This would suggest that these transportation categories either be given different names or acknowledged to contain these stationary combustion emissions. In summary, although these five points question the accuracy of the emissions inventory on which the calculation of diesel particulate matter depends, it remains the most recent and best available and is used in the present work.

# Table 5.4-1 Metropolitan Phoenix PM<sub>2.5</sub> Emissions Inventory for 1995, with elemental and

organic carbon in metric tons per year

Abbreviations: EC, elemental carbon; OC, organic carbon; g, gasoline; d, diesel; ng, natural gas; EC:OC, ratio of elemental to organic carbon in the emission stream; LDGT2, light-duty gas trucks-large; LDGV, light-duty gas vehicles; HDGV, heavy-duty gas vehicles; MC, motorcycles; LDGT1, light-duty gas trucks-small; HDDV, heavy-duty diesel vehicles; LDDV, light-duty diesel vehicles; LDDT, light-duty diesel trucks.

Emission type	Fuel FC.O	FC.OC	metric tons per year			
Emission type	ruei	LC.OC	PM <sub>2.5</sub>	OC	EC	
offroad gas						
boats	g	0.32	4	3	1	
recreational vehicle	g	0.32	4	3	1	
lawn & garden	g	0.32	178	132	42	
subtotal offroad gas			186	138	44	
on-road gas - exhaust						
LDGT2	g	0.32	36	27	9	
LDGV	g	0.32	80	60	19	
HDGV	g	0.32	63	47	15	
MC	g	0.32	1	1	0	
LDGT1	g	0.32	33	24	8	
subtotal - onroad gas			214	159	51	
gas total			400	297	95	
offroad diesel						
external combustion	d	3.96	91	18	71	
airport ground support	d	3.96	229	45	179	
locomotives	d	3.96	241	48	189	
construction exhaust	d	3.96	135	27	106	
indus/light comm equip	d	1.13	1,996	918	1,038	
agricultural equipment	d	3.96	87	17	68	
subtotal offroad diesel			2,780	1,073	1,651	
onroad diesel						
HDDV	d	3.96	1,182	234	925	
LDDV	d	1.13	16	7	8	
LDDT	d	1.13	40	18	21	
subtotal onroad diesel			1,238	259	954	
diesel total			4,017	1,332	2,605	
gas total			400	297	95	
gas + diesel total			4,417	1,629	2,699	
EC:OC gas + diesel ratio		1.66				
stationary source						

Emission true	Fuel	ECOC	metric tons per year			
Emission type	Fuel	EC:UC	PM <sub>2.5</sub>	OC	EC	
industrial processes	misc		275			
comm./inst natural gas	ng	0.34	78	57	19	
internal combustion	ng or d	0.34	235	172	58	
residential natural gas	ng	0.34	63	46	16	
industrial natural gas	ng	0.34	35	25	9	
industrial fuel oil	ng	0.34	2	2	1	
industrial total			688	302	103	
Geological						
paved road dust			7,395	*	*	
construction activity fugitives			3,077			
unpaved road dust			2,992			
agricultural tilling			1,182			
trackout reentrainment			407			
cattle feedlots			113			
process fugitives			75			
agricultural harvesting			0			
others			20			
geological total			15,262			
biomass burning						
residential wood		0.28	230	180	51	
waste/open burning		0.28	29	23	6	
structural/vehicle fires		0.28	66	52	15	
charbroiling/frying meat		0.14	215	189	26	
soil/microbial activity			0	0	0	
wild fires		0.28	23	18	5	
biomass burning total		0.22	565	462	103	
Grand total			20,931	2,393	2,905	
industrial: % of total			3.3	12.6	3.5	
all of diesel EC					2,605	
diesel EC:fraction of all EC					0.90	

\*paved road dust likely contains unknown amounts of carbonaceous emissions

# 5.5 Apportionment to Source Categories

Source apportionment is a set of related statistical methods employed to determine the contribution that various emission source categories make to ambient concentrations of air pollutants. In the early 1990s the first models developed and applied to ambient concentrations of particulate matter can be termed "receptor models." The second type, called "factor analyses", came a few years later. Considered complementary, these two types of source apportionment models have been applied to Phoenix  $PM_{2.5}$  and to Phoenix  $PM_{10}$ . Two of the more recent studies, discussed in this section, are factor analyses (29, 30).

- 1. S. G. Brown et al, "Source Apportionment of Fine Particulate Matter in Phoenix, AZ, Using Positive Matrix Factorization", *J. of Air & Waste Management Association*. 57:741-752, June 2007
- 2. C. W. Lewis et al, "Source Apportionment of Phoenix PM<sub>2.5</sub> Aerosol with the Unmix Receptor Model", *J. of Air & Waste Management Association*. 53:325-338, March 2003.

For a number of reasons, results from different source apportionment studies tend to be difficult to reconcile without invoking too many simplifications; nonetheless, such an averaging has been done for the two cited studies (Table 5.5-1). Together they demonstrate that about half of the wintertime Phoenix  $PM_{2.5}$  comes from fossil fuel combustion, one quarter stems from secondary nitrate, one eighth from both soil and "transport/secondary sulfate", and four percent from biomass burning.

<b>Table 5.5-1</b>	Wintertime Phoenix PM2.5	Apportioned to its	Principal	Emission	Source
Categories					

Source category	Study 1	Study 2 with NO3	Average of 1 and 2 with NO3
Fossil fuel combustion: motor vehicle(1)/ gasoline(2) + diesel + stationary source	54	47	51 ± 3
combustion			
Nitrate	21	21	$21\pm0$
Soil	9	15	$12 \pm 3$
Transport/secondary sulfate	15	9	$12 \pm 3$
Bio-burning	1	7	$4\pm3$

Additional details (Table 5.5-2) warrant some discussion. First, the two studies, based on their midpoints, are five and one half years apart: January 1997 versus July 2002. While this difference may appear to be important, it is not: the general emission rates and speciated profiles of all emission sources do not change that rapidly. Second, the number of samples analyzed is comparable and sufficient (250 versus 789). Third, while there were two different sites involved, their air pollutant concentrations and their chemical composition of PM are similar. Fourth, although employing different estimates of "wood smoke", the two studies yield comparable, low-percentage contributions from this source. Fifth, the difference in "winter definition" can lead to problems, as the first study defines winter as December through February, while the second defines it as October through March. Because October and March concentrations of PM<sub>2.5</sub> are generally lower than those of November through February, one might suspect that differences would arise in the source apportionment work. Sixth, for the two studies, there is a mismatch of contributing source categories: the first has nine while the second has five, perhaps indicative of the differences in the resolving power of the two statistical methods. In Table 5.5-1, four components of Study #1 were combined: (1) "copper/nickel/ vanadium", (2) "regional power generation", (3) "secondary transport", and (4) "arsenic/lead/selenium", to be termed collectively as "transport/secondary sulfate." Seventh, the "motor vehicle", "gasoline", and "diesel" contributions have been combined, and renamed as fossil fuel combustion, and, by name only, now include the emissions from fuel burning by stationary sources. Last, in Tables 5.5-1 and 5.5-2, the "soil" or geological percentage of  $PM_{25}$  is 12%, lower than the 20% given in the discussion on emissions. This difference arises from the higher concentration and percentage contribution of wintertime nitrates, compared with a lower annual nitrate contribution that leads to the higher 20% geological share. These differences in the two studies should not be overlooked; nonetheless, they agree reasonably well for all source categories. These source apportionment results shed light on any interpretations of the measured, JATAP particulate matter concentrations and clearly show that, at least in the Phoenix urban core, fossil fuel combustion, itself dominated by mobile sources, generates one half of the ambient fine particulates.

Remarks/source category	Study 1	Study 2
Sampling period	April 2001 - October 2003	March 1995 - June 1998
Sampling duration (months)	31	40
Sampling midpoint	July 2002	January 1997
Winter definition	Dec - Feb	October - March
Monitoring site	Phoenix Supersite	West Phoenix
Sampling frequency	Every third	Daily
n Samples	250	789
Wood smoke treatment	$K_w = [K] - 0.6[Fe]$	$K_w = [K] - 0.15[Si]$
Numerical model	Positive Matrix Factorization	UNMIX

**Table 5.5-2** Wintertime Phoenix PM2.5 Apportioned to its Principal Emission SourceCategories in Greater Detail

	Percent contribution to PM <sub>2.5</sub>						
Source categories - detailed	Study 1	Study 2	Average				
Motor vehicle(1)/gasoline(2)	42	33	38				
Nitrate	21	21	21				
Diesel	12	14	13				
Soil	9	15	12				
Cu/Ni/V	7						
Regional power generation	4						
Secondary sulfate/transport	2	9	6				
As/Pb/Se	2						
Biomass burning	1	7	4				
Motor vehicle(1)/gasoline(2) + diesel	54	47	51				

Source categories combined	Percent contribution to PM <sub>2.5</sub>					
20mmer caregories comonica	Study 1	Study 2	Average			
Fossil fuel combustion: motor	54	47	51 ± 3			
Nitrate	21	21	$21 \pm 0$			
Soil	9	15	$12 \pm 3$			
Transport/secondary sulfate	15	9	$12 \pm 3$			
Biomass burning	1	7	4 ± 3			

# 5.6 Ambient Concentrations of Particulate Air Toxics

As one might infer from the preceding sections, the calculations to convert the annual average speciated  $PM_{2.5}$  concentrations actually measured in the JATAP into their  $PM_{10}$ counterparts are somewhat involved, especially for diesel particulate matter. For the elements with chronic health-based guidelines, the high percentage of laboratory values reported as "nondetectable" - manganese had the lowest nondetectable frequency of 0-13% while cadmium had the highest (60-70%) – dictates that the concentration be expressed as a range. The lower value in the range comes from setting the nondetectable values to zero; the higher, from setting them to one half of the method detection limit (MDL). For the diesel particulate matter concentrations, discussed generally in a previous section, the complexities are multiplied. That the MDLs for carbon are much lower than the lowest ambient concentrations eliminates the complication of calculating annual averages from sets of individual samples with unacceptably high frequencies of non-detects. (Note that the elemental carbon concentrations in Table 5.6-1 have been corrected for the two different analytical methods (see the discussion on pages 71 - 72), so they are roughly 20% higher than the uncorrected concentrations in Tables 4.5.1-1 and 4.5.1-2.) Nonetheless, for the reader who is not a specialist, Table 5.6-1 summarizes the toxic components of particulate matter quantified in this project. Perhaps the simplest way to understand the health implications of Table 5.6-1 is to compare its concentrations with the standard or guideline value. Dividing the concentration by the standard or guideline value gives numbers less than 1.0 for ambient concentrations within the standard or guideline; and gives numbers greater than 1.0 when a concentration exceeds it (Table 5.6-2). Besides the subject of health effects, urban versus background concentrations demonstrate that urban emissions elevate ambient concentrations several times above background (Table 5.6-3).

			Sites						
Species	Standard or Guideline*	Supersite	VEI	W. PHX.	Salt R. SC	Gila R. SJ	Tonto		
Date began		1/1/2005	1/4/2005	1/4/2005	2/3/2005	2/4/2005	1/4/2005		
Date ended		12/30/2005	12/30/2005	12/30/2005	2/4/2006	2/4/2006	12/30/2005		
n samples		118	59	59	62	57	120		
PM <sub>10</sub>	50,000	32,800	NM	45,100	52,800	NM	9,500		
PM <sub>2.5</sub>	15,000	10,718	10,734	12,434	10,184	9,377	4,109		
[Arsenic] <sub>2.5</sub>	$0.20^{1}$	0.79-1.27	0.81 - 1.23	0.89 - 1.52	0.58 - 1.10	0.67 - 1.02	0.35 - 0.38		
[Cadmium] <sub>2.5</sub>	$0.6^{1}$	2.7 - 6.35	2.78 - 7.33	1.52 - 5.58	2.21 - 6.69	2.34 -6.53	NM		
[Chromium VI]	$0.08^{1}$	0.07 - 0.08	0.06 - 0.08	0.07 - 0.07	0.06 - 0.07	0.04 - 0.05	.001-0.002		
[Manganese] <sub>2.5</sub>	40 <sup>2</sup>	3.50 - 3.62	4.67 – 4.76	5.01 - 5.07	4.36 - 4.50	3.34 - 3.42	1.27 – 1.27		
[Nickel] <sub>25</sub>	90 <sup>2</sup>	0.91 – 1.21	0.91 – 1.35	1.27 – 1.43	0.69-1.06	0.54 - 0.85	0.10 - 0.12		
[DPM] <sub>2.5</sub>	100 <sup>3</sup>	1108	1092	1628	656	554	178		
[EC] <sub>2.5</sub>	None	1231	1214	1809	729	615	197		
[OC] <sub>2.5</sub>	None	5,425	4,841	6,306	3,715	3,081	796		

**Table 5.6-1** Annual Average PM<sub>10</sub>, PM<sub>2.5</sub>, and Selected Air Toxics (units are nanograms per cubic meter (ng/m3))

**Bold values** exceed NAAQS for the PM mass by size fraction and guideline values for their toxic components. Guideline values, from the U.S. EPA's Integrated Risk Information System (IRIS) and the Agency for Toxics Substances and Disease Registry, except for [DPM], which is from The Air Resources Board (California), are inhalation based and strictly speaking apply to the fine fraction. Note that the annual  $PM_{10}$  standard was revoked by EPA, but not until 17 December 2006 (it still serves as a useful benchmark of particulate air quality, even though annual levels above this concentration cannot be associated with health effects).

1. Arsenic and cadmium guidelines: 1 in million cancer benchmark from IRIS

2. Manganese and nickel guidelines: minimum risk levels from ATSDR (non-cancer effects)

3. DPM guideline: 1 in million cancer benchmark from Air Resources Board, California

NM = not monitored; DPM - diesel particulate matter; EC - elemental carbon; OC = organic carbon

Note 1: [DPM]<sub>2.5</sub> is diesel particulate matter 2.5 microns and smaller – a calculated value

Note 2:  $[EC]_{2.5}$  is the concentration of elemental carbon 2.5 microns and smaller – a value calculated for all sites except Tonto from the thermal optical transmittance (TOT) measurements.

Note 3: [OC]<sub>2.5</sub> is the concentration of organic carbon 2.5 microns and smaller – a measured value

	Standard or	Sites					
Species	Guideline (ng/m3)	Supersite	VEI	W. PHX.	Salt R. SC	Gila R. SJ	Tonto
1		A					
n samples		118	59	59	62	57	120
PM <sub>10</sub>	50,000	0.66	NM	0.90	1.06	NM	0.19
PM <sub>2.5</sub>	15,000	0.71	0.72	0.83	0.68	0.63	0.27
Arsenic (ND=0)	0.20	4.79	4.91	5.40	3.52	4.06	2.12
Arsenic (ND=1/2	0.20	7.70	7.46	9.22	6.67	6.19	2.31
Cadmium (ND=0)	0.29	22.39	6.66	3.64	5.30	5.61	NM
Cadmium (ND=1/2	0.29	52.55	17.59	13.39	16.05	15.67	NM
Chromium VI (ND=0)	0.08	0.91	0.81	0.83	0.72	0.54	0.02
Chromium VI (ND=1/2	0.08	1.00	0.94	0.93	0.87	0.66	0.02
Manganese (ND=0)	50	0.31	0.41	0.44	0.38	0.29	0.11
Manganese (ND=1/2	50	0.32	0.42	0.44	0.39	0.30	0.11
Nickel (ND=0)	4	0.56	0.56	0.78	0.42	0.33	0.06
Nickel (ND = $\frac{1}{2}$ MDL)	4	0.74	0.82	0.87	0.65	0.52	0.07
[DPM] <sub>2.5</sub>	100	11.08	10.92	16.28	6.56	5.54	1.78

**Table 5.6-2** Particulate Air Toxics, Divided by their Standard or Guideline Values (bold values exceed a guideline)

Potential health effects, specifically lifetime cancer risk in excess of 1 in 1,000,000, are associated with those sites that have pollutant ratios greater than 1.0, which in Table 5.6-2, are shown in bold. (Health effects investigators and the EPA employ at least three sets of cancer risk levels: 1 excess case per 1,000,000; 1 case per 100,000; and 1 case per 10,000 population. There is no consensus on which risk scale is most suitable.) The  $PM_{10}$  standard is exceeded at one site, the Salt River Senior Center. Arsenic concentrations exceed the health-based guideline from two to nine times, with even the background site of Tonto in excess. Cadmium concentrations exceed the health-based guideline from four to 53 times.

NM Not monitored; ND Nondetects; MDL Method Detection Limit

Hexavalent chromium (chrome VI) concentrations, on the other hand, are just within the guideline, while the manganese and nickel concentrations are well within it. Diesel particulate matter concentrations exceed the California Air Resources Board guideline from two to 19 times.

	Annual average concentration (ng/m3)								
Species									
	Supersite	VEI	W. PHX.	Salt R. SC	Gila R. SJ	Tonto			
[DPM] <sub>2.5</sub>	1,108	1,092	1,628	656	554	178			
[CPM] <sub>2.5</sub>	6409	5811	7770	4282	3554	993			
[Arsenic] <sub>2.5</sub>	1.27	1.23	1.52	1.1	1.02	0.38			
[Cadmium] <sub>2.5</sub>	6.36	7.34	5.59	6.7	6.54	NA			
[ChromiumVI] <sub>2.5</sub>	0.08	0.08	0.07	0.07	0.05	0.002			
[Manganese] <sub>2.5</sub>	15.82	20.80	22.16	19.66	14.95	5.55			
[Nickel] <sub>2.5</sub>	2.95	3.30	3.49	2.59	2.07	0.29			
	(Concentration) ÷ (Tonto)								
Species									
~~~~~	Supersite	VEI	W. PHX.	Salt R. SC	Gila R. SJ	Tonto			
[DPM] <sub>2.5</sub>	6.22	6.13	9.15	3.69	3.11	1.00			
[CPM] <sub>2.5</sub>	6.45	5.85	7.82	4.31	3.58	1.00			
[Arsenic] <sub>2.5</sub>	3.34	3.24	4.00	2.89	2.68	1.00			
[Cadmium] <sub>2.5</sub>	NA	NA	NA	NA	NA	NA			
[ChromiumVI] <sub>2.5</sub>	40	40	35	35	25	1.00			
[Manganese] <sub>2.5</sub>	2.85	3.75	3.99	3.54	2.69	1.00			
[Nickel] <sub>2.5</sub>	10.08	11.25	11.92	8.83	7.08	1.00			

 Table 5.6-3
 Urban Toxic Particulate Concentrations Normalized to Tonto

# 5.7 Human Health Risk from Particulate Air Toxics

### Cancer risk

Some components of ambient PM have respiratory and other health effects; have had their non-cancer and cancer effects quantified through toxicological research programs; and have had these numerical risk factors codified in the EPA's Integrated Risk Information System (IRIS) (<u>http://www.epa.gov/ncea/iris/index.html</u>, and in the Agency for Toxics Substances and Disease Registry (<u>http://www.atsdr.cdc.gov/</u>). The risks estimated in this report are based on "guideline values" from IRIS or the ASTDR, except for DPM, which comes from the Air Resources Board (California).

The following discussion is based only on the fine fraction  $(PM_{2.5})$ . Table 5.7-1 presents the lifetime excess cancer risk from the 2005 aerosol concentrations that exceeded the cancer benchmark values. The two elements of arsenic (As) and cadmium (Cd) do contribute to the overall risk of PM<sub>2.5</sub>, but their contributions are less than ten percent of the total risk (90% is attributed to DPM). Three other elements with chronic health-based guidelines have low enough concentrations that they pose no risk: hexavalent chromium (Cr VI), manganese (Mn), and nickel (Ni). The carbonaceous components of the fine PM account for nearly all of the risk. Considering just DPM plus arsenic and cadmium, DPM drives 91 to 97% of the total risk; if all carbonaceous aerosol is considered – and that consists of DPM, elemental carbon from sources other than diesel fuel combustion, and all of the organic carbon – over 99% of the total risk comes from carbon. Depending on the site, the overall risk from the two elements and DPM varies from about 200 to 500 excess cancer cases per one million population, taken over an average 70 years of exposure. This risk increases five-fold when all of the carbon is assigned the same risk as DPM. As one would expect, the urban core sites have concentrations that pose the highest risk; the two urban-fringe sites, both on tribal lands, have overall risk about 50% lower than the average of the urban core; and the background site of Tonto National Monument has by a wide margin the lowest risk. The risk from toxic PM<sub>2.5</sub> in the urban core is about seven times that at Tonto; the risk at the two tribal sites is three to four times that of Tonto.

These risk estimates, however, may under-estimate the risks to which various populations actually experience. The reason for this lies in the difference between measured ambient concentrations at a fixed monitoring site and "exposure concentrations"— the concentrations to which people are actually exposed. Indoor air pollutant concentrations differ from those in the outdoor air, and most people spend more time inside than outside. Except for the very young and old, most people do not stay in one house or even in one neighborhood throughout a day: they attend school, go to work, engage in shopping, and variously move around portions of the metropolitan area. Most metropolitan-wide investigations into air pollution risk include an exposure analysis, in which various sub-populations are "tracked" (numerically) to determine their exposure times in the different environments (The JATAP study reported on here lacked such an analysis.). While earlier investigations suggested that for typically large US cities the exposure concentrations are about one half of the measured ambient concentrations, subsequent research and reviews (33 and 34) depict a vastly different picture. Based on multiple studies, indoor concentrations of many important air toxics

exceed their outdoor counterparts. For example, of seven air toxics species or species groups, only two had concentrations consistently lower indoors. In contrast, benzene, 1,3butadiene, and the two aldehydes (formaldehyde and acetaldehyde) - all implicated as important contributors to the overall health risk from air toxics – had indoor concentrations from three to over ten times higher than outdoor concentrations. Furthermore, for those people spending considerable time commuting on major freeways or arterial streets, the roadway corridor concentrations of many air pollutants are from three to ten times higher than those measured at fixed monitoring sites near the roadways (35). On the other hand, the single study reporting indoor (school classrooms) versus outdoor concentrations of elemental carbon showed that indoor concentrations were about one half of the outdoor ones (36). With most of the community-wide risk assessments assigning most of the risk to diesel particulate matter, whose surrogate is elemental carbon; this finding suggests that the overall risk based on exposure concentrations might be half of the risk based on ambient concentrations. This suggestion, however, is weakened for two reasons: (1) because cooking was absent from these classrooms and cooking inside residences produces carbonaceous particulates; and (2) organic carbon particulates, represented by a group called polycyclic aromatic hydrocarbons (PAH), are much higher indoors than out of doors. Considering all of these differences among indoor, outdoor, and roadway concentrations, the concentrations measured by the ambient air monitoring networks could be considered lower bounds for the actual exposure concentrations.

While the preceding discussion concerned under-estimates of risk, the other side of the story – over-estimates – also needs to be considered. All of the cancer benchmarks are based on 70 years of continuous exposure, but most people do not live their lives at a single location. Those people who do live in a few or several different cities and towns are likely to experience at least some years with lower air pollution levels than those in a relatively polluted urban area. For these people the lifetime exposure would be somewhat to considerably shorter than 70 years, so the cancer benchmarks would result in risk estimates that are too high for these more mobile populations.

# **Table 5.7-1** Excess Lifetime Cancer Cases per Million Population from Fine Particulates(PM2.5) in Metropolitan Phoenix

(Based on measured, not exposure concentrations. Abbreviations: As, arsenic; Cd, cadmium, DPM, diesel particulate matter; TC, total carbon, which consists of DPM, elemental carbon not from diesel, and organic carbon)

Percent risk from											
Ex	As +	Cd in									
						As + Cd	As + Cd	As + Cd	As + Cd		
	As	Cd	AS + Cd	DPM <sub>2.5</sub>	TC <sub>2.5</sub>	+	+	+	+		
JATAP site			Cu			DPM <sub>2.5</sub>	TC <sub>2.5</sub>	DPM <sub>2.5</sub>	TC <sub>2.5</sub>		
West	65	10.0	165	100	2425	505	2452	2	1		
Phoenix	0.3	10.0	10.5	400	2455	303	2432	3	1		
Phoenix	5 4	11.4	16.9	222	1007	240	2014	5	1		
Supersite	5.4	11.4	10.8	332	1997	549	2014	5	1		
Vehicle											
Emissions	5.2	13.2	18.4	328	1817	346	1835	5	1		
Inspection											
Salt River											
Senior	4.7	12.0	16.7	197	1333	214	1350	8	1		
Center											
Gila River	1.2	117	16.0	1.00	1100	100	1105	0	1		
St. John's	4.5	11./	16.0	100	1109	182	1125	9	1		
Tonto	1.6	0.0	1.6	53	298	55	300	3	1		

# Non-cancer risk

Many air toxic concentrations pose risk not only for cancer, but for a variety of non-cancer health effects, including damage to the liver, kidneys, and cardiovascular system, as well as causing problems in the neural system and in fetal development. Unlike the cancer effects, these non-cancer effects cannot be quantified so precisely, principally because they encompass so many different physiological systems. Nonetheless, the common practice that has emerged relies on toxicological studies to determine airborne concentrations of air toxics that present a minimum risk level (MRL), sometimes called the reference concentration dose (RfC). Measured (or exposure) concentrations are divided by these minimally safe levels to yield ratios of the measured (or exposure) concentration to the MRL. Sometimes this ratio is called the "Hazard Ratio"; other investigators use the term "benchmark quotient". Ratios less than 1.0 simply mean that the ambient or exposure concentrations present little or no non-cancer health risk; those ratios exceeding 1.0 may have adverse health effects, depending on how high the ratio is and on the particularities of the population being studied. In spite of the wide variety of physiological pathways and target organs and systems, most investigators add the benchmark quotients from all the various air toxic species to produce a "benchmark index", merely the cumulative effect of all the species on non-cancer risk. For particulate air toxics species in 2005, Table 5.7-2 shows that none of the annual concentrations exceeded the minimum risk level values from the EPA's Integrated Risk Information System, the Agency for Toxic Substances and Disease Registry, or, in the case

of diesel particulate matter, the Air Resources Board of California. All particulates concentrations were low enough to present no non-cancer health risks.

# Table 5.7-2 Non-Cancer Benchmark Values and Annual Concentrations of Particulate Air

# Toxics in nanograms per cubic meter

(MRL, minimum risk level from EPA's IRIS or ASTDR; NAAQS, National Ambient Air Quality Standard: annual standards for  $PM_{10}$  and  $PM_{2.5}$  only; all others are MRLs; the  $PM_{10}$  annual standard was retracted by EPA in 2006, but it remains a useful measure of particulate air quality, even though it can no longer be associated with any health effects.; NA, not assessed; As, arsenic; Cd, cadmium; Cr VI, hexavalent chromium; Mn, manganese; Ni, nickel; DPM, diesel particulate matter; EC, elemental carbon; OC, organic carbon)

			Sites							
	MRL									
	or									
	NAAQS	Supersite	VEI	W. PHX.	Salt R. SC	Gila R. SJ	Tonto			
n samples		118	59	59	62	57	120			
$PM_{10}$	50,000	32,800	NM	45,100	52,800	NM	9,500			
PM <sub>2.5</sub>	15,000	10,718	10,734	12,434	10,184	9,377	4,109			
					0.58 –					
[As] <sub>2.5</sub>	NA	0.79-1.27	0.81 - 1.23	0.89 - 1.52	1.10	0.67 - 1.02	0.35 - 0.38			
					2.21 -					
$[Cd_{2.5}^{*}]$	10*	2.7 - 6.35	2.78 - 7.33	1.52 - 5.58	6.69	2.34 -6.53	NM			
					0.06 -					
[Cr VI] <sub>2.5</sub>	100	0.07 - 0.08	0.06 - 0.08	0.07 - 0.07	0.07	0.04 - 0.05	0.001-0.002			
					4.36 -					
[Mn] <sub>2.5</sub>	50	3.50 - 3.62	4.67 - 4.76	5.01 - 5.07	4.50	3.34 - 3.42	1.27 - 1.27			
[Nickel] <sub>2.5</sub> *	90*	0.91 - 1.21	0.91 - 1.35	1.27 - 1.43	0.69-1.06	0.54 - 0.85	0.10 - 0.12			
[DPM] <sub>2.5</sub> **	5,000**	1,108	1,092	1,628	656	554	178			
[EC] <sub>2.5</sub>		1,231	1,214	1,809	729	615	197			
[OC] <sub>2.5</sub>		5,425	4,841	6,306	3,715	3,081	796			

\*MRLs are from EPA's IRIS, except Cd and Ni, which are from the ASTDR

\*\*DPM's MRL is from the Air Resources Board of California

# 5.8 Ambient Concentrations and Human Health Risk from Gaseous Air Toxics

To complete the air toxics picture, this section discusses the non-cancer and cancer risk from gaseous air toxics. Table 5.8-1 gives the non-cancer benchmarks for chronic inhalation exposure along with the annual (2005) average concentrations. In contrast to the gaseous concentrations presented in Table 4.5.2-2, which are in units of parts per million by volume, the concentrations in this section are in micrograms per cubic meter ( $\mu$ g/m3). (Gaseous concentrations are commonly expressed in either of the two units Table 5.8-2 presents the non-cancer benchmark quotients for each gaseous air toxic species. Unlike the case for particulates, one gaseous air toxic species at one site (formaldehyde at Greenwood) has a high enough concentration to pose non-cancer health effects. The last row of the table is the

cumulative non-cancer benchmark index, which is the sum of the individual species' benchmark quotients. As a benchmark index of 1.0 or less indicates no or minimal health effects, the non-cancer benchmark indices at the four urban sites (Greenwood, Supersite, South Phoenix, and West Phoenix), which are between 1.0 and 3.0, indicate the possibility of some moderate non-cancer health effects. Of the two Indian Communities, the Salt River Community incurs slightly more non-cancer health effects than the Gila River Community.

					GR	SR		
	MRL	Green-	Super-	Oueen	St.	Senior	S.	W.
	(RfC)	wood	site	Valley	Johns	Center	PHX	PHX
1,3-Butadiene	2	0.62	0.47	< 0.09	< 0.09	< 0.09	0.64	0.71
Acetaldehyde	9	5.07	3.13	NM	NM	NM	3.15	NM
Benzene	9.3*	2.79	2.5	0.38	0.61	1.65	2.33	2.43
Carbon tetrachloride	100	0.63	0.62	0.61	0.56	0.57	0.6	0.54
Chloroform	94.5*	0.33	0.59	0.05	0.11	0.35	0.32	0.34
Dichloromethane	1008.4*	1.15	0.83	0.12	0.26	0.46	0.64	1.04
Ethylbenzene	252.1*	2.06	1.61	0.82	0.37	0.71	1.12	2.38
Formaldehyde	9.5*	9.81	5.61	NM	NM	NM	4.2	NM
Hexachlorobutadiene	None	< 0.41	< 0.41	< 0.41	< 0.41	< 0.35	< 0.45	< 0.47
m,p-Xylene	100	5.43	4.32	0.82	0.88	1.83	3.46	4.84
o-Xylene	100	2.08	0.78	0.38	0.36	0.79	1.2	1.67
Styrene	824.4*	1.71	0.76	0.11	0.35	1.96	0.4	0.82
Tetrachloroethylene	262.5*	0.89	1.43	0.18	< 0.05	< 0.05	1.32	0.94
Toluene	291.7*	8.82	7.18	0.59	2.51	7.23	6.86	12.87
Trichloroethylene	None	0.27	0.18	0.09	< 0.05	< 0.05	< 0.05	< 0.04
Vinyl chloride	100	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.01	< 0.02

**Table 5.8-1** Non-Cancer Benchmarks (reference concentration for chronic inhalation exposure (RfC) in  $\mu$ g/m3) with 2005 Annual Averages of Gaseous Air Toxics ( $\mu$ g/m3) (shaded values may pose non-cancer health effects; NM, not measured)

\*MRLs are from the Agency for Toxic Substances and Disease Registry (ASTDR); otherwise, from EPA's IRIS archive

**Table 5.8-2** Non-Cancer Benchmark Quotients and (in the last row) the Non-Cancer Benchmark index for the 2005 Annual Average Concentrations of Gaseous Air Toxics (shaded values indicate non-cancer health effects; for sites without aldehyde measurements, the average of Supersite and West Phoenix has been substituted; for values in Table 5.7-3 reported as "less than (<)", half of the numerical value has been substitued )

					GR	SR		
	MRL	Green-	Super-	Queen	St.	Senior	S.	W.
	(RfC)	wood	site	Valley	Johns	Center	PHX	PHX
1,3-Butadiene	2	0.31	0.24	0.02	0.02	0.02	0.32	0.36
Acetaldehyde	9	0.56	0.35	0.35	0.35	0.35	0.35	0.35
Benzene	9.3	0.30	0.27	0.04	0.07	0.18	0.25	0.26
Carbon tetrachloride	182.6	0.003	0.003	0.003	0.003	0.003	0.003	0.003
Chloroform	94.5	0.003	0.006	0.001	0.001	0.004	0.003	0.004
Dichloromethane	1008.4	0.001	0.001	0.000	0.000	0.000	0.001	0.001
Ethylbenzene	1000	0.002	0.002	0.001	0.000	0.001	0.001	0.002
Formaldehyde	9.5	1.03	0.59	0.52	0.52	0.52	0.44	0.52
Hexachlorobutadiene	None							
m,p-Xylene	100	0.05	0.04	0.01	0.01	0.02	0.03	0.05
o-Xylene	100	0.02	0.01	0.004	0.004	0.01	0.01	0.02
Styrene	82.4	0.02	0.01	0.001	0.004	0.02	0.00	0.01
Tetrachloroethylene	262.5	0.00	0.01	0.001	0.000	0.00	0.01	0.00
Toluene	291.7	0.03	0.02	0.002	0.01	0.02	0.02	0.04
Trichloroethylene	None							
Vinyl chloride	100	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Non-cancer index <sup>1</sup>		2.35	1.54	0.95	0.98	1.15	1.45	1.61

1. Non-cancer index: the sum of the non-cancer benchmark quotients for all the listed species. Values greater than 1.0 may pose non-cancer health risks.

The cancer risk from gaseous air toxics, calculated as the product of the inhalation unit risk (IUR) level and the annual concentration, is given in Table 5.8-3. As with the particulate air toxics, these risk estimates given in Table 5..8-4 may actually under-estimate the actual ones, because exposure and ambient concentrations usually differ, with most indoor concentrations of gaseous air toxics being higher than outdoor concentrations (see discussions in Section 1.1, page 10and Section 5.7, pages 83 - 84).

**Table 5.8-3** Cancer Benchmarks in  $\mu$ g/m3, Reference Concentrations for Chronic Inhalation Exposure (RfC) in  $\mu$ g/m3 (for non-cancer effects), and inhalation unit risks (IUR) in  $(\mu$ g/m3)<sup>-1</sup>

	Cancer Benchmark	RfC	IUR x 10 <sup>-6</sup>
1,3-Butadiene	0.03	2	30
Acetaldehyde	0.5	9	2.2
Benzene	0.13	9.3	7.8
Carbon tetrachloride	0.07	182.6	6
Chloroform	0.04	94.5	23
Dichloromethane	2	1008.4	0.47
Formaldehyde	0.08	9.5	13
Hexachlorobutadiene	0.05	NA	22
Vinyl chloride	0.23	100	8.8

Table 5.8-4         Lifetime excess cancer risk from gaseous air toxics								
			Queen	GR St.	SR Senior	South	West	
	Greenwood	Supersite	Valley	Johns	Center	Phoenix	Phoenix	
1,3-Butadiene	18.6	14.1	1.4	1.4	1.4	19.2	21.3	
Acetaldehyde*	11.2	6.9	6.9	6.9	6.9	6.9	6.9	
Benzene	21.8	19.5	3.0	4.8	12.9	18.2	19.0	
Carbon tetrachloride	3.8	3.7	3.7	3.4	3.4	3.6	3.2	
Chloroform	7.6	13.6	1.2	2.5	8.1	7.4	7.8	
Dichloromethane	0.5	0.4	0.1	0.1	0.2	0.3	0.5	
Formaldehyde*	127.5	72.9	63.8	63.8	63.8	54.6	63.8	
Hexachlorobutadiene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Vinyl chloride	0.1	0.1	0.1	0.1	0.1	0.0	0.1	
Total	191.0	131.2	79.9	82.9	96.7	110.2	122.6	

\* For sites without aldehyde measurements (Queen Valley, Gila River St. Johns, Salt River Senior Center, and West Phoenix), acetaldehyde and formaldehyde concentrations were set equal to the average of Supersite and South Phoenix.

# 5.9 Human Health Risk from Both Gaseous and Particulate Air Toxics

Discussed separately in the previous two sections, the overall risk to human health is the combined effects of the gaseous and particulate air toxics concentrations. Although synergistic effects between the gaseous and particulate species may be at work, the state of the science has not advanced to the point where such effects could be quantified. The overall risk, expressed as the sum of risk from the gaseous species and the risk from the particulate species, is given in Table 5.9-1. The actual risks in this table are based on exposure concentrations that are assumed to be one half of the measured ambient ones, in spite of the evidence to the contrary presented in the discussion of indoor, outdoor, and freeway corridor air toxics concentrations on pages 83 and 84. The top half of the table presents risks excluding organic carbon particulates; the bottom half includes the risk from this group, equating the risk from organic carbon to that of elemental carbon. Carbonaceous particulates consist of both elemental carbon (mostly diesel exhaust or DPM) and of organic carbon. If this complex mixture of organic carbon particulates is assigned a toxicity similar to its elemental counterpart (and a considerable body of health effects studies suggests that it should be, although the scientific jury remains out), then the overall risk from air toxics increases substantially. These higher risk estimates must be considered provisional for two reasons: (1) the U.S. EPA has yet to assign any cancer risk to DPM, although the Air Resources Board of California did so over ten years ago; and (2) the scientific communities investigating the health effects of organic carbon have yet to arrive at anything remotely resembling a consensus. In the next section (5.9) the excess lifetime cancer risk in metropolitan Phoenix is compared with risks determined in other cities.

# **Table 5.9-1** Total Risk of Excess Lifetime Cancer Cases per One Million Population

from both Gaseous and Particulate Air Toxics (shown with the risk from arsenic, cadmium, diesel particulate matter (DPM), and gaseous air toxics (above); and with arsenic, cadmium, DPM, elemental carbon from sources other than diesel, and organic carbon (below); exposure concentrations are set to one half of ambient)

	Based on	ambient co	Based on exposure concentrations, rounded off	
JATAP site	As, Cd, DPM	Gaseous	Total risk	Actual risk
Greenwood <sup>1</sup>	505	191	696	350
West Phoenix	505	123	628	300
South Phoenix <sup>2</sup>	427	127	554	300
Phoenix Supersite	349	131	480	250
VEI <sup>3</sup>	346	127	473	250
Salt River Senior Center	214	97	311	150
Gila River St. John's	182	83	265	150
Queen Valley <sup>4</sup>	59	80	139	70
Tonto <sup>5</sup>	59	80	139	70

	0			1
	PM*	Gaseous	Total risk	Actual risk (all C)
Greenwood <sup>1</sup>	2452	191	2643	1300
West Phoenix	2452	123	2575	1300
South Phoenix <sup>2</sup>	2233	127	2360	1200
Phoenix Supersite	2014	131	2145	1100
VEI <sup>3</sup>	1835	127	1962	1000
Salt River Senior Center	1350	97	1447	750
Gila River St. John's	1125	83	1208	600
Queen Valley <sup>4</sup>	304	80	384	200
Tonto <sup>5</sup>	304	80	384	200

\*PM: arsenic, cadmium, DPM, elemental carbon from sources other than diesel, and organic carbon

1) Greenwood: PM, not measured, is set equal to West Phoenix.

2) South Phoenix: PM, not measured, is set to the average of West Phoenix and Supersite.

3) VEI: gaseous, not measured, is set equal to South Phoenix.

4) Queen Valley: PM, not measured, is set equal to Tonto.

5) Tonto: gaseous, not measured, is set equal to Queen Valley.

# 5.10 Comparison of the Cancer Risk from Air Toxics in Phoenix with Other Cities

Since the mid 1990s, air toxics studies have been conducted in many cities throughout the United States, although their many differences make comparisons somewhat difficult. In this discussion only cancer risk among the several studies is compared (non-cancer risk is not discussed). Although not all studies quantify this cancer risk in the same way, most express this risk as the number of excess lifetime cancer cases per 1,000,000 population. Some studies express the risk as relative to a health-based benchmark, and others do not quantify it at all. Further differences arise for various reasons, such as (1) not all studies measure the same groups of gaseous or particulate air toxics; (2) not all studies consider diesel particulate matter, which tends to account for about three fourths of the total risk; (3) some of the earlier studies measured only gaseous air toxics but neglected the particulate species; (4) different studies have analytical chemistry results for both gaseous and particulate air toxics with different Method Detection Levels and with different methods of treating the non-detectable values; and (5) some risk estimates are based on measured concentrations, while others rely on either simulated ambient concentrations or on simulated exposure concentrations. Because none of the other studies reported risks from organic carbon, the Phoenix risk estimates for this inter-city comparison exclude the risk from organic carbon. Table 5.10-1 summarizes the cancer risk estimated in the various studies. In metropolitan Phoenix this risk tends to be higher than the national average and higher than many other studies. As expected, it is much lower than the risk in Houston and Los Angeles; but it is about equal to that in Seattle and Detroit, while much higher than the reported risk in Louisville.

**Table 5.10-1** Cancer Risk in Metropolitan Phoenix, AZ (from the JATAP) and Other Air Toxics Assessments throughout the United States (numbers of sites in parentheses; see notes A & B for the meaning of the USA risk numbers)

		Lifetime exercise			
Area	Study	USA and C	Notes		
	period	Gaseous	Particulate		
		air toxics	air toxics	Combined	
USA	2002			>10 - >100	А
USA	2005			>10 - >100	В
Seattle &	Nov	85 110	270 360		
Tacoma,	2008 –	63 - 119	270, 300,	355 - 569	С
Washington	Oct 2009	(0)	450 (5)		
	July			$50^{\text{tn}}: 7, 66,$	
Portland,	1999 –			350	D
Oregon	July			90 <sup>th</sup> : 13,	D
	2000			86, 430	
Houston, TX	2005	1144 (1)	105, 468, 1122		Е
Greater Los Angeles, California	2005	167 (10)	1,073 (10)	1,240 (10)	F
		1.1, 4.0			
Camden,	2002	for 2	2-48 for		G
New Jersey	2002	gaseous	5 metals		U
		species			
Minnesota	1996 -	25 - 58	Not		н
	2001	(35)	measured		**
	Sept		Measured,		
Albuquerque,	2007-	0.15	but no risk	0.15	Ι
New Mexico	March		attributed		
	2009	2	to PM		
Vancouver,		3 gaseous species, 3	2 metals		
Columbia	2005	semi-	2 metals		J
Canada		volatile	posed lisk		
Canada		species			
Detroit, Michigan	2007	62.3, 62.0.231.0	218		Κ
West	• • • • •				
Louisville.	2000 -	50 – 125	45 - 70	95 – 195	L
Kentucky	2001	(5)	(5)		
	2005	85 - 175	170 - 490	260 675	м
JATAP	2005	(5)	(5)	200 - 073	IVI

A & B: As the notes on the following pages indicate, the National Air Toxics Assessments (NATA) report that nationwide 25 million people are exposed to benzene concentrations that pose a risk greater than 10 lifetime cancer cases; that 1 million are exposed to concentrations of 1,3-butadiene, arsenic compounds, chromium VI, coke oven emissions, hydrazine, tetrachloroethylene, PAHs and naphthalene that together pose the same risk as benzene; and that 10,000 people incur a risk of greater than 100 cases from the same group of compounds.

These national assessments for both 2002 and 2005 tend to under-estimate the overall risk, because they exclude diesel particulate matter. For example, the 2005 assessment assigns a risk of 68 lifetime cancer cases to Maricopa County, and a maximum value anywhere in the USA of 150, considerably lower than the risk from the individual studies given in the table.

C: Seattle & Tacoma risks are from ambient measurements at individual sites.

D: Portland risks are from simulated exposure concentrations throughout the metropolitan area and are the minimum, mean, and maximum of all grids for the  $50^{th}$  and  $90^{th}$  percentile concentrations.

E: Houston, Texas risks are from the maximum concentration sites. The risks from particulate air toxics are only from diesel particulate matter. The risks of 468 and 1122 are from 1997 – 1998, while the 105 value is from 2005 at a suburban site with moderate, not maximum, concentrations.

F: Greater Los Angeles risks are the average from ten monitoring sites. Note that the NATA 2005 (see note A) assessment assigned risks of 61 to 110 for the four counties comprising the airshed.

G: Camden, New Jersey: numbers are relative risk, i.e. the concentration divided by the health benchmark concentration. Values greater than 1.0 indicate a risk to human health. Of the 34 air toxics concentrations (all come from dispersion modeling), two gaseous species (hydrogen sulfide and dioxin) and five metals (arsenic, cadmium, lead, manganese, and nickel) had relative risks greater than 1.0.

H: The Minnesota study had one sampling site in each of 35 different cities and towns. Only gaseous air toxics were measured and risk assigned. All particulate air toxics (including diesel particulate matter) were excluded.

I: The Albuquerque, New Mexico study limited its risk characterization to two gaseous species – benzene and methylene chloride. Particulate and semi-volatile organics were measured, but (apparently) their concentrations were too low to present any risk.

J: The Vancouver study relied on measurements of gaseous, semi-volatile, and particulate air toxics species; the study compared concentrations with health benchmarks, but did not quantify risk.

K: The Detroit study relied on measurements of diesel particulate matter (1 site), metals (arsenic, cadmium, and nickel) at 2 sites, and of 8 gaseous species at 3 sites.

L: West Louisville, Kentucky (2000 – 2001): 5 sites, metals (arsenic, cadmium, chromium, nickel); gaseous species (11 altogether); no diesel particulate matter

M: JATAP risks are based on five sites for particulates (West Phoenix, Phoenix Supersite, Vehicle Emissions Inspection, Salt River Senior Center, and Gila River St. Johns) and five sites for gaseous toxics (Phoenix Supersite, Salt River Senior Center, Gila River St. Johns, Greenwood, and South Phoenix). These risk estimates exclude those from organic carbon; instead, they are based on the gaseous concentrations, on arsenic and cadmium, and on diesel particulate matter.

Six studies reported risk as excess lifetime cancer cases per 1,000,000 population and included the risk from diesel particulate matter. Five of these studies involved multiple air monitoring sites, so the lowest risk, the average risk, and the highest risk are shown in Figure 5.10-1. The Houston study reported only the risk from a maximum concentration site.



**Figure 5.10-1** Comparative Cancer Risk from Air Toxics in the United States, including the JATAP for Phoenix, AZ

# 5.11 Conclusions on Risk, Based on Neighborhood Monitors Only

- Given as the number of lifetime excess cancer cases per one million population, the combination of gaseous and particulate air toxics results in from 250 to 350 in central Phoenix and about half of that on the urban perimeter.
- This risk is based on exposure concentrations which are assumed to be one half of the ambient concentrations.

- For the particulate phase, this risk comes from arsenic, cadmium, and diesel particulate matter. If, however, all carbonaceous particulates are considered, and gaseous air toxics are included as well, the lifetime excess cancer cases per one million population in central Phoenix increase to 1,000 1,300.
- In central Phoenix three fourths of the risk comes from particulate air toxics; this share increases to over 90% if organic carbon particulate is included.
- Gaseous air toxics and their emission sources posing the greatest risk are
  - formaldehyde (vehicle exhaust, fuel combustion, and a photochemical reaction product),
  - o 1,3-butadiene (vehicle exhaust and fuel combustion),
  - Acetaldehyde (vehicle exhaust, fuel combustion, and a photochemical reaction product), and
  - Benzene (motor vehicle exhaust, fuel combustion, solvents).
- Even 60 miles east of central Phoenix, at Tonto National Monument and Queen Valley, arsenic, cadmium (by inference), and diesel particulate matter concentrations exceed their guideline values, as do four gaseous species. Risk at the background sites is 70 -200 excess lifetime cancer cases per million population (the higher risk includes the organic carbon particulate).
- Within metropolitan Phoenix, the three components of particulate matter posing the greatest chronic health threat are diesel particulate matter (90% of the total risk), and arsenic and cadmium, considered together (the remaining 10%).
- Even though the annual National Ambient Air Quality Standards for  $PM_{10}$  and  $PM_{2.5}$  are met for both size fractions at all sites, except for the former at the Salt River Senior Center, various components of these particles still pose a legitimate lifetime health threat.
- Three of the six species of airborne particulate matter with chronic, health-based guidelines exceeded these levels in metropolitan Phoenix in 2005: arsenic, cadmium, and diesel particulate matter.
- Concentrations of both gaseous and particulate species were generally higher in the urban core than in the two more peripherally situated tribal sites.
- Depending on the site and particulate species, urban core and tribal concentrations of particulate air toxics were enriched three to 40 times above background.

# 6.0 Appendix A. Meteorological Modeling

This appendix retains the table and figure numbers of the original memorandum (7); as a scanned document, however, page numbers of the present report have been substituted for the original ones.

# ENVIRON

### MEMORANDUM

To:	Leonard Montenegro, ADEQ; and Dennis Pagano, USEPA
From:	Chris Emery
Date:	27 January 2009
Subject:	Development of Gridded Meteorological Fields for the JATAP Study Utilizing CALMET and MM5

### Introduction

The Joint Air Toxics Assessment Project (JATAP) is a consortium of federal, state, local, and tribal air pollution control officials designed to address the risk from air toxics in the greater Phoenix Metropolitan area. Participants include the U.S. Environmental Protection Agency (EPA) Region 9, the EPA Office of Air Quality, Planning, and Standards (OAQPS), Arizona Department of Environmental Quality (ADEQ), the Maricopa County Environmental Services Division, the Pinal County Air Quality Control District (PCAQCD), the Intertribal Council of Arizona, the Gila River Indian Community (GRIC), the Salt River–Pima Maricopa Indian Community (SRPMIC), and the Fort McDowell Yavapai Nation. The purpose of the study is to determine which air toxics are of most concern to South Phoenix and tribal communities. The measurements made in 2005 are the second phase of the study. Phase I consisted of air toxics measurements at the South Phoenix and West 43rd Avenue sites from August 2001 through March 2004. The ultimate goal of this consortium is to obtain a metropolitan-wide assessment of the risk associated with airborne toxics in greater Phoenix.

The Arizona Department of Environmental Quality (ADEQ) intends to conduct air quality modeling to analyze source contributions to hazardous air pollutants (HAPs or toxics) at monitor locations within Phoenix and on nearby tribal lands. The modeling will be used for human exposure assessments. ADEQ is considering conducting this study in two phases:

- <u>Phase I</u>: Use AERMOD in a screening-mode assessment of major point sources "near" (< 10 km) each receptor (monitor) to identify contributions of specific facilities to human exposure; and
- <u>Phase II</u>: Expand the assessment to urban-wide on-road mobile sources (and possibly other sources).

ENVIRON has proposed using a photochemical grid model (CAMx) for the broader-scale modeling to be conducted in Phase II<sup>1</sup>. As a prerequisite to estimating on-road and biogenic emissions, as well as performing the gridded chemical modeling for Phase II, ADEQ requires gridded meteorological data fields to be produced. In ongoing discussions with ADEQ, ENVIRON has proposed utilizing data from Mesoscale Meteorological Model (MM5) annual simulations and local/regional meteorological observations, which are combined using the CALMET diagnostic model, to produce the high-resolution gridded inputs for the CAMx model. This Technical Memorandum documents the approach and data sources, and summarizes the results.

#### Work Tasks

The objective of the this work was to develop high resolution gridded meteorological files for the entire year of 2005 that encompasses the Phoenix Metropolitan Area to support the Phase II emissions and CAMx modeling work associated with the JATAP human risk assessment. Figure 1 shows the geographic extent of the various non-attainment areas that cover the Phoenix Metropolitan Area and the State of Arizona.

ENVIRON performed the following tasks in developing the meteorological fields:

- A modeling domain was developed that encompasses the Phoenix Ozone Non-Attainment Area to facilitate the use of pre-existing photochemical precursor emissions inventories;
- Hourly MM5 data fields covering the entire modeling domain at 12 km grid spacing were extracted and formatted for CALMET for the entire year of 2005 (January 1 to December 31);
- Hourly local meteorological data from a National Weather Service dataset were extracted and formatted for CALMET for the entire year of 2005;
- Hourly local meteorological data from the Maricopa Flood Control District's meteorological monitoring network were procured and formatted for CALMET for the entire year of 2005;
- CALMET version 5.8 was run in two ways to develop gridded data fields for the modeling domain:
  - An integrated observation-MM5 mode;
  - o An MM5-only mode;
- Quality assurance review was performed on the input data and on the final output data sets.

A more detailed discussion of each task is presented below.

<sup>&</sup>lt;sup>1</sup> Emery, C., G. Mansell, G. Yarwood, A. Pollack. 2008. Draft White Paper: Modeling Hazardous Air Pollutants in Phoenix. Prepared for Leonard H. Montenegro, Arizona Department of Environmental Quality, Phoenix, AZ. Prepared by ENVIRON International Corporation, Novato, CA (February 21, 2008).



Figure 1. Arizona regional map with regulatory air quality area designations.

### **Technical Approach**

### Modeling Domain Development

In developing a modeling grid for this project we wanted to ensure that the Phoenix metropolitan area and its surrounding areas were covered by the final domain. In addition, we wanted to ensure that the domain dovetailed with additional projects that have and will be completed in the area. As a result we decided to utilize the <u>Universal Transverse Mercator (UTM) projection</u> domain that was developed for the latest ozone SIP submission and covered the current Maricopa 8-hour ozone non-attainment area shown in Figure 1.

The final modeling domain was defined as having a southwest corner origin of 297 km Northing and 3652 km Easting, consisting of 29 by 50 grid cells with 4 km spacing (Figure 2). CAMx will be applied on this 4 km domain along with an additional 1 km nested grid, as depicted by the white inset in Figure 2. This nested grid is intended to allow for high resolution modeling over the urban core of the Phoenix Metropolitan Area. While emissions have been developed for the 4 and 1 km grids, meteorological outputs have only been developed for the 4 km grid.

### Extraction of Gridded MM5 Data

In order to maximize three-dimensional data coverage over the modeling grid, and to ensure meteorologically "consistent" fields going into CALMET, we extracted 12-km gridded MM5 output fields that are being used to support concurrent regional ozone and particulate modeling for the Four Corners Air Quality Task Force. The data were extracted from January 1, 2005 through December 31, 2005 for a domain that covered the entirety of Arizona. Specifically, MM5 data were extracted for latitudes between 31°N and 37°N and longitudes between 104°W and 115°W. The extraction process was completed utilizing CALMM5, a preprocessing program that extracts and reformats three dimensional gridded data from MM5 outputs specifically for CALMET. For this project CALMM5 version 2.6 (build 060330) was used to produce CALMET ready files. The resultant gridded "soundings" were used as a first guess in CALMET. This process will be discussed further in the CALMET section of this document.

### Surface Meteorological Observations

In addition to the inputs derived from MM5, regional/local meteorological observations were obtained to fill in gaps between the 12-km meteorological model "soundings" and to ensure that local small-scale influences were appropriately reflected in the CALMET fields. In order to accurately describe the local weather for each day and hour of 2005, multiple surface observations were obtained for locations distributed throughout the modeling domain, with particular emphasis on choosing sites that filled otherwise data-sparse areas. The observations used in the CALMET processing were derived from two sources. The first was the NWS/NCAR DS472 dataset, and the second was the Flood Control District of Maricopa County. Each of the data sources had to be processed separately due to vastly differing collection methodologies and data formats. A discussion of each follows. Additionally, both surface observation dataset were

Page 4



**Figure 2**. JATAP meteorological modeling domain; this domain is consistent with the latest ozone SIP and consists of 50 by 29 4-km grid cells. The white inset indicates the coverage of a 1 km nested grid to be used in CAMx.

quality controlled to ensure completeness and reasonability. This process ensured that data were within reasonable bounds for the given observations and that sufficient hours of station data were available to produce a reasonable description of the meteorological condition in area.

### DS472

The DS472 dataset contains hourly meteorological observations for all Canadian and United States airfields and includes approximately 1000 stations in total. The dataset includes a wide array of meteorological parameters, including surface sir temperature and dewpoint, surface pressure, surface wind speed/direction, visibility, cloud information, among others. It is updated half yearly and was available for all of 2005. For the purpose of this analysis, temperature, dew point and pressure were extracted for 5 stations throughout the Phoenix metropolitan area. The stations utilized were KGYR (03186), KIWA (23104), KLUF (23111), KPHX (23182) and

KSDL (03192). These specific stations were chosen because they were dispersed throughout the region. The stations are mapped in Figure 3 below as purple starred dots. After extracting the station data from the DS472 database, the data were quality controlled and reformatted for use with CALMET. The reformatting was accomplished utilizing a two step process, first converting the native DS472 format to the NCDC's Solar and Meteorological Surface Observational Network format. This format is supported by the CALMET SMERGE preprocessor, which was utilized as step two to develop CALMET-ready surface observations.

### Maricopa Flood Control District

The Maricopa County Flood Control District maintains a network of 24-hour rain, stream and weather stations that provide "real-time" information on rainfall, floods and weather conditions in Maricopa County. The network operates in the National Weather Service ALERT (Automated Local Evaluation in Real Time) format. The ALERT system uses "automatic" telemetry gauges for data collection. The gauges transmit their information to the District base computers via VHF radio. The computers then compile the information and maintain a data record. The Flood Control District started the ALERT system in 1980 and currently maintains a network of 302 automatic rain gages, 154 automatic stream gages, and 32 automatic weather stations throughout Maricopa and neighboring counties.

Due to the vast regional extent of the network and its long established nature, we concluded that utilizing data from the Flood Control District would provide additional reliable surface observations for use in CALMET. ENVIRON contacted the District's Volunteer Observer Coordinator and gained access to data from 6 meteorological stations that provided hourly or sub-hourly observations. The stations were chosen because they were widely spaced and would help accurately characterize the surface weather patterns in the outer areas of the domain. Figure 3 shows the locations of the Flood Districts Stations (red starred dots) that were used in this analysis. The data were quality controlled and reformatted for use with CALMET, similarly as described for DS472 data.

#### CALMET Set-up and Options

The CALMET model was first run to integrate the mesoscale meteorological (MM5) model output fields at 12 km spacing and observational data from the 11 surface meteorological stations. The 12 km MM5 data were specified to be used as the initial guess field (IPROG=14). CALMET then performed a "Step 1" procedure that included accounting for diagnostic wind model effects using the 4 km terrain and land use data to simulate blocking and deflection, channeling, slope flows, etc. USGS 1:250,000-Scale Land Use and Land Cover (LULC) data, and USGS 1-degree Digitized Elevation Model (DEM) data were used for land use and terrain input fields. In "Step 2" of the CALMET modeling, the surface meteorological observations were incorporated into the Step 1 wind fields.



**Figure 3**. MM5 grid points (black dots) and surface observation locations (colored stars) utilized in the analysis: DS472 data sites are mapped in purple and Maricopa County Flood District Sites are mapped in red.

CALMET was then run a second time using just the MM5 three-dimensional data, without any additional observations. This run was performed to identify the impact of including the relatively sparse observation data among the much higher density of MM5 grid points. Because MM5 is a prognostic model, it does not exactly replicate observations on a site-by-site and hourby-hour basis. Therefore, deviations from actual conditions can occur, and when combined with observational data in an interpolative, diagnostic manner such as CALMET, there can be many hours where the few observations generate "bullseyes" (circular depressions or bulges) in the meteorological fields. This has been commonly reported by EPA and the federal land managers from their Class I assessments. A far better approach is to use "nudging" in MM5 to control model drift from actual conditions; this is a process (as used in the Four Corners MM5 application) where observational data are used to nudge the model to observations in time and space, allowing the model to respond in a mass-consistent fashion.

Photochemical grid models such as CAMx rely on self-consistent meteorological fields that

properly characterize the three-dimensional state of the atmosphere in terms of winds and density (i.e., temperature, pressure, and moisture). These models are not particularly sensitive to relatively small, mostly uniform biases in temperatures (within ~2-5 K) and winds (within ~2 m/s, 30 degrees) relative to observed conditions, especially for seasonal and annual applications. Photochemical models are far more sensitive to small-scale density and momentum gradients and inconsistencies since they adjust for these by modifying local vertical wind profiles. Resulting vertical motion perturbations can be quite large, and can result in detrimental impacts to three-dimensional transport patterns. Therefore it was necessary in this project to gauge the extent to which the observational data generated such inconsistencies.

The CALMET modeling system has numerous options that need to be specified. These options were defined following EPA-recommended regulatory default options as given by Atkinson and Fox (2006), with exceptions that are explained in the bullets below. Table 1 below lists the EPA-recommended regulatory default options and the option definitions that were used in the project; deviations from EPA-recommended defaults are indicated by bold in Table 1 and are as follows:

- The EPA-recommended default is not to use any MM5 data (IPROG=0), whereas, for this project, 12 km MM5 data were utilized (IPROG=14). Use of MM5 data is believed to produce more representative meteorological fields and is now encouraged by federal land managers and EPA. Input MM5 data frequency is 1 hour (ISTEPPG).
- Because CALMET utilized a wealth of MM5 input data, IEXTRP was set to 1 to keep surface winds from being extrapolated to upper levels. The EPA recommended default (-4) is to extrapolate the surface wind observations aloft using similarity theory, which makes more sense if there is no MM5 data available.
- The maximum mixing height was set higher (4,500 m AGL) than the EPA-recommended regulatory default value (3,000 m AGL). Although a 3,000 m AGL maximum mixing height may be appropriate for the eastern U.S., mixing heights are higher in the western U.S. and therefore have been adjusted upward.
- The number of smoothing passes was ramped up from 1 to 4 over the lowest five layers, whereas EPA suggests 1 pass in the surface layer and 4 passes for all remaining layers.
- Several other new options are available in CALMET v5.8 that post-date the EPA recommendations these are denoted with "n/a" in the EPA default column. We set these parameters to CALMET default values.

Table 2 lists the vertical layer structure in CALMET. Twenty-four layers are set to match the input MM5 layer structure up to approximately 4000 m, which was set as the model top (and will be the top of CAMx). The only exception is layer 1, which CALMET requires to be set to 20) meters.)

Variable Description **EPA** Default Project Values **IBYR** Beginning year User Defines 2005 User Defines IBMO Beginning month 1 IBDY Beginning day **User Defines** 1 **User Defines** 0 **IBHR** Beginning hour User Defines 7 (MST) IBTZ Base time zone User Defines IRLG Number of hours to simulate 24/day IRTYPE Output file type to create (1 = all fields) 1 1 LCALGRD Are 3-D w-components and temperature needed? Т Т User Defines UTM PMAP Map projection UTM Zone **User Defines** 12 **IUTMZN** North UTMHEM **UTM Hemisphere** User Defines NAS-C DATUM Datum-region for output coordinates **User Defines** 50 User Defines NX Number of east-west grid cells Number of north-south grid cells **User Defines** 29 NY DGRIDKM Grid spacing **User Defines** 4 km User Defines 297km XORIGKM Southwest grid cell X coordinate 3652km User Defines YORIGKM Southwest grid cell Y coordinate 24 Number of vertical Layers **User Defines** NZ ZFACE See Table 2 User Defines Vertical cell face heights (NZ+1 values) Save met data fields in an unformatted file? Т т LSAVE **IFORMO** Format of unformatted file (1 for CALPUFF) 1 1 Observation data mode (1 = use surface sites, use 1 1 NOOBS MM5 data aloft w/o upper air observations) 0 NUSTA User Defined Number of upper air data sites 11 NSSTA Number of stations in SURF.DAT file **User Defines** User Defines NPSTA Number of stations in PRECIP.DAT 0 User Defines 0 NOWSTA Number of over-water surface stations Are cloud data to be input as gridded fields? (0 = no 0 ICLOUD 0 cloud information processed) 2 Format of surface data (2 = formatted) 2 **IFORMS** Generate winds by diagnostic wind module? (1 = Yes) 1 IWFCOD 1 Adjust winds using Froude number effects? (1= Yes) 1 1 **IFRADJ** 0 0 **IKINE** Adjust winds using Kinematic effects? (1 = Yes) Use O'Brien procedure for vertical winds? (0 = No) IOBR 0 0 **ISLOPE** Compute slope flows? (1 = Yes) 1 1 Extrapolate surface winds to upper layers? (-4 = use **IEXTRP** similarity theory and ignore layer 1 of upper air station -4 1 data; 1 = no vertical extrapolation of surface winds) 0 ICALM Extrapolate surface calms to upper layers? (0 = No) 0 NZ\*0 NZ\*0 BIAS Surface/upper-air weighting factors (NZ values) Using prognostic or MM-FDDA data? (0 = No, 14 = use IPROG 0 14 MM5 as first-quess field) ISTEPPG 1 Timestep of input MM5 data (hours) n/a F Use varying radius to develop surface winds? F LVARY RMAX1 User Defines 75 Max surface over-land extrapolation radius (km) RMAX2 Max aloft over-land extrapolations radius (km) **User Defines** 75 100 RMAX3 Maximum over-water extrapolation radius (km) User Defines 0.1 RMIN Minimum extrapolation radius (km) 0.1 TERRAD User Defines 12. Radius of influence of terrain features (km) 10.0 **R1** Relative weight at surface of Step 1 field and obs User Defines

 Table 1. CALMET configuration used in the JATAP project and comparison with EPA regulatory default settings as given by Atkinson and Fox (2006). (Deviations from EPA recommended defaults are indicated by **bold text.**)

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Page 9

Variable	Description	EPA Default	Project Values	
R2	Relative weight aloft of Step 1 field and obs	User Defines	25.0	
DIVLIM	Maximum acceptable divergence	5.E-6	5.E-6	
NITER	Maximum deceptable divergence minimization	50	50	
NSMTH	Number of passes in smoothing (NZ values)	2,4*(NZ-1)	1,2,2,3,3, 4*(NZ-5)	
NINTR2	Max number of stations for interpolations (NA values)	99	99	
CRITEN	Critical Froude number	1	1	
ALPHA	Empirical factor triggering kinematic effects	0.1	0.1	
IDIOPT1	Compute surface temperatures from observations (0 = yes)	0	0	
ISURFT	Surface station to use for surface temperature (between 1 and NSSTA)	User Defines	11	
IDIOPT2	Compute domain-average lapse rates? (0 = yes)	0	0	
IUPT	Station for lapse rates (between 1 and NUSTA)	User Defines	1	
ZUPT	Depth of domain-average lapse rate (m)	200	200	
IDIOPT3	Compute internally initial guess winds? (0 = True)	0	0	
IUPWND	Upper air station for domain winds (-1 = 1/r**2 interpolation of all stations)	-1	-1	
ZUPWND	Bottom and top of laver for 1st guess winds (m)	1,1000	1,1000	
IDIOPT4	Read surface winds from SURF.DAT? (0 = True)	0	0	
IDIOPT5	Read aloft winds from UPn.DAT? (0 = True)	0	0	
CONSTR	Neutral mixing height B constant	1.41	1.41	
CONSTE	Convective mixing height E constant	0.15	0.15	
CONSTN	Stable mixing height N constant	2400	2400	
CONSTW	Over-water mixing height W constant	0.16	0.16	
FCORIOL	Absolute value of Carioles parameter	1.E-4	1.E-4	
IAVEZI	Spatial averaging of mixing heights? (1 = True)	1	1	
MNMDAV	Max averaging radius (number of grid cells)	1	1	
HAFANG	Half-angle for looking upwind (degrees)	30	30	
ILEVZI	Laver to use in upwind averaging (between 1 and NZ)	1	1	
IMIXH	Convective mixing height method (-1 = Maul-Carson for land cells only	n/a	-1	
THRESHL	Threshold buoyancy flux	n/a	0.05	
DPTMIN	Minimum capping potential temperature lapse rate	0.001	0.001	
DZZI	Depth for computing capping lapse rate (m)	200	200	
ZIMIN	Minimum over-land mixing height (m)	50	50	
ZIMAX	Maximum over-land mixing height (m)	3000	4500	
ZIMINW	Minimum over-water mixing height (m)	50	50	
ZIMAXW	Maximum over-water mixing height (m)	3000	4500	
ITPROG.	3-D temperature interpolation (1 = use surface data and MM5 data aloft)	n/a	1	
IRAD	Form of temperature interpolation (1 = 1/r)	1	1	
TRADKM	Radius of temperature interpolation (km)	500	500	
NUMTS	Max number of stations in temperature interpolations	5	5	
IAVET	Conduct spatial averaging of temperature? (1 = True)	1	1	
TGDEFB	Default over-water mixed layer lapse rate (K/m)	-0.0098	-0.0098	
TGDEFA	Default over-water capping lapse rate (K/m)	-0.0045	-0.0045	
JWAT1	Beginning land use type defining water	999	999	
JWAT2	Ending land use type defining water	999	999	
Layer Index	Layer Interface (m)	Layer Thickness (m)		
-------------	---------------------	---------------------	--	--
24	4210	570		
23	3640	530		
22	3110	510		
21	2600	390		
20	2210	280		
19	1930	270		
18	1660	180		
17	1480	180		
16	1300	170		
15	1130	170		
14	960	170		
13	790	80		
12	710	80		
11	630	80		
10	550	80		
9	470	80		
8	390	80		
7	310	80		
6	230	70		
5	160	40		
4	120	40		
3	80	40		
2	40	20		
1	20	20		
0	0	Surface		

Table 2. CALMET vertical layer structure used in JATAP meteorological modeling.

#### **Evaluation of CALMET Output**

CALMET-generated fields of winds, temperatures, and boundary layer heights were evaluated by animating these fields in several vertical layers over the course of the 2005 simulation year. This process was performed for both the CALMET MM5-only run and the CALMET MM5+observation run. Since surface data were the only source of observations used in the latter run, and CALMET was instructed not to extrapolate observed winds aloft, the wind fields in layer 2 and higher reflected the MM5-only patterns in both runs. The CALMET-induced terrain impacts on the horizontal winds were strongest near the surface, and quickly decreased with altitude such that the CALMET winds were entirely based on un-modified MM5 input wind fields within about 3-6 layers, depending on the inversion strength.

Temperatures through the boundary layer represented a blend of MM5 and observations, but were entirely based on the MM5 input fields above the boundary layer. In general, MM5 tended to under predict daytime temperatures, and thus the CALMET run with observations generated a warmer daytime boundary layer than the MM5-only run. Interestingly, the PBL heights were very similar among the two CALMET configurations, even though the PBL temperatures were often different by as much as 5 C.

The CALMET results were specifically analyzed to evaluate the impact of observations on the CALMET-derived MM5 first guess fields of winds and temperature, and their impacts on PBL

depth and vertical velocity. As stated above, MM5 tended to under predict daytime temperatures by several degrees (C) much of the year, which is consistent with our experiences with MM5 in dozens of applications across the U.S. Additionally, MM5 exhibited some error in replicating wind speed and direction at times, but did well in replicating the synoptic-scale influences on winds over Phoenix since MM5 was nudged toward coarse (~40-km) observational analyses prepared by the NWS. Therefore, differences in wind speed/direction did not appear to be as consistently problematic as for temperature, except when some obvious issues were noted in the observed winds at certain sites.

Figure 4 shows a particular hour on May 28, 2005 in which local differences between the MM5 and observational data are particularly large for both temperature and winds. In the CALMET MM5+observation run, note that the temperature field is dominated by two observation points reporting rather different temperatures at this hour (Figure 4a). The temperature field around the two sites shows the "bullseye" effect due to their temperature differences, and result in artificial interpolation patterns well away from them. The run including observations is fairly constant across the domain well away from the two observation sites (indicating that only two sites reported valid data at this hour), with no obvious altitude cooling effect in the higher terrain to the north and east. In CALMET, the temperature observations completely replace the MM5 temperatures at the surface and tend toward the MM5 fields aloft (MM5 temperature are used solely above the boundary layer). In contrast the MM5-only run is cooler by a few degrees on the valley floor, although it exhibits a more believable spatial pattern devoid of obvious interpolation artifacts; the effects of higher terrain to the northeast are obvious.

Note also that the wind field is impacted by a rogue wind observation in the southeast portion of the domain (Figure 4b). This effect on the winds is completely removed in layers 2 through 24, where the observations are not used whatsoever. Terrain deflections on the wind field away from the rogue data site are evident in both runs, and exhibit blocking effects on the valley floor due to a stabilizing boundary layer.

The observation "bullseyes" in both temperature and wind fields raise concern for causing artificial PBL mixing and three-dimensional transport patterns. These were further evaluated by plotting PBL heights and vertical velocity patterns. Figure 5 shows both at the same hour as the plots in Figure 4. The PBL depth shows a local maximum over the wind/temperature observation site in the southeast, which is much higher than surrounding areas and obviously not generated in the MM5-only run. Furthermore, the vertical wind at the top of layer 1 also exhibits a local maximum in the same area due to acceleration and deceleration patterns surrounding the same site. Since vertical velocity is determined form the vertical integration of horizontal accelerations from the ground up, this perturbation in vertical velocity propagates to the top of the model. At this hour, the observation data are causing artificial mixing and three-dimensional transport patterns in the local area.





Page 14



**Figure 4b.** CALMET layer 1 wind fields on May 28, 2005 at 21 LST: CALMET MM5-only run (top); CALMET MM5+observation run (bottom). Wind vectors are plotted every other grid cell and show both direction and speed (vector length), while the color patterns indicate wind speed.

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Figures 6 and 7 show temperature and wind comparisons for other dates and hours to give an example of some of the most egregious patterns arising from the use of the observations in combination with MM5. The temperature patterns are shown for May 20 at 09 LST and the MM5+observation run exhibits very large range of temperature impacted by the various sites with non-missing data. The wind patterns are shown for May 27 at 21 LST and indicate that MM5 missed the strong southwest winds in the southeastern portion of the domain. The impact of the resulting horizontal divergence/convergence patterns result in large vertical velocities in those areas.

We conducted standard quality assurance checks on the observational data, which include "neighbor" and minimum/maximum range checks to ensure that the data were within reasonable ranges on an hour-by-hour basis. It is a nearly impossible task to evaluate each and every data point throughout a year and establish if it is "acceptable" relative to the other observations in the domain. Indeed the observations that appear outside a reasonable range in the plots shown here are quite likely "valid"; this area is characterized by complex terrain and widely varying meteorology can and does occur across the domain at the same hour (effects of high elevation, localized thunderstorms, etc.). To invalidate observations would require in-depth knowledge of what exactly occurred at a given site at a given hour. Therefore, we are left with using the data at hand and relying on CALMET to perform the interpolations and to mix with the MM5 fields that deviate typically 10-20% from the observations. Much effort is required to "tune" CALMET by varying its multitude of control parameters to alleviate the most egregious patterns that result. In this project, we maintained these parameter settings at values recommended by EPA and federal land managers for regulatory and environmental impact assessments in complex terrain - these in turn have been defined according to a wealth of experiences by these agencies with CALMET over the past decades.

As stated earlier, much of the performance issues that we see in the CALMET MM5+observation run do not present problems for the associated CALPUFF model. However, we are concerned with these impacts on three-dimensional mass conservation and mass consistency calculations within Eulerian photochemical grid models such as CAMx. The EPA CMAQ model does not support the use of diagnostic models (such as CALMET) to generate meteorological input fields for these very reasons. While CAMx is designed to accommodate all types of meteorological models to maximize its flexibility across a wide spectrum of applications and available data, we strongly caution the use of diagnostic models.

As a result of our analyses, our recommendation is to use the CALMET MM5-only run as the source of meteorological input fields for JATAP CAMx regional toxics modeling. The MM5-only run has generated consistent wind and temperature fields in which the CALMET diagnostic routines are used to interpolate 12-km MM5 data to the 4-km CAMx grid while including stability-dependent terrain-adjustments that are important in an area characterized by complex topography. The MM5-only run, while reflecting the various biases and errors in the MM5 wind and temperature fields, are self-consistent and remove the "bullseyes" and related artificial spatio-temporal gradients brought about by mixing in observational data that can falsely impact transport patterns.

Page 16



**Figure 5a.** CALMET PBL heights on May 28, 2005 at 21 LST: CALMET MM5-only run (top); CALMET MM5+observation run (bottom).

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**Figure 5b.** CALMET layer 1 vertical velocity on May 28, 2005 at 21 LST: CALMET MM5-only run (top); CALMET MM5+observation run (bottom).



**Figure 6.** CALMET layer 1 temperatures on May 20, 2005 at 09 LST: CALMET MM5-only run (top); CALMET MM5+observation run (bottom).



**Figure 7a.** CALMET layer 1 winds on May 27, 2005 at 21 LST: CALMET MM5-only run (top); CALMET MM5+observation run (bottom). Wind vectors are plotted every grid cell and show both direction and speed (vector length), while the color patterns indicate wind speed.

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# 7.0 Appendix B. Averages, Non-Detects, and the Method Detection Level (MDL)

D. R. Helsel (2005) (reference 10 of this report) explains how best to calculate averages, and other measures of central tendency, from sets of measured environmental concentrations which contain copious non-detectable values. First he debunks the commonly used substitution methods, in which each non-detect is arbitrarily set to zero, one half of the method detection level (MDL), or to the MDL itself. Second, in Table 6.11, page 78, he offers the following recommendations for calculating averages plagued by numerous non-detects (Table 7.0-1).

	Amount of available data				
Percent non-detects	Fewer than 50 values	More than 50 values			
< 50%	Kaplan-Meier	Kaplan-Meier			
50-80%	Robust MLE or ROS	Maximum likelihood			
		Report only % above (or			
		below) a meaningful			
	Report only % above (or	threshold; do not present			
	below) a meaningful	summary statistics (e.g.			
> 80%	threshold; do not present	mean).			
	summary statistics (e.g.	For large data sets it may be			
	mean).	possible to calculate the			
		upper range of percentiles,			
		e.g. $90^{\text{th}}$ or $95^{\text{th}}$			

 Table 7.0-1
 Recommended Methods for Estimating Summary Statistics

At most monitoring sites in 2005 the air toxics measurements exceed 50 samples, the lone exception being the gaseous air toxics at Queen Valley, where 31 samples were collected and analyzed. Kaplan-Meier and regression on order statistics (ROS) could have been applied to the Queen Valley data; Kaplan-Meier and maximum likelihood estimation (MLE) to the other sites. For those data sets with 80% or more of non-detects, only the percentages of values below and above the MDL are reported; no central tendency statistics are calculated because of their unreliability. Although these statistical methods were not used in this work, the annual averages for those gaseous species with greater than 70% non-detectable values are reported as less than the average MDL (see Table 5.7-3). For particulate air toxics (Table 5.6-1) the annual average concentrations are reported as a range, with the lower value calculated by setting non-detectable values to zero and the upper value by setting non-detectable values to one half of the method detection level. Tables 7.0-2 and 7.0-3 give the percentage of non-detectable values for the gaseous and particulate air toxics from the 2005 air monitoring campaign.

_	Green-	Phoenix	Queen	Gila	Salt	South	West
Compound	wood	Supersite	Valley	River	River	Phoenix	Phoenix
1,3-Butadiene	0	0	81	88	68	23	17
Acetaldehyde	0	0	NM	NM	NM	2	0
Benzene	0	0	0	0	0	0	0
Carbon Tetrachloride	0	0	0	2	5	12	15
Chloroform	2	0	45	42	7	23	15
Dichloromethane	0	0	3	15	5	2	2
Ethylbenzene	0	0	6	22	3	7	7
Formaldehyde	0	0	NM	NM	NM	2	0
Hexachlorobutadiene	98	96	100	100	100	100	98
p-Xylene	2	0	6	9	0	5	3
m-Xylene	0	0	3	9	0	5	3
o-Xylene	0	0	13	20	3	5	5
Styrene	2	0	71	49	3	37	22
Tetrachloroethylene	0	0	16	71	63	45	38
Toluene	0	0	0	0	0	0	2
Trichloroethylene	10	16	61	92	75	83	80
Vinyl Chloride	98	100	100	85	97	97	97
n < 50%	15	15	11	10	10	14	14
n: 50 - 80%	0	0	2	1	3	0	0
n > 80%	2	2	3	4	2	3	3

**Table 7.0-2** Percentage of Non-Detectable Values for Gaseous Species (number of samples  $\approx 60$ )

NM = not measured

Table 7.0-3 Percentage of Non-Detectable	Values for Particulate Species (number of
samples $\approx 60$ )	

		Tonto	Gila	Salt	VEI	West
	Phoenix	National	River	River		Phoenix
Compound	Supersite	Monument				
Arsenic	42	34	34	47	36	46
Cadmium	62	NM	64	69	70	68
Elemental carbon	0	0	0	0	0	0
Organic carbon	0	0	0	0	0	0
NM - not measured						

NM = not measured

## 8.0 Appendix C. History of the Joint Air Toxics Assessment Project

Beginning as an idea to build partnerships between various government agencies that had had little contact with one another, officials in EPA's North Carolina Office of Air and Radiation in 1999 agreed upon a concept and wrote a document explaining their vision and goals. The support of these officials led to the eventual birth of the Joint Air Toxics Assessment Project (JATAP) in Arizona, which, with federal financial, administrative, and technical support, carried out a multi-year effort to characterize the health risk from air toxics in Phoenix. The governmental entities involved were, on the one hand, state, county, and local environmental agencies; and, on the other, their tribal counterparts, most notably two native American Indian communities: the Salt River Pima Maricopa and Gila River Indian Communities. Before JATAP these two sets of air pollution officials had seldom interacted. Twelve years after the initial idea this comprehensive report attempts to describe the project's technical findings, most of which are based on an extensive field campaign --conducted cooperatively between tribal and anglo staff and managers -- to measure air toxics concentrations in 2005 and early 2006. Subsequent work has consisted of various emissions, meteorological, and air quality modeling analyses. Community outreach needs to be the next step. A brief history of the project can be gleaned from the two following tables, the first being a short version of the second.

Year	Activity
1999 - 2000	USEPA Assistant Administrator for the Office of Air and Radiation and
	"Joint Statement on Vision and Goals": strategy to build partnerships
	among co-regulators through collaboration on specific projects.
2001	JATAP is formed
2001 - 2002	Blueprint for air toxics assessment of metropolitan Phoenix
2002 - 2003	More planning for an air toxics monitoring campaign
2003 - 2004	Pilot air toxics monitoring project (3 sites, S. PHX & Gila River I. C.)
2005 - 2006	Full-scale air toxics monitoring campaign (9 sites, gaseous & PM)
2006	Interpretation and analysis of gaseous air toxic concentrations in 2005
2008	Gridded emissions and meteorological fields for air quality modeling
2008 - 2010	PM air toxics and their risk; one report for gaseous and PM air toxics
2010	Emissions reanalysis with a more useful report
2009 - 2011	Air quality modeling
2010 - 2011	Comprehensive JATAP report

#### Table 8.0-1 Joint Air Toxics Assessment Project, a Brief Chronology

		-
Year	Activity	Remarks
1999 –		This group issued a report in
2000	USEPA Assistant Administrator for the	December 2000, titled "Joint
	Office of Air and Radiation convened a	Statement on Vision and Goals".
	planning group of senior federal, state.	Contained in this document was a
	local and tribal air quality directors to	strategy which included a key
	begin looking at a vision for air quality	element for building partnerships
	management for the next decade	among co-regulators through
	management for the next decade.	collaboration on specific projects
2001	The Joint Air Toxics Assessment	conaboration on specific projects.
2001	Droiget (IATAD) for the greater Dhooniy	
	Project (JATAP) for the greater Phoenix	
	area, the first multi-jurisdictional effort	
	to be undertaken in response to this	
	strategy, was formed with the	
	participants being the Arizona	
	Department of Environmental Quality,	
	Maricopa and Pinal Counties, U.S.	
	Environmental Protection Agency, Gila	
	River Indian Community, the Ft.	
	McDowell Yavapai-Apache Tribe and	
	the Salt River Pima-Maricopa Indian	
	Community. The Institute for Tribal	
	Environmental Professionals at	
	Northern Arizona University served as	
	the project manager with financial	
	assistance from EPA Region 9	
2001 -	Phase 1 of the JATAP provided a	One of the more difficult
2002	blueprint for a comprehensive air toxics	problems to overcome was
	assessment of the greater Phoenix	procuring chemistry laboratories
	metropolitan area. The blueprint was	that could provide Method
	developed with the guidance of a	Detection Levels (MDL) low
	Steering Committee made up of	enough to quantify several of the
	representatives from each of the	particulate and gaseous air toxics
	governments involved.	species.
2002 -	Phase 2 of JATAP consisted of selecting	*
2003	the compounds of interest, designing	
	the monitoring network, and writing the	
	quality assurance project plans for the	
	emission inventory and monitoring	
	activities This phase required	
	cooperation coordination and	
	collaboration among several different	
	antitias (three tribes, two counties, the	
	state and the federal accomments	
1	state, and the rederal government).	

 Table 8.0-2
 Joint Air Toxics Assessment Project, a Detailed History

Year	Activity	Remarks
2003 - 2004	ADEQ and the Gila River Indian Community jointly initiated an air toxics monitoring pilot project with support from EPA Region 9. It involved three monitoring sites south of downtown Phoenix, one of which was on the Gila River reservation and was operated by Gila River Indian Community personnel. Monitoring was conducted in 2003 and 2004.	Contractor builds an air toxics emissions inventory for the study domain and interprets the measurements, especially concerning the prevalence of concentrations below the Method Detection Level (MDL).
2005 - 2006	Air toxics monitoring field campaign, for both gaseous and particulate air toxics. A contractor analyzed the gaseous air toxics data and completed a report and gave one or more presentations to the JATAP interested parties.	"Analysis of Air Toxics Collected as Part of the Joint Air Toxics Assessment Project Final Report" STI-905039.03-3016-fr Sonoma Technology, Inc. prepared for the Arizona Department of Environmental Quality, Phoenix, AZ December 2006
2008	A contractor (ENVIRON) develops (1) a gridded emissions inventory, and (2) meteorological fields for subsequent air quality modeling for the JATAP	Memorandum from ENVIRON, a contractor, to Leonard Montenegro, ADEQ; and Dennis Pagano, USEPA, November 2008
2008 - 2010	Work proceeded on the risk assessment with analysis of particulate air toxics and their risk, complementing the earlier work on gaseous air toxics.	" Joint Air Toxics Assessment Project (JATAP) 2005: the Risk from Airborne Gaseous and Particulate Air Toxics in Metropolitan Phoenix", July 16, 2010
2010	This emissions analysis, which expanded on the work done by a contractor, was funded by the Gila River Indian Community and the Salt River Pima Maricopa Indian Community.	"Air Toxics Emissions in the Gila River Indian Community, in the Salt River Pima Maricopa Indian Community, and in metropolitan Phoenix, Arizona", prepared for the JATAP by R. Dimitrova and P. Hyde, 26 August 2010
2009 - 2011	Air quality modeling for 2005 Phoenix air toxics is carried out.	
2011	Comprehensive technical report is issued	"Phoenix Air Toxics Assessment Final Report", 30 September 2011

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