Urban Community Air Toxics Monitoring Project, Paterson City, NJ (UCAMPP)

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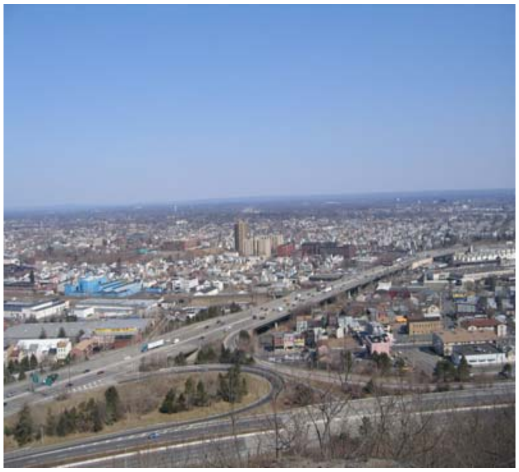

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This final report is dedicated to the memory of Randy England (NJDEP), whose contribution to setting up the monitoring sites and assuring safety at those sites was invaluable.

The Great Paterson Falls

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I. ACRONYMS

AIRS	Aerometric Information and Retrieval System
AQS	Air Quality Subsystem
ATSDR	Agency for Toxic Substance Disease Registry
BAM	Bureau of Air Monitoring
BAQEv	Bureau of Air Quality and Evaluation
BTS	Bureau of Technical Services
COC	Chain of Custody
Cr(VI)	Hexavalent Chromium, chromium VI
DEM	Digital Elevation Model
DNSH	Dansylhydrazine
DQA	Data Quality Assessment
DQI	Data Quality Indicator
DPM	Diesel Particulate Matter
DQO	Data Quality Objectives
DSRT	Division of Science, Research and Technology
EC	Elemental Carbon
EDD	Electronic Data Deliverables
EJ	Environmental Justice
USEPA	United States Environmental Protection Agency
ERG	Eastern Research Group, Inc.
EOHSI	Environmental and Occupational Health Science Institute
FRM	Federal Reference Method
GC	Gas Chromatography
GC/FID/MS	Gas Chromatograph/Flame Ionization Detector/Mass Spectrometry
GIS	Geographic Information System
HAP	Hazardous Air Pollutant
HI	Hazard index
HPLC	High Performance Liquid Chromatography
HQ	Hazard quotient
IC	Ion Chromatography
ICPMS	Inductively Coupled Mass Spectrometry
L	Liter
Lpm	Liters per minute
LULC	Land Use Land Cover
MB	Method Blank
MDL	Method Detection Limit
mg	milligram(s)
mL	milliliter(s)
MM5	Mesoscale Model 5
NCEP	National Center Environmental Predictions
ND	not detected
NESHAP	National Emissions Standards for Hazardous Air Pollutants

NOAA	National Oceanic Atmospheric Administration
NIST	National Institute of Standards and Technology
NJDEP	New Jersey Department of Environmental Protection
NJEMS	New Jersey Emissions Management System
NJDHSS	New Jersey Department of Health and Senior Services
nm	nanometer
OQA	Office of Quality Assurance
PAH	Polycyclic aromatic hydrocarbons
PAKS	Passive Aldehyde Ketone Sampler (uses DNSH for derivitization)
p-dichlorobenzene	1,4-dichlorobenzene
PM_{10}	Particulate Matter with aerodynamic diameter smaller than10 microns
ppbv	parts per billion (by volume)
PTA	Parents and Teachers Association
PUF	Polyurethane foam
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RfC	Reference concentration
RIOPA	Relationship of Indoor, Outdoor and Personal Air
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
RT	Retention Time
RTI	Research Triangle Institute
RUC	Rapid Update Cycle
SD	Standard Deviation
SOP	Standard Operating Procedure
SRM	Standard Reference Material
STP	Standard Temperature and Pressure
TAD	Technical Assistance Document
TO-11A	USEPA method for aldehydes uses DNSH for derivitization
UCAMPP	Urban Community Air Toxics Monitoring Project, Paterson City, NJ
URF	Unit risk factor
USGS	United States Geological Survey
UTM	Universe Transverse Mercator
VOC	Volatile Organic Compound(s)

II. EXECUTIVE SUMMARY

★Overall Objective/ Specific Aims

The overall objectives of the Urban Community Air Toxics Monitoring Project, Paterson City, NJ, (UCAMPP) was to provide information and develop tools and methods so that the NJDEP and communities can better address exposure and risk issues related to air toxics through the characterization of local air associated with different land use patterns in a highly industrialized urban community. Three air monitoring stations were set up on the rooftops of three buildings in Paterson, with the aim of capturing industrial, commercial and mobile source-dominated emissions over the course of one year. The background monitoring site was located ~45 km WSW of Paterson in Chester, NJ. UCAMPP's specific aims were to 1) characterize the spatial resolution of local air toxics; 2) determine concentration gradients; 3) identify source signatures from various land uses; 4) evaluate modeling results using monitoring data; 5) field test new sampling and analytical techniques for air toxics that are currently difficult to quantify; 6) characterize the concerns of an Environmental Justice (EJ) type community; 7) identify risk reduction strategies, and 8) implement feasible strategies. This study will serve as a pilot project and provide valuable information that can be applied to other communities around the state and the nation.

★Why was this project undertaken?

In 2003, NJDEP priorities included "Protecting Communities from Toxics". Also in 2003, the USEPA's competitive grant program "National Air Toxics Monitoring Program-Community Assessments" became available. This program was designed to fund pilot projects to help communities and governments develop tools and methods to help characterize, track and reduce air toxics. The UCAMPP project was ranked #1 nationwide out of approximately 60 submitted proposals.

★What was measured?

A total of 132 air toxics were targeted. This list includes 4 aldehydes, 48 elements, hexavalent chromium, elemental and organic carbon, 16 polycyclic aromatic hydrocarbons, PM_{10} mass, 60 volatile organic compounds and limited meteorological information. Monitoring began in November, 2005 and finished in December, 2006 at three sites in Paterson meant to represent commercial, industrial and mobile source dominated land use and at one background location in Chester, NJ, a rural site. Two of the sites in Paterson were located at Paterson public schools which allowed UCAMPP to measure ambient levels of air pollution that school children, a sensitive subpopulation, may be exposed to. Monitoring took place about every 6 days to try and coincide with the NJDEP air toxics monitoring program at other locations around the state. 89%-93% of the collected samples were considered valid.

★What was done with the data?

Descriptive and comparative statistics were computed. Comparative statistics looked for differences between; Paterson, an urban community, and the NJDEP rural background site in Chester, NJ; weekdays vs. weekends; the three sites in Paterson; and the seasons.

★ Results

✳For aldehydes, no differences were found except for acrolein which was higher on weekdays than weekends in Paterson. This is most likely due increased emissions during the week from anthropogenic activities.

✳As expected, the following air toxics had annual average concentrations that were statistically significantly higher in Paterson, (urban), than at the background (rural) site and higher concentrations on weekdays than on weekends in Paterson; aluminum, calcium, iron, magnesium, manganese, silicon, titanium, elemental carbon, fluoranthene, pyrene, dichloromethane, MEK, Methyl Isobutyl Ketone, MTBE, tetrachloroethylene, and toluene. This does not necessarily mean that these concentrations posed a health risk.

✳As expected, the following air toxics had statistically significantly higher concentrations in Paterson (urban) than at the background (rural) site but did not exhibit weekday/weekend differences; bromine, chlorine, copper, lead, nickel, potassium, sodium, strontium, vanadium, zinc, zirconium, organic carbon, all PAHs except benzo(b)fluoranthene, PM_{10} mass, 1,1 trichloroethane,1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,3-butadiene, acetylene, acrolein, benzene, chloroethane, chloroform, dichlorodifluoromethane, ethyl benzene, m,p-xylene, n-octane, o-xylene, p-dichlorobenzene, propylene, styrene, and trichlorofluoromethane. Overall, most annual average concentrations were highest at the commercial site, even if not statistically significant. This does not necessarily mean that these concentrations posed a health risk.

✳Only carbon disulfide and acetonitrile were higher at the background site than in Paterson and they did not pose a health risk.

✳Seasonal differences varied by compound. Acetylene, benzene, MTBE, benzo(a) pyene concentrations were higher in the winter in both Paterson and the background site. The following air toxics had concentrations that were higher in Paterson in the winter: bromine, chlorine, copper, iron, lead, nickel, zinc, zirconium, EC, OC, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(a,h,)anthracene. Levels of many air pollutants are elevated in the winter due to meteorology, e.g., low wind speeds and mixing height, higher frequency of inversions etc., and the increase in fuel combustion for space heating.

✹These results suggest the impact of anthropogenic activities on air quality in Paterson, provides evidence of an urban footprint and indicates Paterson air quality is not only influenced by mobile sources but that point and area sources are important contributors to air pollution in an urban environment like Paterson.

★Evaluate Modeling with Monitoring Data.

The results from a dispersion model, i.e., Calpuff, and NATA 2002 were compared to monitoring data. Results varied by pollutant. This report included an example of a newly developed model, Bayesian Maximum Entropy.

★ Characterize Air Quality in an Urban, Environmental Justice Type, Community.

✳Risk Assessment: Out of 132 air toxics that were selected to be measured during UCAMPP, only 1 compound measured at the commercial site in Paterson, p-dichlorobenzene, showed a significant increase in concentration during 2 months (Mid October through mid December, 2006) of the 14 month monitoring period. During that two month period, the levels of p-dichlorobenzene increased by up to three orders of magnitude over the levels observed during the twelve other months of monitoring. The last two measurements for p-dichlorobenzene obtained at the commercial site towards the end of December 2006**,** returned to the levels that were observed during the rest of the sampling period. Due to the time frame for sample analysis and data processing, the data showing both the increase and subsequent decrease in the levels of p-dichlorobenzene were received at the same time. While the concentrations observed during the period of elevation did not pose an immediate health risk to the community, as soon as NJDEP was aware of the spike in concentrations, staff worked to identify any potential sources by reviewing NJDEP databases, informing enforcement and modeling wind direction on those days. The investigation is on-going and NJDEP is working with local and county health departments to identify the source(s). NJDEP has applied for additional funding from USEPA to perform another year's worth of monitoring to determine if concentrations p-dichlorobenzene become elevated again or if this excursion was an isolated event.

If the annual average concentrations of p-dichlorobenzene, observed at the commercial site during the entire monitoring period that included the two-month elevation, continued for a 70 year lifetime exposure, the cancer risk would be 205 in a million. NJDEP uses 1 in a million as a health benchmark when assessing cancer risk. The cancer risk at the other sites in Paterson from p-dichlorobenzene ranged from 3-4 in a million with the background site having <1 in a million.

With the exception of p-dichlorobenzene at the commercial site, benzene is the major contributor to cancer risk with a risk ranging from 9 to14 in a million in Paterson. At the background site, benzene posed a risk of 4 in a million. Carbon tetrachloride was the major contributor to risk at the background site with a risk of 9 in a million. This is the risk for both the background and the three sites in Paterson. The same pattern held true for chloromethane, i.e., the risk is the same in Paterson as at other locations around the state. Other air toxics with risk levels above the NJDEP health benchmark of 1 in a million are chloroform (ranging from 4 to 8 in a million in Paterson vs. 2 in a million at the background site), ethyl benzene (ranging from 1 to 3 in a million in Paterson vs. < 1 in a million at the background site), 1,3-butadiene (ranging from 4 to 9 in a million in Paterson vs. <1 in a million at the background site), tetrachloroethylene (ranging from 3 to 4 in a million in Paterson vs. < 1 in a million at the background site) and arsenic (ranging from 6 to 7 in a million in Paterson vs. 4 in a million at the background site). For naphthalene, the cancer risk marginally exceeded the health benchmark with lifetime cancer risk at two sites in Paterson ranging from 1.3 to 1.1 in a million. The risk posed by nonmobile source generated air toxics, i.e., p-dichlorobenzene, tetrachloroethylene, chloroform, chloromethane, carbon tetrachloride and arsenic**,** show that although mobile sources are important risk drivers in an urban environment, area and point sources also contribute to the risk. There was no short term (24 hr) or long term (lifetime, i.e., 70 yr) exceedances of noncancer health benchmarks (e.g., Reference Concentrations) for any of the sites in Paterson or the background location.

Nine air toxics measured in Paterson had concentrations that were similar to concentrations measured at the other NJDEP air toxics monitoring sites around the state. These locations are: Camden, an urban residential site; Elizabeth, the mobile source site; and New Brunswick, the suburban site. Chester is also part of the NJDEP air toxics monitoring network as the NJDEP designated rural, background site. Since the same air toxics of concern in Paterson are the same air toxics of concern at other locations around the state, and the fact that they have concentrations within the same order of magnitude in Paterson as around the state, this indicates that our NJDEP monitoring network is able to capture and characterize over 90% of New Jersey's air quality issues. However, community based projects are still important to identify and characterize air quality issues specific to individual communities. Naphthalene, which was marginally above the health benchmark at two sites in Paterson, could not be compared to the other three NJDEP air monitoring sites because comparable measurements were not made at those sites.

There are many local state and federal programs that are specifically targeting many of these compounds to reduce concentrations and improve air quality. For example, local initiatives include bans on wood burning, and NJDEP programs include diesel retrofits, anti-idling legislation, and the dry cleaning rule, which will reduce the use of tetrachloroethylene. Federal programs (USEPA) include but are not limited to; cleaner motor vehicles, cleaner burning fuel, and cleaner wood burning stoves.

✳Implemented risk reduction strategies were based on outreach and education.

Formal presentations describing the project were made early in the study to students at PANTHER Academy in Paterson, about 70 Nurses from Paterson school district, Paterson school board, Paterson Environmental Revitalization Committee (PERC), New Jersey Clean Air Council, NJDEP's Air Toxics Steering Committee, NJDEP's Division of Air Quality, North East States for Coordinated Air Use Management (NESCAUM), Mid-Atlantic Regional Air Management Association, Inc., (MARAMA) and two USEPA sponsored conferences. Informal presentations were made to Paterson Community Health Center, Association of Community Organizations for Reform Now (ACORN) in Paterson, Hispanic Multi-Purpose Service Center, and Kamau Khalfani from the Learning Tree/WBAI, Passaic County Health Department and facility owners/managers during site visits.

Final results will be presented to USEPA Region 2, the Mayor of Paterson, federal, state and locally elected officials, local and county health departments, etc., in addition to interested community members, the NJ Clean Air Council, the Environmental Justice Advisory Council and any other interested parties.

✳A student intern module was developed for students at PANTHER academy. They attended a series of lectures, collected information on attitudes towards air pollution and received a stipend for their efforts.

✳During site visits, most risk reduction strategies were based on outreach and education on how to reduce air toxics. Two other risk reduction strategies were implemented. Three facilities bought multiple anti-idling signs for their facilities around the state. The other involved informing a facility that the crushing of fluorescent bulbs on site not only potentially emits mercury vapor but definitely creates a hazardous waste. Enforcement followed up and that facility stopped this practice.

★One of the many successes of UCAMPP was the ability to leverage state resources by using data that were collected and paid for by the NJDEP /USEPA at the background site as part of the state's on-going air toxics monitoring program, using equipment purchased with UCAMPP funds for other USEPA funded projects, using UCAMPP data to assist USEPA in their current School Air Toxics monitoring program, assisting New Jersey Department of Health and Human Services by delivering their occupational surveys during UCAMPP site visits, and directing the NJDEP funded survey "Awareness of and Exposure to Air Pollution in an Urban Environment" to be administered in Paterson.

★Conclusion/Recommendations/Lesson Learned**:**

One of the most important lessons is that the NJDEP air toxics monitoring network captures and characterizes over 90% of air quality issues in New Jersey, including urban community air quality. However, community based projects are still important to pinpoint local issues, such as the p-dichlorobenzene issue in Paterson.

For community based projects, it may be best to complete emissions inventory, site visits and screening type of modeling/monitoring before finalizing monitoring locations and targeting air toxics. Local meteorological measurements should be collected at every site. More detailed information on actual emissions in permits and emissions statements would have been helpful in compiling the emission's inventory. A more timely assessment of the data would be helpful to enforcement if there were issues that required their attention.

One lesson learned from this and previous projects is that unless there are preexisting community groups who have come together to specifically address air quality issues, it is difficult to organize a community group in a short (2-3 year) time frame.

USEPA has recognized this difficulty and provides two tier funding through their Community Action for a Renewed Environment (CARE); the first is to provide resources to organize the community and the second is to actually address some environmental concern. UCAMPP was not funded under the CARE grant program and did not have the resources to organize the community. However, the project was able to have many meetings with potential stakeholders (citizens/groups/ businesses) and provide basic outreach and education.

Another important lesson is that what is perceived is not always what the actual measurements show. For example, the commercial site was impacted more from stationary emissions than the industrial designated site; risk from air toxics in an urban environment are not driven only by mobile source air toxics; emissions inventory and modeling information can't always predict monitoring data; and generally, in Paterson, the air quality was similar to that observed around the state. Although mobile source air toxics, i.e., benzene, remain the largest risk driver in this urban community and around the state, area and point sources are important contributors to local air quality.

Finally, UCAMPP provided an excellent opportunity to gather information and determine which tools and resources are most valuable for community based air toxics projects. These tools will assist NJDEP, USEPA and other state and local governments in refining the scope of such projects to better utilize existing resources and expertise.

III. INTRODUCTION

A. Project Background/ Objectives

In 2003, the USEPA began a competitive grant program "National Air Toxics Monitoring Program-Community Assessments" in order to fund pilot projects which would help communities characterize, track and reduce air toxics. This solicitation required that applicants monitor for certain air toxics, i.e., benzene, carbon tetrachloride, chloroform, 1,3-butadiene, 1,2-dichlropropane (propylene dichloride), dichloromethane, tetrachloroethylene (perchloroethylene), trichloroethylene, vinyl chloride, arsenic, beryllium, cadmium, hexavalent chromium, lead, manganese, nickel, acetaldehyde, formaldehyde and acrolein. This requirement was meant to provide a consistent database for characterization of air toxics and analyses of long term trends. This occurred after NJDEP made "Protecting Communities from Toxics" one of it's top priorities. Both of these initiatives afforded the perfect opportunity for staff from the Division of Science Research and Technology (now known as the Office of Science in the Policy, Planning and Science program) to apply for USEPA funding for the 'Urban Community Air Toxics Monitoring Project, Paterson City, NJ (UCAMPP). The UCAMPP project was ranked #1 out of approximately 60 submitted proposals.

The general purpose of UCAMPP was to provide information and develop tools so that the New Jersey Department of Environmental Protection and communities could better address exposure and risk issues related to air toxics. The main objective of UCAMPP is to characterize local air toxics related to different land use patterns in a highly industrialized urban community. This objective was accomplished by strategically placing air toxics monitoring stations in community-oriented locations that attempted to capture industrial, commercial and mobile source dominated emissions. Two of the monitoring stations were located at Paterson public schools allowing UCAMPP to measure the community's potential for exposure, especially children, a susceptible subpopulation. Specifically, UCAMPP set out to: 1) characterize the spatial resolution of local air toxics; 2) determine concentration gradients; 3) identify source signatures from various land use(s); 4) evaluate modeling results using monitoring data; 5) field test new sampling and analytical techniques for air toxics that are currently difficult to quantify; 6) characterize air quality in an urban community; 7) identify and implement risk reduction strategies. This study serves as a pilot project to provide information that can be applied to other communities around the state and the nation.

Prior to UCAMPP, the Division of Air Quality initiated the Camden Waterfront South Air Toxics Pilot Project in Camden NJ. This Camden Waterfront South Air Toxics Pilot Project was the first NJDEP community based air toxics project. This project developed tools that were used and expanded upon during the UCAMPP project. During this time frame, the NJDEP also started on what was called Compliance and Enforcement Sweeps, first in Camden and then in Paterson. This afforded the opportunity to leverage resources and focus multiple efforts in one community. Paterson was chosen for this funding cycle because NJDEP wanted to have at least 3 community-based toxics projects, one in the south, the central and the northern part of the state.

B. Why Paterson ?

Paterson City (Paterson) in Passaic County, NJ, was chosen for this project because it is a mixed-use urban community with high population density that has many of the characteristics of an environmental justice community. The United States Environmental Protection Agency (EPA) defines environmental justice as "the fair treatment and meaningful involvement of all people regardless of race, color, national origin, or income with respect to the development, implementation, and enforcement of environmental laws, regulations, and policies. Fair treatment means that no group of people, including a racial, ethnic, or socioeconomic group, should bear a disproportionate share of the negative environmental consequences resulting from industrial, municipal, and commercial operations or the execution of federal, state, local, and tribal programs and policies."

Paterson was the first planned industrial city in the United States because of the energy available from the Great Paterson Falls. NJDEP had previously dedicated resources to this community. For example in December, 2003, NJDEP conducted 1400 inspections with 123 inspectors from NJDEP, USEPA, Passaic County and the Passaic Valley Sewerage Commission during a Compliance & Enforcement Initiative. This Initiative helped ensure inner-city residents equal protection under environmental laws. (http://www.state.nj.us/dep/enforcement/specialprojects.html). Additionally, the NJDEP has a $PM_{2.5}$ monitor located in Paterson. Paterson has many sources of air toxics from industrial (e.g., textiles; dyes; chemicals; metal fabrication, refinishing and recovery; plastics; printing; electronics; paper and food products, etc.), commercial (e.g., dry-cleaning, fast food restaurants, photo labs, commercial heating/boilers, salons, print shops, etc.), and mobile source (US I-80, Route 19 and County Routes 649, 639 and 648) dominated sectors. All of these areas either contain or are fringed by residential land use, allowing for neighborhoods scale air toxics monitoring.

Paterson has a disproportionately large percentage of families living at or below the poverty level, i.e., nineteen percent of the families in Paterson live at or under the poverty level compared to 6.3% for the state. Paterson has a high population density and rich ethnic diversity. According to 2000 U.S. Census data, there are about 149,000 residents, of which 1/3 are white, 1/3 black and the balance are some other race. Fifty percent of the population considers themselves to be Hispanic or Latino. In 2005, the population density in Paterson was over 17,210 people per square mile. If the population trends over the past two decades continue, then the population density could increase by an additional 500 people per square mile by 2010.

Paterson has more than three times the state average for hospitalization rates due to asthma (Wallace, 2003). A study in Paterson (Freeman et al., 2002) found that 21% of participating third graders had been diagnosed with asthma or related health problem. Paterson is located in Passaic County, which has the fifth highest hospitalization rate for asthma among New Jersey counties (NJDHSS, 2003). About twenty-five air toxics (Leikauf, 2002) could potentially be associated with asthmatic symptoms. UCAMPP monitored for about eleven of these air toxics. Ambient concentrations of these air toxics that may cause exacerbations of asthma are currently unknown although many of these have been measured in urban air around the nation. Additionally, the USEPA's 1996 National Air Toxics Assessment (NATA) identified fourteen air toxics which may cause elevated cancer and noncancer risks (NJDEP, 2003) in Passaic County. Of these fourteen air toxics, 1,2-dibromomethane and 1,3 dichloromethane were never detected during UCAMPP. UCAMPP did not measure diesel particulate matter (DPM) because there is no air monitoring method that can differentiate diesel particulate matter from other kinds of particulate formed from by the other types of combustion in an urban setting. The remaining eleven air toxics were measured during UCAMPP. Please see http://www.nj.gov/dep/airtoxics/passaic_96.htm for more detailed information.

C. Project Partners

In addition to the many different program areas within the NJDEP, partnerships were developed with the Environmental and Occupational Health Sciences Institute (EOHSI) and the Paterson School District.

Researchers at EOHSI have developed new and advanced techniques for measuring air toxics such as acrolein and hexavalent chromium. EOHSI also donated some of the equipment and the personnel necessary for sample collection, a portion of the sample/data analyses, and a small pilot study to field-test their new methods.

UCAMPP also partnered with the Paterson Public Schools District. They agreed to allow UCAMPP to place air toxics monitoring equipment on the roof at two of their public schools, to capture mobile and industrial source-oriented emissions. The NJDEP already had monitoring equipment at the background and commercial sites.

D. Outreach Efforts

Community based projects require outreach and education to the community. At least two of the specific aims of UCAMPP required some level of outreach and education to the community; 1) characterize the air quality of an urban environment; 2) provide information and develop tools so that the New Jersey Department of Environmental Protection (NJDEP) and the local community can better address exposure and risk issues related to air toxics.

1. Student Intern Module

A student intern module was designed and implemented as part of UCAMPP. The primary objective was outreach and education to the Paterson community. Specific goals included providing an opportunity to teach the students about 1) air toxics, 2) how to administer a survey and 3) to earn a stipend. Educational sessions included an overview of the UCAMPP project, explanation of what air toxics are, health effects, regulation, risk reduction strategies, employment opportunities, how to administer a survey, and a debriefing after the students completed the surveys. The survey was designed by Dr. Branden Johnson, a Research Scientist at NJDEP as a teaching tool. Dr. Johnson taught the educational sessions related to the survey. Seven students completed the survey component and received a stipend of $320.00 through PANTHER Academy. In 2007, the NJDEP funded Dr. Johnson to collect information in Paterson. The project was called "Awareness of and Exposure to Air Pollution in an Urban Environment" and was aimed to identify the degree and factors in Paterson residents' beliefs, attitudes and behaviors regarding outdoor air pollution, self-protection, and pollution reduction. A final manuscript is currently being prepared for submittal to a peer-review journal.

2. Additional Outreach Efforts

During this project, there were many opportunities for outreach and education. Formal presentations were made to students at PANTHER Academy, nurses and the school board of the Paterson School District, the Paterson Environmental Revitalization Committee, the New Jersey Clean Air Council, the NJDEP Air Toxics Steering Committee, the NJDEP Division of Air Quality, Northeast States for Coordinated Air Use Management (NESCAUM), the Mid-Atlantic Regional Air Management Association (MARAMA) and at two USEPA-sponsored Air Monitoring National Meetings. The project was discussed (no formal presentation) with the

Paterson Community Health Center, ACORN, the Hispanic Multi-Purpose Service Center, Kamau Khalfani from the Learning Tree/WBAI, Passaic County Health Department and facility managers/owners during site visits.

Site visits provided an excellent opportunity for outreach and education. Handouts were provided to the facilities which included USEPA pamphlets ("Reducing air pollution from…") the NJDEP hotline 1-877-WARN-DEP, and New Jersey's anti-idling regulations. Most people were not aware of the laws restricting idling.

After the final UCAMPP report has been approved by NJDEP and USEPA, the final results will be presented to any of the above-mentioned groups who are interested. Currently, the list includes but is not limited to; elected officials, Paterson school superintendent, school board, PTA, Paterson Act Congregations Together, NJDEP Air Toxics Steering Committee, NJDEP Air Summit, the NJ Clean Air Council, USEPA Region 2, NESCAUM, MARAMA, the USEPA National Air Monitoring Conference, New Jersey Environmental Justice Alliance, and the NJDEP Environmental Justice Advisory Council.

E. Site Selection

Since the overall objective of the Urban Community Air Toxics Monitoring Project, Paterson City, NJ, (UCAMPP) was to characterize local air toxics related to different land use patterns in a highly industrialized urban community, three air monitoring stations were set up on the rooftops of three buildings in Paterson with the aim of capturing industrial, commercial and mobile source-dominated emissions over the course of 1 year. These locations were chosen because of their proximity to industrial, commercial and mobile sources and to: 1) characterize the spatial resolution of local air toxics; 2) determine concentration gradients; and 3) identify source signatures from various land uses.

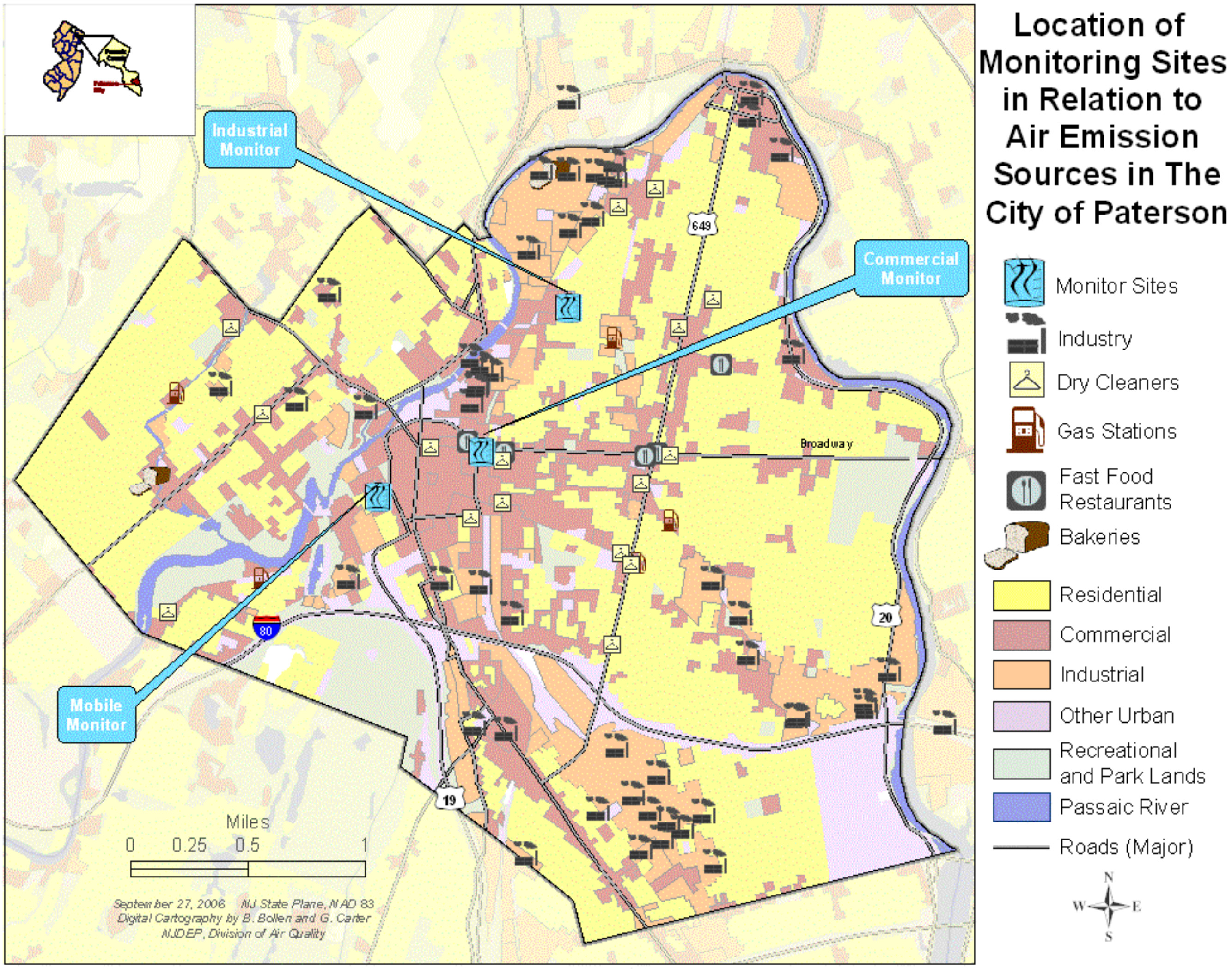
Paterson is roughly 6 km in diameter and is composed of sectors that are dominated by industrial, commercial and mobile sources in which residential units are scattered throughout. Potential monitoring locations were determined using Geographic Information System (GIS) layers of population density, and source location and identification obtained from an emissions inventory developed specifically for this project. Land use, school locations and a wind rose (see Figure 1) were also used to assess potential monitoring sites. The final three locations in Paterson were selected were based on accessibility (flat roofs, maneuverable stairs, access on weekdays and weekends), safety and security for field staff and equipment, and proximity to industrial, commercial and mobile source-oriented land use. Although the best approach for community exposure monitoring is to collect samples around 1.5 to 2 meters above ground, the monitors were placed on the roof /upper floor of the buildings due to limited availability of ground level space in an urban environment and the safety and security of the equipment and field sampling staff. The three monitoring sites were located around Paterson at the neighborhood spatial scale, i.e., approximately 0.5 km to 4.0 km from each other. In order to assess whether an urban environment is more polluted than non-urban areas, a non-urban background site was sited for comparison at the NJDEP air toxics monitoring site located in Chester NJ. This site has been operating since 2001 and is about 58 km west/southwest of Paterson. The NJDEP Chester air toxics monitoring location was selected as the background site because it is generally upwind of Paterson and is the NJDEP-designated "background" monitoring station for the state air toxics network. Please note that in Chester, the monitoring occurred at 1.5 to 2 meters above ground.

Table 1 summarizes each of the sites and briefly describes why each was chosen as a background, commercial, industrial and mobile source dominated site. Following Table 1 is additional information about each site.

Table 1: Characteristics of monitoring sites and stations

Monitoring		Dominant Source	Sampler		Site Characteristics
Site	Location		Placement	Height	
Background	Chester	No identified local sources	NJDEP air toxics monitoring site	Ground level	- 58 km away from Paterson - Designated background site for State urban air toxics monitoring
Commercial	Paterson	Area sources	Top of local health department building	≈10m	- Near downtown, ~1/4 mile from the center of the commercial district in Paterson - major intersections, - close to active railway, -
Industrial	Paterson	Stationary sources	Roof of a public school	≈13m	- Heavily industrial impacted area known as Bunker Hill - near industrial facilities
Mobile	Paterson	Mobile sources	Roof of a public school	≈13m	- Close to US Route 80 & 19 and County Route 639, 673 & 648 - Near a NJ Transit Bus Depot

Figure 1. Map of Paterson, Sources and Monitoring Locations



September 27, 2006 NJ State Plane, NAD 83
Digital Cartography by B. Bollen and G. Carter
NJDEP, Division of Air Quality

1. Industrial Land Use/Stationary Source-Dominated Site

The industrial source-dominated site (I site) was located on the roof of Public School #10 (PS#10) at 48 Mercer Street in Paterson. Monitoring at the school allowed UCAMPP to measure ambient levels of air pollution that school children, a sensitive subpopulation, may be exposed to. This location is SSE (0.1 to 1 km) of a highly industrialized area known as Bunker Hill.

Local meteorology was measured at this site for part of 2006. This site is located in the northern section of the city.

48 Mercer Street, Paterson, NJ. Public School #10 (PS#10)
Industrial Source-Dominated Site (I site)

2. Commercial Land Use/Area Source-Dominated Site

The designated commercial source-dominated site (C site) was located at 176 Broadway, a four story building about 1/4 mile from the center of the shopping district in downtown Paterson. This site is surrounded by typical urban downtown sources such as fast food restaurants, commercial heating/boilers, major intersections and an active railway. The site has housed the NJDEP $PM_{2.5}$ monitor since November 1998.

176 Broadway, Paterson, NJ. Paterson's Public Health Department
Commercial Source- Dominated Site (C site)

3. Mobile Land Use-Dominated Site

The designated mobile source-dominated site (M site) was located at 22 Passaic Street on the roof of a three story building, Public School # 2 (PS#2). Monitoring at the school allowed UCAMPP to measure ambient levels of air pollution that school children, a sensitive subpopulation, may be exposed to. PS#2 is located between 0.1 km to 0.8 km from major mobile sources such as U.S. Interstate Route 80, Route 19, and a major NJ Transit Bus Depot, and is surrounded by County Routes 639, 673 and 648. This site is located in the southwestern part of the city.

22 Passaic Street, Paterson, NJ. Public School #2 (PS#2)
Mobile Source Dominated Site (M site)

4. Background Site

The background site was located thirty-six miles WSW of Paterson in Chester, New Jersey. Chester is the NJDEP designated background/rural site for the federal Urban Air Toxics Monitoring Program (UATMP) and it not expected to be influenced by any urban sources. Additional monitors were set up at this site to match the monitoring systems at the Paterson sites. Please note that these monitors were at ground level.

Chester, N.J. Background Site (B site)

F. Sampling Schedule

Sampling was conducted from November 18, 2005, to December 20, 2006 by the EOHSI team with assistance from NJDEP. Sampling frequency was one in every six days to avoid collecting multiple samples that have been influenced by a single episode or event (e.g., release or inversion) and to coincide with the UATMP monitoring conducted by NJDEP (at Chester, Camden, Elizabeth, and New Brunswick). The UCAMPP Data Quality Objectives sampling goal was 44 weekday and 16 weekend measurements, for a total of 60 samples at each site throughout the year. Some scheduled sampling days were missed due to equipment malfunction and inability to access sites. Additional sampling days were added to get approximately the same number of weekday and weekend sample days in all four seasons. Between 197 and 206 samples for each group of air toxics were collected throughout this project. Please refer to Tables 17 and 18 for number of valid samples and seasonal/weekday/weekend breakdown.

G. Analyte Selection

UCAMPP identified a suite of air toxics from 1) an initial NJ emissions inventory; 2) the analytes targeted in the grant solicitation; and 3) analytes measured at the four existing NJDEP air toxics monitoring sites. Total number of analytes was limited by financial considerations. UCAMPP measured the same analytes, i.e., selected aldehydes, elements, hexavalent chromium, elemental and organic carbon, selected PAHs, PM_{10} mass and selected VOCs at all four sites. Please refer to Table 19 for the selected air toxics.

1. Emissions Inventory

The following is a list of databases and resources that were available which were used to construct the final emissions inventory for UCAMPP. Many of these databases have overlapping information because they were constructed for use in other programs, and not necessarily for air dispersion modeling. Only permitted sources are in the emissions inventory.

a. Facility site visits confirmed/clarified the information obtained from the sources listed below; identified any grandfathered sources not listed in any databases; speciated emissions by source; and allowed an opportunity for outreach/education and identification and implementation of risk reduction strategies.

b. A "Windshield Inventory" consisted of a drive through Paterson to identify sources not in databases, and eliminate sources that had closed but were still listed in the inventory as active.

c. NJDEP's 2005 Release and Pollution Prevention Report (RPPR): contains information obtained by the New Jersey Community Right To Know (RTK) program. This database is populated with actual stack and fugitive air emissions on a facility-wide basis. Emissions from individual sources within a facility (such as specific stacks) are not provided.

d. NJDEP's Emission Statement Program: actual emissions on a facility-wide basis for 36 Hazardous Air Pollutants (HAPS) from major sources. These HAPs were chosen for reporting from the HAP list in the Clean Air Act by NJDEP, based on prevalence and toxicity. 2005 data was used. It would be more useful if more than 36 HAPS were reported, emissions were listed by source instead of facility-wide, and all sources were required to submit Emission Statements, not just major sources.

e. New Jersey Emissions Management System (NJEMS): NJDEP's permitting database. It contains allowable (permitted) emissions, otherwise known as "potential to emit," and stack parameters. The database provides potential to emit emissions by Emission Unit for criteria pollutants only. Potential to emit for speciated HAPs is facility-wide and not stack or emission unit specific. It would be useful to have stack and emission unit specific information.

f. NJDEP's Site Masterfile: used to find the address and latitude and longitude coordinates for facilities included in the study.

g. USEPA's 2005 Toxics Release Inventory (TRI): provided facility-wide actual emissions. Emissions listed by source instead of facility-wide would be an improvement.

h. A facility's chemical usage (for 2005 and the first half of 2006) was used for generating and speciating emissions through MSDS, site visits and questionnaires. Information was sometimes limited due to "proprietary information."

i. NJDEP's Multi-Media Release Report (MMRR) database search engine compiles emissions from different NJDEP emission sources.

j. Emissions factors from USEPA (AP-42) were used for generating and speciating emissions. Speciation was based on source operations/category code. Often facilities had multiple codes or were not included in AP-42.

k. Stack test data from active facilities was obtained from the NJDEP Bureau of Technical Services (BTS).

l. USEPA's 2002 National Emissions Inventory (NEI): contains source-specific data.

m. For a limited number of facilities, NJDEP facility-specific air quality dispersion modeling was used to supplement the emissions inventory when applicable.

n. The 2005 Paterson Sweep was an enforcement action which inspected 227 facilities in Paterson. This effort assisted in identifying which facilities were still operating/had closed.

The above-mentioned databases identified 123 point sources and 53 other sources, such as bakeries, dry cleaners, fast food restaurants, gas stations, nail salons and small printing operations. 61 point sources and 11 "other sources" were eliminated due to one or more of the following: facility had closed; insufficient emissions; proximity to monitors; and lack of emission factors. All nail salons and small printing operations were removed because of a lack of emissions data. An informal phone survey of nail salons revealed that they were unwilling to provide information regarding number of employees, and many operators did not speak English. It was also observed that many salons were open one day and closed the next.

Site visits provided much of the information needed to complete a comprehensive emissions inventory. Many of the data sources listed above provided only limited permit and emissions information. For example, 1) only 36 HAPs are required to be reported by major facilities through the Emission Statement Program, 2) "potential to emit" information was usually significantly greater than a facility's actual emissions, 3) many permits listed "total VOCs" for the entire facility, and 4) permit reporting thresholds were not risk-based. Please note that currently NJDEP is working to increase the number of reported HAPs, improve speciated data, and revise permit reporting thresholds based on risk.

H. Monitored Analytes

132 air pollutants were measured during UCAMPP:

- 60 volatile organic compounds, using TO-15 method, analysis by ERG, Inc., a USEPA national contract laboratory;
- 48 metals using x-ray fluorescence, analysis by RTI, a USEPA national contract laboratory;
- EC/OC using thermal/optical transmittance carbon analyzer, by RTI;
- 4 carbonyls using Passive Aldehydes and Ketones Sampler Method (PAKS), a DNSH method by EOHSI (Zhang et al., 2000), additional acrolein measurement using TO-15 method, at the background site only, carbonyls using TO-11A, a DNPH method, both by ERG, Inc.
- 16 PAHs using USEPA TO-13 method, by EOSHI;
- Hexavalent chromium (EOHSI analysis method); (Fan., Z., et al., 2008)
- PM_{10} mass, by EOHSI, donated effort (40 CFR, part 50, appendix J).

Meteorological data was also collected at the I site for approximately 6 months. Due to the limited collection time, this meteorological data was of limited use.

IV. SAMPLING AND ANALYTICAL METHODS

The Partisol Speciation Sampler-Model 2300 (Thermal Fisher Scientific) was used for PM_{10} sample collection. The PM_{10} sampler has 4 channels. Two PTFE-coated inlets were used for elemental and hexavalent chromium analysis, and a clear anodized inlet was used for combined PAH and EC/OC collection. The fourth channel was used for duplicates. The sampling flow rate was 16.7 LPM, and the sampling period was from midnight to midnight, for a sampling duration of 24 hours, leading to sample volumes of around 24 m^3. Prior to each sampling event, the flow rate was checked by a Streamline flow meter (Thermal Fisher Scientific) to make sure the flow rate was equal to the designated flow rate of 16.7 LPM ± 5%.

Partisol Speciation Sampler-Model 2300

The canister method (TO-15) was used for VOC measurements, which included acrolein in 2006. The Passive Aldehydes and Ketones Sampler Method (PAKS) (Zhang et al., 2000; Herrington et al., 2005) was used to measure four aldehydes, including acrolein. At the background site, TO-11A was also used to measure aldehydes. In 2006, ERG, Inc., switched from TO-11A to TO-15 for the quantification of acrolein.

A. Aldehydes

During UCAMPP, the PAKS method (Zhang et al., 2000) was used for the measurement of formaldehyde, acetaldehyde, propionaldehyde, and acrolein. PAKS is a diffusive, tube-type sampler, which utilizes a dansylhydrazine (DNSH)-coated silica-based bonded C_{18} sorbent to collect airborne aldehydes.

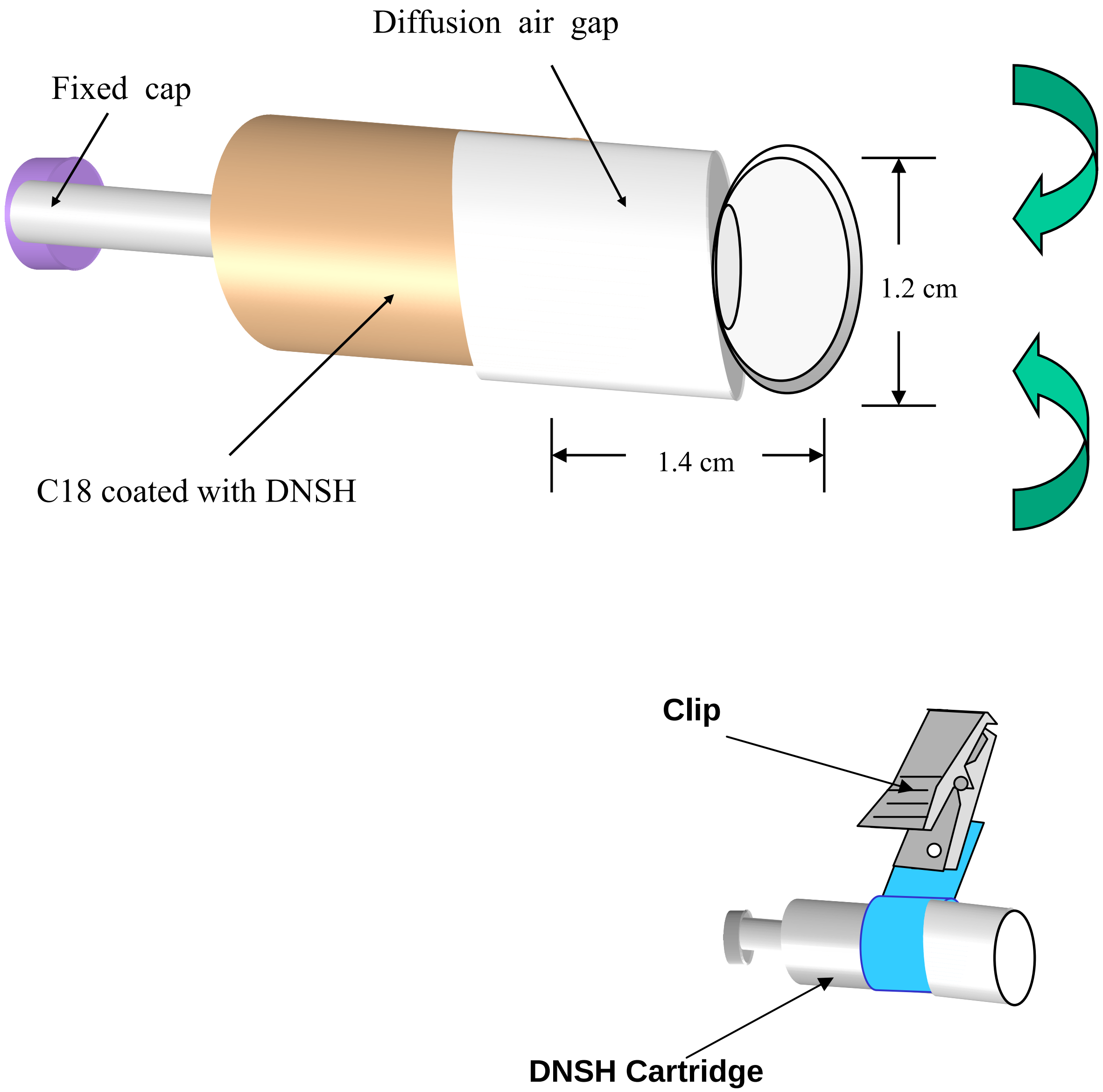


Figure 2. PAKS - DNSH-based Passive Sampler

Since it was not feasible to automate the start of sampling with a passive method, the PAKS samplers were deployed in the field for 48 hours beginning at around 10 am on each setup day and retrieved at 10 am on sample pick-up day. During passive sampling, aldehydes react with DNSH to form corresponding hydrazone derivatives which are sensitive to fluorescence. The derivatives are extracted and quantified using a High Performance Liquid Chromatography

(HPLC)-fluorescence technique. The analytical instrument included an HPLC system [Waters 600E System Controller, Waters 717 Autosampler, Waters 470 Programmable Fluorescence Detector, and Waters Nova-Pak C_{18} column (3.9×300 mm, 60A, 4 µm)] and a guard cartridge (Nova-Pak, 4 µm, 60Å, C18 Guard-Pak, SUPELCO). The HPLC analytical conditions are described in Table 2 below.

Table 2: HPLC Analytical Conditions for Measurement of Aldehydes

Time (min)	% A (pH 7.80) Water/Acetonitrile/Tetrahydrofuran 80/10/10 v/v with 0.68 g/L KH_2PO_4 and 3.48 g/L K_2HPO_4	% B (pH 8.70) Water/Acetonitrile/Tetrahydrofuran 40/30/30 v/v with 0.68 g/L KH_2PO_4 and 3.48 g/L K_2HPO_4
0	100	0
30	70	30
60	60	40
80	60	40
85	100	0
Flow Rate	1 mL/min	
Injection Volume	20 µL	
Detector	Excitation wavelength 250 nm	Emission wavelength 525 nm

Based on previous field and laboratory evaluation conducted by EOHSI (Lioy et al., 2008), field blank concentrations of aldehydes varies by batch. To control the variability of background concentrations of the target compounds, the samplers used for sampling during each month were prepared from the same batch, and at least one field blank was collected. Further, all the samples and field blanks collected during the same month were processed together, and the sample concentrations were corrected by the field blank concentrations obtained from each month to account for variability of the field blanks. This was done to reduce the noise of the PAKS method to the analytical noise, that is, the PAKS MDL was defined as three times the standard deviation of seven repeat analyses of a low concentration standard.

It is necessary to note that during the final data analysis and our internal quality assurance audit, we discovered two errors associated with reported concentrations of aldehydes. The first error was a discrepancy between the designed and manufactured ratio of the cross-sectional area to diffusion length (A/L). The A/L by design should be 0.785 cm for PAKS cartridges. This was the value when cartridges were physically prepared at the EOHSI laboratory. However, when cartridges were pre-cut by the cartridge suppliers, A/L was not maintained at 0.785 cm. We obtained an average A/L ratio of 0.917 ± 0.025 cm after measuring eighty used cartridges which were randomly selected from a few thousand pre-cut cartridges that had been purchased over the past several years. Because PAKS sampling rates are directly proportional to the A/L ratio, the aldehyde concentrations that were previously determined were overestimated. In this final report, calculated concentrations using the designed sampling rate (with A/L = 0.785) were corrected with the average A/L ratio (i.e. 0.917). Due to the variability of the A/L ratio, there is some additional uncertainty associated with the reported concentrations.

The second error was more substantial, especially for formaldehyde. Formaldehyde presents as a monomer in the gas phase but can form a polymer in solution. It was estimated that liquid standards, either 37% formaldehyde solution or the 15-carbonyl mix, contained more than 50% polymerized formaldehyde. Recently it was discovered that DNSH can effectively react with both formaldehyde monomer and polymers. As shown in Figure 3, three peaks of formaldehyde-DNSH derivatives were observed when a calibration standard was prepared by directly spiking a known amount of formaldehyde standard solution into a DNSH-coated PAKS cartridge. The peak area of the monomer derivative was approximately 20% of the sum of the three peaks.

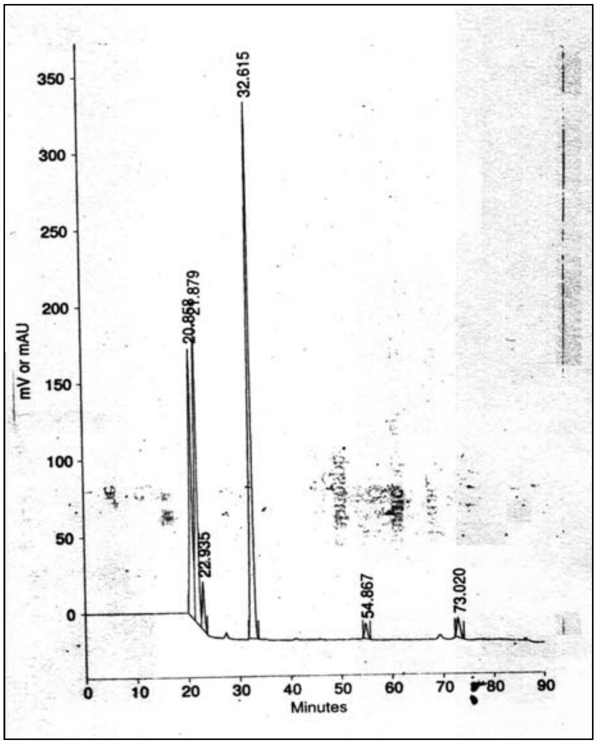


Figure 3. Three peaks of formaldehyde-DNSH derivatives were observed when a calibration standard was prepared by spiking a known amount of formaldehyde standard solution into a DNSH-coated PAKS cartridge: the monomer derivative at retention time (RT) of 20.858 min, the dimmer derivative at RT 21.879 min, and the trimer derivative at RT 32.615.

In the last three years, the calibration standards were a liquid mixture of fifteen carbonyls that were purchased from one company. Calibration curves for individual target aldehydes (formaldehyde, acetaldehyde, acrolein, and propionaldehyde) were prepared through syringe spiking of a diluted 15-carbonyl mixture standards into PAKS cartridges. The formaldehyde mass used for establishing the calibration curve corresponded to both monomer and polymer formaldehyde derivatives. However, only the peak area of the formaldehyde monomer derivative was used for the calculations, which overestimated the formaldehyde concentration in the sample.

To correct this error, calibration curves were established using gas-phase standards of each species which contained only 90% or more of the monomer. More specifically, the aldehyde-

DNSH derivative of each individual species was prepared *in situ* by placing PAKS cartridges in a dynamic gas calibration system containing known concentrations of aldehydes for 12 hours. The samplers were extracted and analyzed for aldehyde concentrations to establish the calibration curves. As shown in Figure 4, the monomer formaldehyde-DNSH peak area generated by a gas standard accounted for > 90% of the total area of the three monomer and polymer peaks generated by a liquid standard as shown in Figure 3. A series of calibration standards (8 levels) were generated and the regression coefficients of the calibration curves obtained were greater than 99% for the four aldehydes being reported. The new calibration curve for each aldehyde was compared against the calibration curve made using the 15-carbonyl mix spikes to generate a calibration correction factor for formaldehyde, and the concentrations determined by liquid calibration standards were corrected by those factors and are presented in this report.

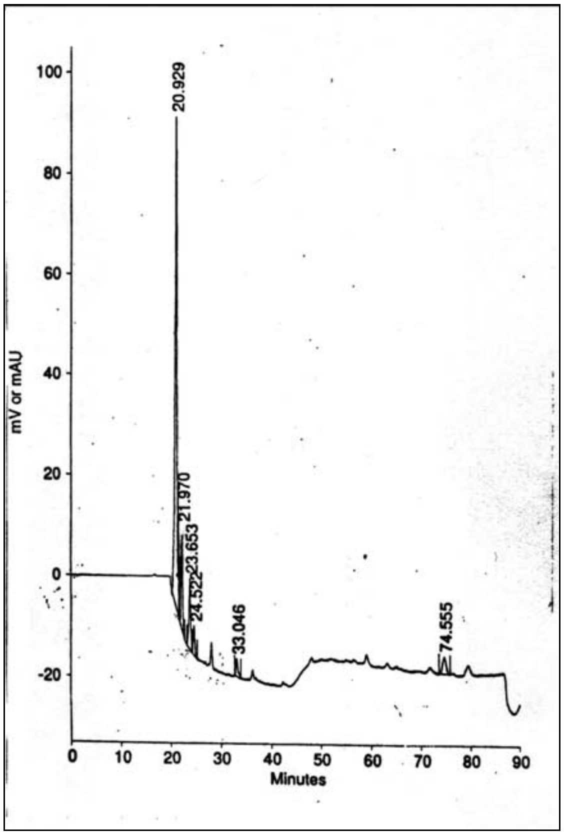


Figure 4: The DNSH derivative of monomer formaldehyde (peak at RT 20.929 min) was dominantly observed, along with a small peak of the dimmer derivative (RT 21.970 min) and almost completely diminished peak of the trimer derivative (RT 33.046 min), when the standard was prepared in a dynamic gas calibration system. Formaldehyde solution was injected through a syringe pump then passed through a glass flask being heated at 120°C before entering the dynamic gas calibration system. DNSH-coated PAKS cartridges were placed in the dynamic gas calibration system where an atmosphere of known formaldehyde concentration was maintained.

B. PM_{10} & Elements

Samples for PM_{10} mass and elemental analyses were collected on a 47 mm Teflon-membrane filter housed in a ChemComb cartridge (Thermal Fisher Scientific). After sample collection, the filters were weighed by a micro-balance (sensitivity is 1 µg) in a temperature (23°C) and humidity (40%) controlled room located at EOHSI. The filter samples were then sent to Research Triangle Institute (RTI) for elemental analysis by Energy Dispersive X-Ray Fluorescence Spectroscopy (ED-XRF).

C. Hexavalent Chromium

UCAMPP provided an opportunity for EOHSI to further develop and field test their newly developed IC-ICPMS method for the measurement of hexavalent chromium (Cr(VI)) in ambient air. Cr(VI) samples were collected on 47mm cellulose filters that were pretreated with 2 g/L sodium bicarbonate ($NaHCO_3$), which helps to prevent the reduction of Cr(VI). After sampling, filters were stored at -15°C in Petri dishes until extraction and analysis. The filters were extracted using 5 mL of nitric acid (HNO_3) solution with pH of 4 and sonicated at 60°C for 40 minutes. After sonication, 100 µL of solution was injected into an ion chromatography (IC) for separation. A Dionex GS50 gradient pump with degasser and a CG5A guard column were used for chromatographic separation of hexavalent and trivalent chromium. The isocratic elution scheme was 40% deionized water and 60% 1 M nitric acid at a flow rate of 1.25 mL/min for 4 minutes. The Cr(VI) concentration was determined by a VG Elemental Plasma Quad 3 (PQ3) inductively coupled plasma mass spectrometer (ICPMS). The dwell time was 300 ms. Under these analytical conditions, a good separation of the species was achieved. The calibration curve had concentrations of 0.5, 1, 2, 5, 10 and 25 ng/mL to determine the concentration in solution.

The analytical detection limit (ADL) 0.12 ppb (ng/mL) was determined as 3 times the standard deviation of 7 repeat analyses of the lowest concentration standard. The ADL is equivalent to 0.05 ng/m^3 air concentration for a sampling volume of 24 m^3. The method detection limit (MDL) was based on three times the standard deviation of trip and field blanks collected over the course of the study. However, elevated field and trip blanks were found in June, July and September, at 0.42, 0.51, and 0.71 ng/m^3, respectively. This was 7 to 12 times higher than the average field and trip blank concentrations for the remaining blank samples collected during the study. The field samples collected during these months were also found to be elevated to a similar extent. Thus, the sample concentrations measured from June to September 2006 were corrected with the corresponding field and trip blanks collected during each month. The field blanks collected from those four months were excluded for the Cr(VI) MDL calculation, and the MDL for Cr(VI) was 0.16 ng/m^3 (see Table 19). These results indicated that the filters should be cleaned prior to sampling.

During the sampling, storage or analysis processes, species interconversion [the reduction of Cr(VI) to Cr(III) or oxidation of Cr(III) to Cr(VI)] can occur. To monitor species interconversion, 16 samples were spiked with stable isotope solutions before sampling and 56 samples were spiked after sample collection before storage and analysis. Four µL of ^{50}Cr(III) and ^{53}Cr(VI) stable isotope solutions (10 ng/µL) were spiked onto the filter samples. These samples were stored, extracted and analyzed using the same methodology as the regular samples.

D. EC/OC

A 1 x 1 cm portion of quartz filter was cut from the filter samples for PAH analysis and sent to RTI for elemental carbon and organic carbon (EC/OC) analysis using the thermal/optical analysis method. The MDLs (0.157 µg/m^3 for both) were provided by RTI.

E. Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbon (PAHs) samples were collected using a sampling protocol similar to USEPA TO-13. The sampling system consists of a quartz filter and polyurethane foam plugs (PUF). Ambient air is pulled through a PM_{10} cyclone and then through a 47 mm quartz fiber filter (QFF) to collect particulate-phase PAHs, after which the air flows through a stainless steel cylinder containing five PUFs (diameter 25mm, height 100mm) to capture gas-phase PAHs. After sampling, PUF plugs are placed in a pre-baked glass jar with aluminum foil-lined lids, while the QFFs were placed in aluminum foil pouches. All samples were transported in a cooler and stored in freezer until analyzed. A 1 x 1 cm portion of the quartz filter was sent to RTI for EC/OC analysis.

The 16 PAHs measured in this study were acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluorene, fluoranthene, indeno(1,2,3,-cd)pyrene, naphthalene, phenanthrene, and pyrene

After sample collection, both filters and PUFs were Soxhlet extracted with dichloromethane for 16 hours. Before extraction, deuterated PAHs, including d_8-naphthalene, d_{10}-phenanthrene, d_{10}-pyrene, d_{12}-benzo(a)pyrene, were added as surrogates to monitor the loss of PAHs during sample processing. The extract was then concentrated to 50-100 µL under a gentle nitrogen stream. After spiking with a known amount of d_{10}-acenaphthene and d_{10}-anthracene as internal standards, the target PAHs were separated and analyzed by a Varian 3900 GC with a Saturn 2000MS ion trap detector.

Compound separation was achieved using a 30m × 0.25mm i.d. × 0.25 µm film thickness VF-5 column. Oven temperature was initially set at 50°C for 10 minutes, then ramped at 25°C/min to 125°C and then 8°C/min to 260°C, and then 3°C/min to 300°C and held for 5 minutes. The injector temperature was 300°C and the injection volume was 1 µL with splitless injection mode. Helium was employed as carrier gas and the flow rate was set at 1.2 mL/min. The detector interface was set at 200°C. The mass spectrometry conditions were as follows: SIM mode; ionization energy, 70 eV; ion source temperature, 200°C. Data were collected using the Varian Chem-Station software.

The calibration curve for each PAH compound was constructed using the ratio of the responses between the target PAHs and the internal standards, and the R^2 was greater than 0.995 for all the target species. The PAH concentrations and the surrogate recoveries were quantified based on the calibration curves. The PAH sample concentrations were corrected with the recoveries of the surrogates. According to the volatility of each PAH species, the recovery of d_8-naphthalene was applied to correct the concentrations of naphthalene, acenaphthylene, acenaphthene and fluorene; the recovery of d_{10}-phenanthrene was used to correct the concentrations of phenanthrene and anthracene; the recovery of d_{10}-pyrene was used to correct the concentrations of pyrene, fluoranthene, benzo(a)anthracene, and chrysene; and the recovery of d_{12}-benzo(a)pyrene was used for the correction of benzo(a)pyrene and the rest of compounds. The recovery of the surrogates was 84.0±45.8 for d_8-naphthalene, 86.7±28.3 for d_{10}-phenanthrene, 101.9±40.9 for d_{10}-pyrene, and 100.3 ± 47.2 for d_{12}-benzo(a)pyrene.

Five- to seven-ring PAHs were not detected in either filter or PUF field blanks. A typical level of naphthalene was about 30ng, equivalent to 1.2 ng/m^3 of naphthalene for sampling at 16.7 L/min for 24 hours in both filter and PUF field blanks. Less than 10 ng (equivalent to < 0.4 ng/m^3 of PAHs in a sampling volume of 24 m^3) of 2- to 4-ring PAHs were detected in the PUF blanks. One field or trip blank was collected per month during a one year sampling period, and the average concentration of the field and trip blanks collected during the whole project was calculated and used for blank subtraction. The MDLs were estimated as 3 times the SD of the field and trip blank for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene. For benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3,-cd)pyrene, benzo(g,h,i)perylene, and dibenzo(a,h)anthracene, the MDLs were derived from the standard deviation of 7 repeat analyses of the lowest concentration of calibration standard because these species were nondetectable in the field and trip blanks.

F. Volatile Organic Compounds

VOCs in ambient air were quantified using the EPA TO-15 method. The ATEC model 2200 canister air sampler was used for VOC collection. Calibration was performed prior to each sampling period following the pre-installed program. After sample collection, the canister was sent to ERG for analysis. For the background site, samples were collected by NJDEP staff as part of the regular air toxics monitoring program. However, not all days matched up exactly with the Paterson sites since there were days where samples could not be collected or the equipment failed. We attempted to make up for this shortfall by sampling additional days (more than 1 in 6) in Paterson to obtain a similar number of weekdays and weekends in the appropriate season.

VOC Sampler at M Site: ATEC 2200; and a canister.

V. DATA HANDLING PROTOCOLS

A. Quality Assurance/Quality Control (QA/QC)

QA/QC included planning, SOPs, QAPP, field sampling and laboratory audits, blanks and controls (spikes), preventive maintenance, correction activities, assessment of precision with duplicates, characterization of data assessments, and % valid samples.

B. Data Validation

For data validation, UCAMPP used QC checks and audits; data screening; statistical analyses; and extensive review of the data with staff in the NJDEP Bureau of Air Monitoring, BTS Air Quality Evaluation Section, and DSRT (now known as Office of Science) QA Project Officers.

C. Statistical Analyses

Prior to data analysis, the non-detect (ND) values were replaced with either 1/2 the MDL, the MDL, or zero, depending on the percent ND of valid samples from all sites combined per analyte.

The following protocol was followed for ND substitution:

1) If %ND was equal to or less then 15%, NDs were substituted with 1/2 of MDL of the target analyte.
2) If %ND was equal to or greater than 50%, no substitution was conducted and only relevant percentiles were reported.
3) If %ND was above 15% and below 50%, two substitutions were applied: one substitution was with the full MDL and the other was with zero. It was found that there were no substantial differences in these results. It was decided to use this approach because if there is only a small number of ND's (i.e., ≤15%) then the effect is minimal. If there is a large number of ND's (≥50%) then it does not make sense to calculate most summary statistics. For moderate numbers of ND's (>15% and <50%), an upper and lower limit on the sample mean could be calculated by using the zero and MDL substitution to cover the range of all possible outcomes.

There were times when values below the MDL were reported by the participating laboratories. Those values were used in the statistical analyses. If a blank subtract resulted in a value equal to or less than zero, those were considered ND.

Descriptive and comparative statistics were performed to characterize the distributions of measured ambient concentrations and to compare ambient concentrations by sampling site, geographical location, season and day of the week.

Since most measurements obtained from the study are non-normal and highly skewed (Shapiro-Wilk test; $p<0.05$), non-parametric approaches were used to examine the spatial and temporal differences between or among the compared groups. Specifically, non-parametric counterparts for t-test or ANOVA (i.e., Wilcoxon Rank Sum test and Kruskal-Wallis test, respectively) were used. For non-parametric multiple comparison tests, a Wilcoxon rank-sum test (two-sided) for each comparison was conducted with the significance determined by Bonferroni's corrected alpha (i.e., 0.05/6=0.0083).

All statistical analyses were conducted using the SAS® Software (version 9.1).

D. Data Processing and Validation

All data including information on field sampling, analytical analyses and meteorological data were entered into a Microsoft Excel worksheet. The field sampling and analytical analyses information were used to identify invalid and suspect samples. For example, samples with 20% more or less than the 24-hour sampling time were considered as invalid. If the difference between initial and final sampling flow rate was greater than 15%, the samples were considered invalid. Any samples found to be invalid were marked in the database and not used in final data analyses. Samples which had some missing sampling or analysis information were considered as suspect samples, were flagged in the database and used in the data analyses.

E. Field Blank Subtraction

Blank subtraction was conducted for all valid field samples except VOCs, to determine the final air concentration of each target analyte. For elements, PAHs, and EC/OC, the average concentration of all the field blank samples was subtracted from each field sample to obtain the final concentration. If a field blank value was greater than 3 times the standard deviation of all field blanks, it was considered an outlier and excluded from analysis by convention.
For aldehydes, the blank subtraction was performed on a monthly basis. For other target analytes, the averaged blank concentrations are: 0.32 µg/m3 for PM_{10} mass concentration; 9.04 ng/m^3 and 0.90 µg/m^3 for EC and OC, respectively; and 0 to 0.29 ng/m^3 for the 48 elements. For PAHs, the average blank concentrations were in the range of 0-1.14 ng/m^3. For Cr(VI), an average of 0.054 ng/m^3 was obtained from 9 blank samples (the 4 summer field blanks were excluded from the MDL calculation).

F. Method Precision

The method precision for the measurement of all analytes was evaluated using the absolute percent difference (%Diff) between collocated regular and duplicate samples. The %Diff was conducted using the following equation:

$$\%Diff = \frac{Abs(regular - duplicate)}{(regular + duplicate)/2} \times 100$$

The reported %Diff in Table 20 is the average of all the pairs. If at least one sample result in the pair was ND, that pair was not used in the calculation of %Diff.

VI. RESULTS AND DISCUSSION

A. Valid Measurements

The total number of samples collected is presented in Table 17 and the details of the number of samples collected during different seasons and weekday and weekend are presented in Table 18. Approximately 220 regular field samples (not including duplicates and field blanks) per sample type were collected and 89% to 93% of those were considered valid. Sample type is defined here as aldehydes, elements, hexavalent chromium, EC/OC, PAHs, PM_{10} or VOCs. Valid duplicates ranged from 4% to 13% for per sample type. Valid blanks (trip and field) ranged from 0% to 9%. Since there were no observed differences in the individual concentrations of the field and trip blanks for all air toxics, the field and trip blanks were processed together for MDL and final sample concentration calculation. No blanks were collected for the VOCs as per the USEPA protocol.

B. Percent Above MDL

Table 19 provides the details on MDL, % detected and %ND. Aldehydes were detected above the MDL between 76% and 97% of the time. Cesium, europium, molybdenum and scandium were never detected. Bromine, calcium, copper, iron, manganese, potassium, silicon, sulfur and zinc were detected 100% of the time. The following elements were detected over 50% of the time: aluminum, arsenic, bromine, calcium, chlorine, copper, gallium, iron, lead, magnesium, nickel, potassium, rubidium, selenium, sodium, strontium, sulfur, titanium, vanadium, yttrium, and zirconium. Cr(VI) was detected above the MDL 86% of the time. EC/OC were always detected. The PAH samples were quantifiable over 50% of the time except for benzo(ghi)perylene and indeno(1,2,3-cd)pyrene which were detected less than 50% of the time. PM_{10} was detected over 99% of the time. For VOCs the following compounds were never measured above the MDL at any monitoring location: 1,1,2,2-tetrachloroethane; 1,1,2-trichloroethane; 1,1-dichloroethane; 1,1-dichloroethene; 1,2-dibromoethane; 1,2-dichloroethane; 1,2-dichloropropane; bromochloroethane; bromodichloroethane; bromoform; chloroprene; cis-1,3-dichloropropene; ethyl acrylate; ethyl tert butyl ether; tert amyl methyl ether; trans-1,2-dichloroethylene; and trans-1,3-dichloropropene. The following VOCs were detected 100% of the time above the MDL: 1,1,1-trichloroethane; benzene; carbon tetrachloride; chloromethane; dichlorodifluoromethane; dichlorotetrafluoroethane; ethylbenzene; m,p-xylene; propylene; toluene; trichlorofluoromethane; and trichlorotrifluoroethane. This was not unexpected as these compounds either have long half lives in the atmosphere (the chlorinated compounds) or are mobile-source generated.

C. Method Precision

Method precision was evaluated using the average percent difference (%Diff) between duplicates which were measured above the detection limit is reported in Table 20. In summary, the %Diff was less than 30% for many target pollutants, e.g. formaldehyde and acrolein by the PAKS method were 30% and 13% respectively, 18% for Al, 8% for Ca, 15% for Cl, 19% for Cu, 9% for Fe, 6% for S, 12% for Zn, 15% for EC, 4% for OC, 23% for Cr(VI), and 8% for PM_{10} mass concentration,. The methods for Cr(VI) and acrolein and formaldehyde by PAKS method are newly developed. The method precision indicates a good reproducibility of the methods developed for the measurement of these two species, considering their low concentrations and instability in ambient air.

Poor precision was obtained for benzo(b)fluoranthene (67%) with the other PAHs having %Diff less than 35%.

Poor precisions were observed for some species, such as total Cr (48%), acetaldehyde (54%), propionaldehyde (50%), and hafnium (54%). Possible reasons for the large %Diff observed for these species could be attributed to low concentrations (for Cr, hafnium and benzo(b)fluoranthene) and low number of measurements that were quantifiable (total Cr and Hf).

Good precision was obtained for most VOCs by the TO-15 method, the majority of compounds having a precision of 20% or less. Overall, the chlorinated and brominated compounds had the best precision, and acrolein by TO-15 had the worst at 55%.

D. Descriptive Statistics, Geographical and Temporal Comparisons

Please note all summary statistics reported in the following text are for when the ND replacement was with zero. Both replacement values (0 and full MDL) are presented in Tables 21-27

1. Aldehydes:

Summary statistics for the ambient concentrations of aldehydes measured by the PAKS method (DNSH) at the four sites are presented in Table 21. The mean ± SD concentrations for acetaldehyde were 7.74 ± 8.39 $\mu g/m^3$ (B site), 7.49 ± 8.93 $\mu g/m^3$ (C site), 7.23 ± 8.14 $\mu g/m^3$ (I site) and 9.70 ± 22.51 $\mu g/m^3$ (M site). The maximum measurement at the mobile site was 157.09 $\mu g/m^3$ which is more than three times the maximum values obtained at the other three sites. Since there was no reason to believe that this value was due to a measurement or human error (e.g., laboratory, data entry), the value was retained. The means ± SD for formaldehyde were 10.94 ± 7.35 $\mu g/m^3$(B site), 11.26 ± 7.67 $\mu g/m^3$ (C site), 10.70 ± 6.71 $\mu g/m^3$ (I site) and 9.94 ± 6.52 $\mu g/m^3$ (M site). The concentrations for acrolein and propionaldehyde were much lower than for formaldehyde and acetaldehyde. The mean ± SD concentrations for acrolein were 0.28 ± 0.39 $\mu g/m^3$ (B site), 0.30 ± 0.27(C site), 0.37 ± 0.60 (I site), and 0.35 ± 0.40 $\mu g/m^3$ (M site). Propionaldehyde values were 1.11 ± 1.65 $\mu g/m^3$ (B site), 1.42 ± 4.00 $\mu g/m^3$ (C site), 0.86 ± 0.94 $\mu g/m^3$ (I site), and 0.96 ± 1.41 $\mu g/m^3$ (M site).

There were no significant differences for any of the aldehydes except acrolein between sites, between Paterson and Chester, between weekday vs. weekend or seasons.

In Paterson, acrolein concentrations were significantly higher during the weekdays (0.38 ± 0.46 μg/m^3) than during the weekends (0.24 ± 0.38 μg/m^3) with p=0.01. These results indicate the impact of higher emissions of acrolein from mobile, commercial and industrial sources.

A seasonal difference, in which summer was greater than winter (0.40 ± 0.42 μg/m^3 vs. 0.26 ± 0.47 μg/m^3 respectively) was observed for acrolein when the ND replacement was 0 (p=0.02), but not for the MDL replacement. It is known that ambient aldehydes can be generated by both primary (motor vehicles) and secondary sources (photochemical reactions). However, they are highly reactive and can decay under sunlight. Seasonal differences in aldehyde concentrations are determined by both generation and degradation processes during each season (Anderson et al., 1996; Christensen et al., 2000; Ho et al., 2002; Sin et al., 2001; Herrington et al., 2007 and 2008).

2. Elements

The spatial variability of elemental concentrations differed by species. Annual average concentrations of aluminum, calcium, iron, magnesium, manganese, silicon, and titanium were statistically significantly higher (up to 2x's higher) at the sites in Paterson than the background site, as well as the concentrations on weekday vs. weekends in Paterson, as seen in Table 22. For example, the annual mean ± SD for aluminum at the background site was 105.78 ± 109.78 ng/m^3 while in Paterson, the sites ranged from 162.51 ± 147.95 ng/m^3 at the M site, 175.99 ± 146.07 ng/m^3 at the I site, and 193.90 ± 158.66 ng/m^3 at the C site. In Paterson, weekday concentrations were statistically significantly higher than on weekends (204.59 ± 162.23 vs. 110.67 ± 86.34 ng/m^3). Sulfur was higher on weekday than on the weekends with no difference between Paterson and the background site. These observed differences provide strong evidence that the concentrations of these elements are influenced by anthropogenic activities, i.e., by industrial, commercial and/or mobile sources. Interestingly, only iron and manganese were listed in the emissions inventory. However, the emissions inventory did not include mobile sources and many of those elements are associated with mobile source emissions. Additional elements had concentrations that were also statistically significantly higher (up to 4x's higher) in Paterson than Chester, but did not exhibit a weekday/weekend difference: bromine, chlorine, copper, lead, nickel, potassium, sodium, strontium, vanadium, zinc, and zirconium. (This is an example of the ND replacement making a difference in the results; both replacements were significant for Paterson vs. Chester but only the 0 replacement found a difference in Paterson weekday/weekend.) These results provide evidence that these elements also indicate an urban footprint.

Copper exhibited a significant difference among the sites in Paterson; the commercial site was statistically significantly higher (18.02 ± 12.83 ng/m^3) than the industrial site (12.35 ± 11.26 ng/m^3) and mobile site (13.4 ± 12.05 ng/m^3). There are two sources of copper in the emissions inventory but neither source is located closer to the commercial site than the other monitoring locations. This could indicate that there is an unknown source of copper in Paterson near the commercial site. Sodium was higher at the mobile site (319.33 ± 357.87 ng/m^3) than the industrial site (267.23 ± 308.87 ng/m^3).

Elements that were statistically significantly higher in winter than one or more of the other seasons are bromine, chlorine, copper, iron, lead, nickel, selenium, sodium, titanium, zinc and zirconium. The elevated concentrations (around two times or more) of these elements could represent change in emissions such as space heating. Although not statistically significantly different, strontium was the only element whose average summer concentration was higher than winter's (3.38 ± 4.40 vs. 2.65 ± 1.96 ng/m^3). Upon further investigation, it was found that the highest measured concentrations in Paterson and the background site were for samples collected on July 4. This is probably because strontium is commonly used in fireworks for its red color (http://en.wikipedia.org/wiki/Strontium).

None of the other elements exhibited differences in weekday/weekend or season for the background site.

3. Hexavalent Chromium

The descriptive statistics for hexavalent chromium [Cr(VI)] are presented in Table 23
The only observed differences were seasonal with the summertime concentrations being statistically significantly higher than 1 or more of the other seasons in both Paterson and the background site. At the background site, the biggest difference was between summer and winter (0.41 ± 0.36 vs. 0.11 ± 0.09 ng/m^3). In Paterson, the largest difference was between summer and spring (0.39 ± 0.28 vs. 0.15 ± 0.12 ng/m^3). It is thought that the higher concentrations of Cr(VI) in summer may be caused by photooxidation, ozone or other co-pollutants such as manganese (ATSDR, 9/2008). Please note that in a subsequent study, this seasonal effect was not observed. More research is needed to identify if the seasonal variability is real or is an artifact.

4. Elemental and Organic Carbon

The descriptive statistics for elemental carbon (EC) and organic carbon (OC) are presented in Table 24. For both EC and OC, the pattern was similar to some of the elements, in that the concentrations in Paterson were about twice those at the background site. For EC in Paterson, concentrations were higher on the weekday vs. the weekend (0.87 ± 0.61 vs. 0.61 ± 0.43 μg/m^3). There were no day of the week differences for EC and OC at the background site and no day of the week difference for OC for Paterson. In Paterson there were higher concentrations of EC in the winter (1.16 ± 0.90) vs. spring (0.61 ± 0.34 μg/m^3). OC was around twice as high in winter than all other seasons, and there was a difference between summer and spring. There was no difference at the background site by season for EC but there was for OC (spring different than summer). These observations suggested higher emissions of EC and OC from combustion sources during the winter, consistent with the literature (Roosli et al., 2001; Karar and Grupta, 2006).

EC is generally formed during combustion. It was not unexpected that higher concentrations were observed in Paterson than at the background site since the background site did not have any stationary sources close by and was impacted much less by mobile sources since it is far from the roadway. The higher EC concentrations on weekdays are consistent with the fact that local sources, such as direct emissions from vehicular traffic and other combustion sources, are more abundant during the weekday than weekend.

In contrast, OC is generated from both primary emissions and secondary formation through photochemical reactions. The secondary formation depends upon many factors, such as meteorology (UV, temperature, and relative humidity) and ozone concentrations. Since ambient OC concentrations are contributed to by both direct emissions from combustion sources as well as secondary formations via atmospheric photochemical reactions, it would be expected that there would be less of a difference in photochemical processes between weekday and weekend, except for the potential weekday and weekend differences in the precursor concentrations.

5. Polycyclic Aromatic Hydrocarbons

The descriptive statistics for polycyclic aromatic hydrocarbons (PAHs) are presented in Table 25. Annual averages of almost all of the PAHs were statistically significantly higher in Paterson than at the background site except benzo(b)fluoranthene which was higher at the background site than in Paterson (0.55 vs. 0.15 ng/m^3). It is unknown at this time why this occurred.

Since PAHs are generated from many combustion sources, such as automobile exhaust and wood smoke (Lopes et al., 1996; Singh et al., 2008; Hellen et al., 2008), the higher PAH concentrations measured in Paterson demonstrate the impact of emissions from traffic, commercial activities and the operation of industrial facilities around the mobile, commercial, and industrial monitoring sites. Within Paterson, concentrations of naphthalene, acenaphthylene, fluorene, and phenanthrene were higher than the heavier PAHs by about an order of magnitude.

In Paterson, there weren't any strong differences among sites. For instance, only dibenzo(a,h)anthracene (with 0 substitution for ND but not full MDL) exhibited a difference among sites, with the M site higher than the C site (0.13 ± 0.26 vs. 0.09 ± 0.16 ng/m^3). Only fluoranthene and pyrene had higher concentrations (by less than a factor of 2) in Paterson during the weekday than on the weekend. This is most likely due to increases sources of combustion during the week. The background site had no day-of-the-week difference.

The seasonal variation of ambient PAH concentrations vary by species, probably due to source variation, reactivity of each PAH compound during each season, and meteorology. As presented in Table 25, in Paterson and the background site, many compounds were higher in winter and fall than other seasons. For example, in Paterson, acenaphthylene was higher in winter (18.24 ± 43.88 ng/m^3) and fall (14.20 ± 37.43 ng/m^3) than spring (1.32 ± 1.39 ng/m^3) and summer (1.06 ± 1.06 ng/m^3), with the background site exhibiting the same pattern except that the concentrations were an order of magnitude lower. Anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluorene, naphthalene, and pyrene also exhibited these patterns; mostly winter was highest, but sometimes it was fall.

This behavior is consistent with previously reported trends (Takeshi et al., 2004). Higher emissions of PAHs are expected from automobile exhaust and space heating during the winter than in summer, and a greater degradation of PAHs occurs in summer than in winter (Baek et al., 1991). However, some lighter PAHs may show higher concentrations in summer due to volatilization from environmental surfaces such as roads, soil, and vegetation (Lang et al., 2002). In Paterson, only fluoranthene was higher in summer than spring, and at the background site, phenanthrene was highest during summer vs. spring and winter (7.70 ± 5.60 ng/m^3 for summer and 2.85 ± 2.59 ng/m^3 in spring and 2.57 ± 1.68 ng/m^3 in winter).

6. PM$_{10}$ Mass

The ambient PM$_{10}$ mass concentrations obtained from the four sampling sites are summarized in Table 26. The ambient PM$_{10}$ concentrations (mean ± SD) were significantly higher in Paterson than at the background site (17.92 ± 11.90 vs. 11.29 ± 6.98 µg/m^3). These observations indicate an impact from the commercial and/or industrial and/or traffic activities in Paterson. There was no significant difference observed for PM$_{10}$ among the three sites in Paterson, which is not unexpected because all sites were surrounded by roads.

There were no statistically significant seasonal or day of the week variations for either Paterson or the background site, although in Paterson the concentration of PM$_{10}$ was 19.02±12.61 µg/m^3 during weekdays vs. 14.99±9.32 µg/m^3 weekends.

7. Volatile Organic Compounds

The summary statistics for VOCs are presented in Table 27. The following compounds had values (mean±SD) that were statistically significantly higher in Paterson compared to the background site: 1,1,1-trichloroethane (0.16±0.11 vs. 0.11±0.02 µg/m^3); 1,2,4-trimethylbenzene (0.76±0.61 vs. 0.09±0.08 µg/m^3); 1,3,5-trimethylbenzene (0.24±0.17 vs. 0.04±0.03 µg/m^3); 1,3-butadiene (0.21±0.20 vs. 0.03±0.04 µg/m^3); acetylene (1.45±1.39 vs. 0.52±0.36 µg/m^3); acrolein (0.87 ± 0.56 vs. 0.56 ± 0.68 µg/m^3); benzene (1.43 ± 0.94 vs. 0.52 ± 0.22 µg/m^3); chloroethane (0.05 ± 0.07 vs. 0.02 ± 0.03 µg/m^3); chloroform (0.24 ± 0.23 vs. 0.07 ± 0.08 µg/m^3); dichlorodifluoromethane (2.97 ± 0.70 vs. 2.73 ± 0.48 µg/m^3); dichloromethane (1.20 ± 1.33 vs. 0.33 ± 0.26 µg/m^3); ethylbenzene (0.78 ± 0.96 vs. 0.14 ± 0.08 µg/m^3); methyl ethyl ketone (2.28 ± 2.29 vs. 1.08 ± 1.25 µg/m^3); methyl isobutyl ketone (0.49 ± 0.54 vs. 0.11 ± 0.16 µg/m^3); methyl tert-butyl ether (0.63 ± 1.28 µg/m^3 vs. ND); m,p-xylene (2.49 ± 4.31 vs. 0.30 ± 0.21 µg/m^3) ; n-octane (0.27 ± 0.21 vs. 0.07 ± 0.06 µg/m^3); o-xylene (0.77 ± 0.81 vs.0.13 ± 0.07 µg/m^3); p-dichlorobenzene (6.22 ± 26.84 µg/m^3 vs. ND); propylene (1.36 ± 1.02 vs. 0.43 ± 0.34 µg/m^3); styrene (0.20 ± 0.17 vs. 0.07 ± 0.06 µg/m^3); tetrachloroethylene (0.65 ± 0.62 vs. 0.13 ± 0.12); toluene (7.52 ± 5.94 vs. 0.70 ± 0.55 µg/m^3); and trichlorofluoromethane (2.27 ± 1.37 vs. 1.53 ± 0.30 µg/m^3). Many of these compounds were not specifically identified in the emissions inventory. Listing total VOCs on the permits rather than speciating individual compounds is a common practice, and the emissions inventory does not include mobile sources. Regardless, these results provide additional evidence that industrial and/or commercial and/or mobile sources impact the air quality in Paterson and that better speciation of VOCs on permits is needed, particularly those that have significant health effects. Although many of these air toxics are emitted from mobile sources, there are many industrial and area source VOCs that are higher in Paterson than the background site. This provides evidence that urban air quality is not driven solely by mobile source emissions, and that the emissions from point and area sources are important contributors to urban air quality, e.g., p-dichlorobenzene and tetrachloroethylene respectively.

Interestingly, there were two compounds that were statistically significantly higher at the background site: carbon disulfide (2.16 ± 0.06 $\mu g/m^3$) and acetronitrile (0.91 ± 0.30 $\mu g/m^3$). Carbon disulfide may be from biogenic activity related to the grass-/wood-/wetlands that surround the background monitoring location. Carbon disulfide is product of microbial processes in plants and soils during the growing season. This hypothesis is loosely supported by our results because, although not statistically significant, spring exhibited the highest value at the background site.

The emissions inventory revealed that there are no permitted sources of acetonitrile in Morris County where the background monitoring location is located even though it is commonly used as a solvent because it is miscible in water. There is a permitted source in Warren County located about 40 miles west southwest of the monitoring station. Acetonitrile is a breakdown product of acrylonitrile. However, there are no known permitted sources of acrylonitrile in the area, so that is not likely to be the explanation for the statistically significantly higher values measured at the background site vs. Paterson. There may be unknown sources in the vicinity of the background site.

The sites in Paterson displayed some statistically significant differences for some species. For example, 1,1,1-trichloroethane, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, ethyl benzene, methyl isobutyl ketone, and o-xylene at the commercial site were about two times higher than the other sites. The most striking difference for the C site was for p-dichlorobenzene which had an average concentration which was two orders of magnitude higher than at the other sites. It can be seen in Figure 5 that the average was driven by very high concentrations observed in the fall of 2006.

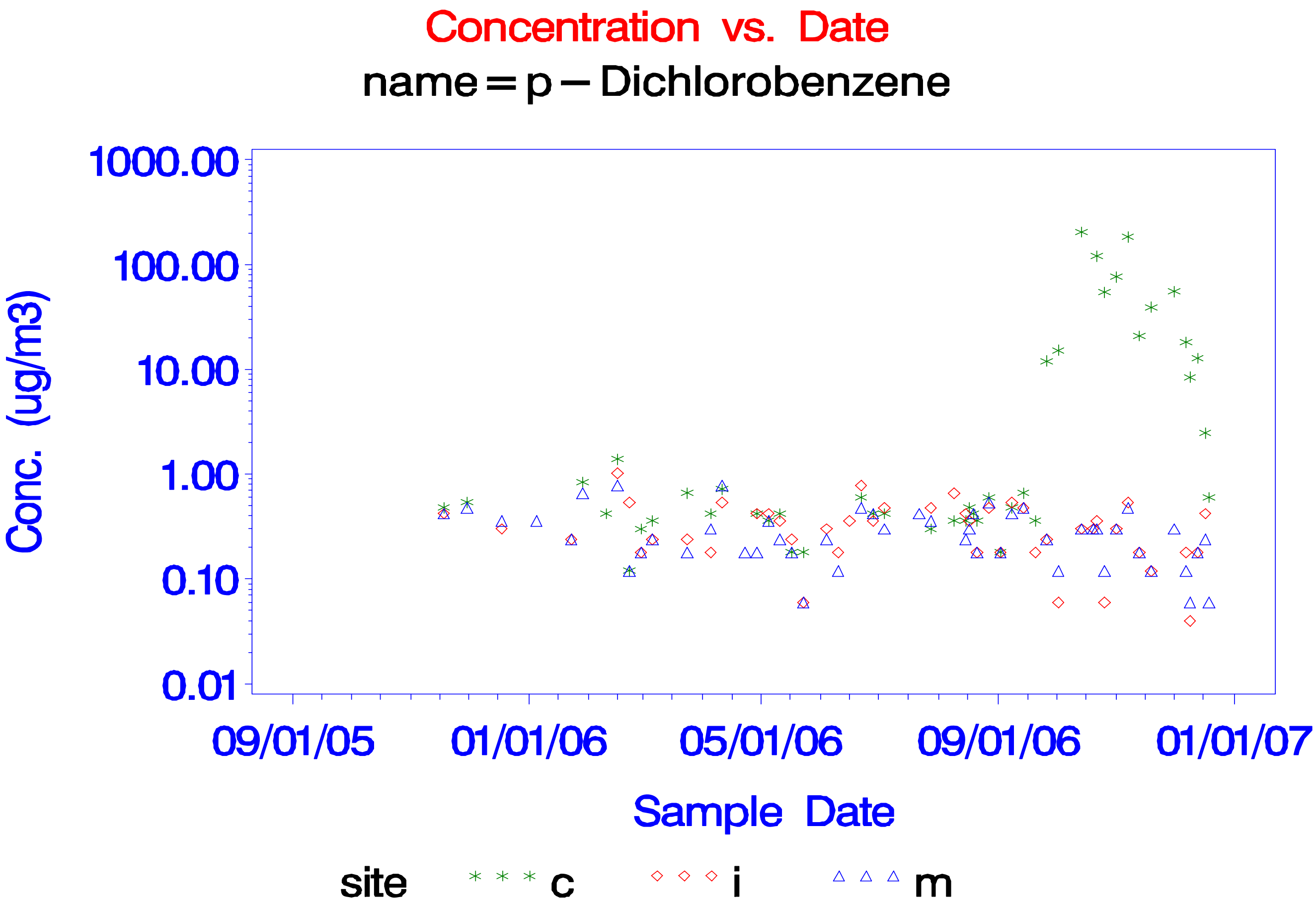


Figure 5: Time Trend for p-Dichlorobenzene Concentrations at the Paterson sites.

Although not statistically significantly different from all other sites in Paterson, the following compounds also had higher annual averages at the C site: 1,3-butadiene, acrolein, benzene, chloroethane, chloroform, dichlorofluoromethane, ethylbenzene, MTBE, propylene, styrene, and tetrachloroethylene.

In general, VOCs showed the same trend as other pollutants that were measured, i.e., the C site had higher concentrations than the other sites for species that are associated with all types of sources, i.e., point, area and mobile.

In Paterson, compounds with statistically significantly higher values during the weekdays were: dichloromethane (1.33 ± 1.39 vs. 0.81 ± 1.05 μg/m^3); methyl ethyl ketone (2.62 ± 2.51 vs. 1.31 ± 1.00 μg/m^3); methyl isobutyl ketone (0.12 ± 0.17 vs. 0.08 ± 0.12 μg/m^3); methyl tert-butyl ether (0.71 ± 1.38 vs. 0.41 ± 0.92 μg/m^3); tetrachloroethylene (0.72 ± 0.68 vs. 0.46 ± 0.31 μg/m^3); and toluene (8.04 ± 6.23 vs. 6.05 ± 4.23 μg/m^3). This provides further evidence that urban air quality is not overwhelmed solely by mobile sources and that area and point sources are important contributors to urban air quality.

At the background site, only acrolein was higher during the weekend vs. the weekday ($p<0.0001$; 0.76 ± 0.98 vs. 0.48 ± 0.48 $\mu g/m^3$). It is unclear why this difference occurred.

Seasonal variability occurred for some VOCs. Interestingly, not all VOCs exhibited seasonal differences at both the background and Paterson sites; that is, sometimes differences occurred at the Paterson sites and sometimes at the background site. The following compounds were statistically significantly higher in the winter than in one or more of the other seasons in Paterson: 1,3-butadiene (two times greater in winter than in the other seasons); acetylene; benzene; propylene; and toluene. This is most likely due to winter heating and/or meteorology, e.g., combustion from heating and inversions, low mixing heights, low wind speed.

Chloroethane was the only VOC that was higher in the summer than one or more seasons for both Paterson and the background site. This could be from volatilization from soil and water (ATSDR, 1998).

For many compounds, spring concentrations were the lowest, whether it was statistically significant or not. Monthly rainfall was checked and it does not appear that levels were excessive during the spring.

VII. FIELD TESTING OF NEW METHODS FOR AIR TOXICS CURRENTLY DIFFICULT TO QUANTIFY

A. Comparison of TO-11A, PAKS, and TO-15 for the Measurement of Aldehydes

One of the objectives of the UCAMPP study was to field test new sampling and analytical techniques for air toxics that are currently difficult to quantify. During UCAMPP, aldehydes were measured with three different methods. At all of the Paterson sites, aldehydes, i.e., acetaldehyde, acrolein, formaldehyde and propionaldehyde) were measured using the EOSHI PAKS method (Zhang et al., 2000) and acrolein was also measured using USEPA method TO-15. At the background site, acrolein was measured using TO-15 and PAKS and the other three aldehydes were measured with PAKS and USEPA method TO-11A. Acrolein has been difficult to quantify by the EPA TO-11A method. In addition, recent finding from an EOHSI study also showed that acetaldehyde was significantly underestimated by the TO-11A when the sampling time was 6 hours and longer when sampling known concentrations of formaldehyde and acetaldehyde (Herrington et al., 2007).

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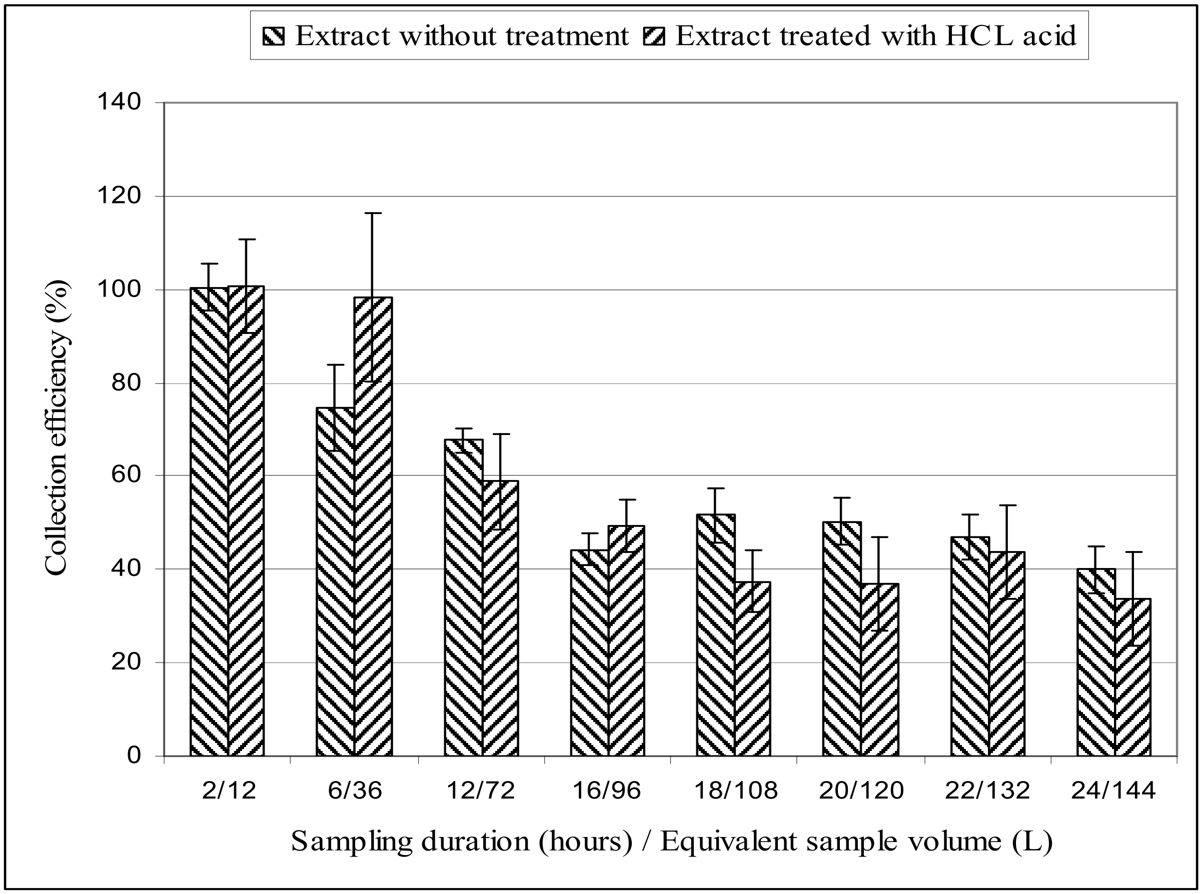


Figure 6: Collection efficiency of acetaldehyde vs. sampling duration

The PAKS method was newly developed at EOHSI and field tested during the UCAMPP study. As described in the methods section, PAKS utilizes the DNSH reagent as a derivatization agent, and the aldehyde-DNSH derivatives are fluorescence-sensitive, while the TO-11A method utilizes derivatization with DNPH, separation by HPLC and detection by UV. The benefit of the PAKS method is that it does not require a sophisticated setup or power supply because it is a compact passive method. This provides more flexibility for field sampling and minimizes loss of samples due to power or sampling pump failures.

To date, laboratory evaluation results have shown that the passive PAKS method is a sensitive, reliable and precise method for the measurement of acrolein (Herrington et al. 2005). During UCAMPP, the reported %Diff (precision measurement) for acrolein by PAKS is 13% while acrolein by TO-15 is 55%. However, the PAKS method may overestimate formaldehyde, acetaldehyde and propionaldehyde concentrations, as seen in Table 3**.** TO-11A is the current USEPA method for quantification of most aldehydes and is used nationwide. 2006 was the first year that acrolein was reported by USEPA method TO-15.

Table 3: Annual Averages for Background Location in µg/m^3

Air Toxic	PAKS	TO-11A[1]	TO-15
Acetaldehyde	7.74[2]	1.19	n/a
Acrolein	0.28[2]	n/a	0.56[2]
Formaldehyde	10.94[3]	1.93	n/a
Propionaldehyde	1.11[3]	0.20	n/a

[1] Values obtained from NJDEP 2006 Air Toxics Summary, 2006 data only, 0 replacement for ND
[2] Value obtained from UCAMPP report, 0 replacement for ND, includes 2 measurements from 2005
[3] Value obtained from UCAMPP report, 1/2 MDL replacement for ND, includes 2 measurements from 2005

Based on the evaluation conducted by Herrington et al., 2007, the discrepancy is partially attributed to the low collection efficiency of the TO-11A method for a sampling duration >6 hours. In addition, a negative association was observed between formaldehyde concentrations measured by the TO-11A method and those by PAKS (Figure 7), i.e. the formaldehyde concentrations measured by the TO-11A method decreased slightly as those measured by PAKS increased.

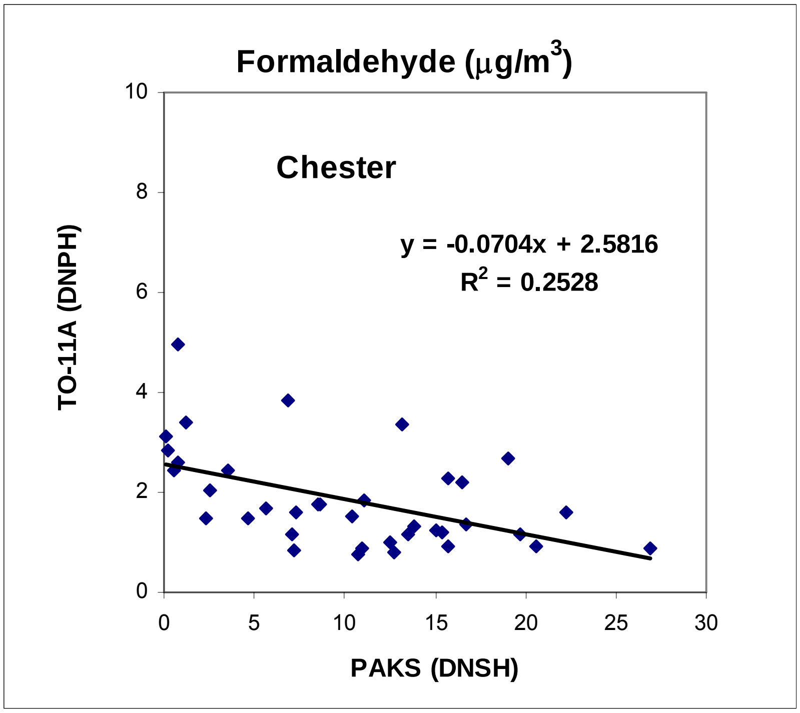


Figure 7: Comparison of formaldehyde concentration measured by TO-11A method and PAKS.

These observations suggest a decrease in collection efficiency of formaldehyde by the TO-11A method when the formaldehyde is high and the sampling duration is 24 hours. Or, these results may indicate that the PAKS method overestimates the concentrations of formaldehyde, acetaldehyde and propionaldehyde when the aldehydes are at high concentrations. More study is needed to determine why the two methods give such different results.

Since it is not feasible to automate the start of sampling with a passive method, the aldehyde passive sampler was deployed in the field for 48 hours beginning at 10 am on each setup day and retrieved at 10 am on the day of sample pick-up. Besides PAKS, formaldehyde, acetaldehyde, and propionaldehyde were simultaneously measured by the TO-11A method at the background site through the NJDEP Urban Air Toxic Monitoring Program. However, the sampling duration for TO-11A is 24 hours, midnight to midnight. Acrolein was measured by the TO-15 method at the four sites, also with the same sampling duration of 24 hours. Field blank concentrations, MDLs, method precision, and sample concentrations for each method are compared and reported below.

1. Field Blank Concentrations and Method Detection Limits

The field blank concentrations obtained from the PAKS and TO-11A are presented in Table 4. No field blank samples were collected by method TO-15.

Table 4: Mean Field blank and MDL for each measurement method (µg/m3)

	TO-11A[1] (n=23)		PAKS[2] (n=17)		TO-15[3]
	Mean	MDL	Mean	MDL[4]	MDL
Acetaldehyde	0.07	0.01	7.6	0.21 / 0.14	N/A
Acrolein	N/A	N/A	0.17	0.28 / 0.23	0.25
Formaldehyde	0.04	0.01	5.71	0.20 / 0.27	N/A
Propionaldehyde	0.001	0.01	0.66	0.17 / 0.55	N/A

[1] Values from 2006 only

[2] Values include 2 measurements in 2005, not all sampling days match exactly with TO-11A

[3] Only acrolein was measured by TO-15 method. The field blank was not collected by TO-15 method.

[4] 1st value is 2005 MDL/ second is 2006 MDL

The mean field blank value for each aldehyde was calculated using the total number of field blank measurements, even if the value was less than the detection limit. Please note that for TO-11A, all field blank measurements for acetaldehyde and formaldehyde were above the MDL. For propionaldehyde the mean field blank value may be underestimated since only two blank values were above the MDL. As can be seen in Table 4, the MDLs for TO-11A were 1 order of magnitude lower than for the PAKs method. The average of the field blank concentrations for formaldehyde, acetaldehyde and propionaldehyde were two orders of magnitude lower for TO-11A than for the PAKS method It has been observed in previous field and laboratory evaluation conducted by EOHSI (Lioy et al., 2008) that the field blank concentrations of aldehydes measured by PAKS (DNSH) had big differences in concentrations that appeared to vary by batch. To control the variability of background concentrations of target compounds, the samplers used each month were prepared from the same batch, and at least one field blank was collected. Further, all the samples and field blanks collected from the same month were processed together.

The sample concentrations were corrected by the field blank obtained for each month to help account for the variability of the field blank levels. Therefore, the noise of the PAKS method was reduced to the analytical noise, that is, the PAKS MDLs were defined as three times the standard deviation of seven repeat analyses of a low concentration standard**.** More work is needed to reduce the concentrations observed in the field blank measurements for acetaldehyde, formaldehyde and propionaldehyde for the PAKs method. Acrolein is observed to have low field blank concentrations for PAKS.

2. Method Precision

The method precision was evaluated by calculating the average of the absolute percent difference for the duplicate samples that had concentrations greater than the MDL. As shown in Table 5, good precision was obtained by the TO-11A method, with mean absolute %difference for formaldehyde, acetaldehyde and propionaldehyde < 20%. For PAKS, a good precision was obtained for acrolein, with a mean %difference of 13%. The precision for formaldehyde is reasonable, with mean %difference of 30%. However, greater variability was observed for acetaldehyde and propionaldehyde, with an average %difference of 54% and 50% respectively. The reasons for the large variability of these two species are not clear. The precision of acrolein measured by TO-15 is also poor, with mean %difference of 55%.

Table 5: The mean relative absolute percent difference of duplicate samples measured by different methods (% difference calculated from duplicates with concentrations > MDL)

	TO-11A (n=7)	PAKS	TO-15 (n=11)
Acetaldehyde	12%	54% (n=17)	NA
Acrolein	NA	13% (n=10)	55%
Formaldehyde	16%	30% (n=22)	NA
Propionaldehyde	9%	50% (n=9)	NA

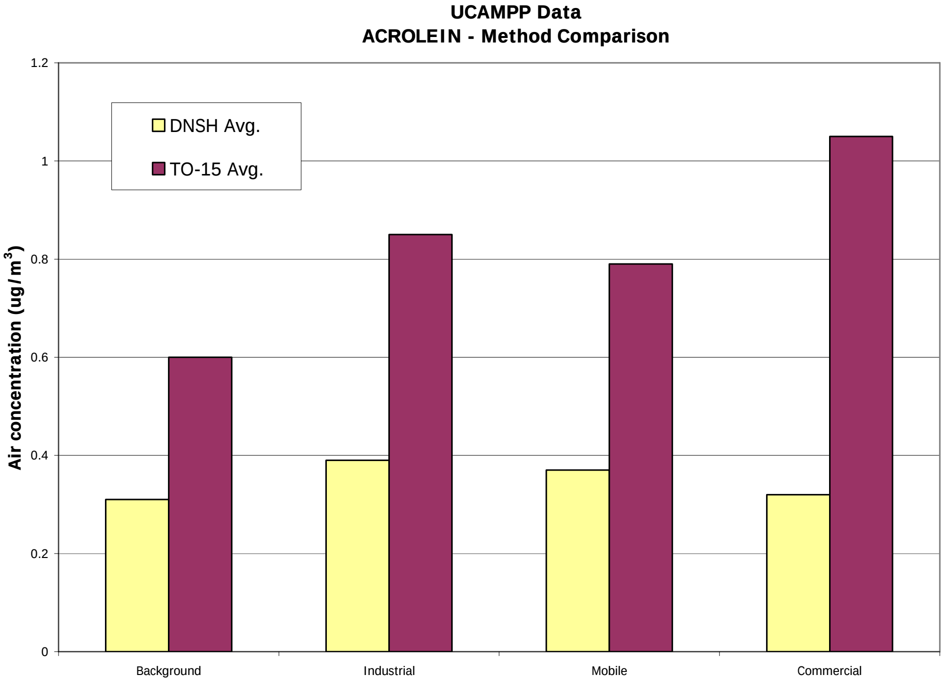


Figure 8: Acrolein Concentrations Measured by Different Methods

The annual average concentrations of acrolein measured at each site by PAKS and TO-15 are presented above in Figure 8**.** It can be observed that concentrations obtained with the TO-15 method were two to three times higher than those obtained by PAKS.

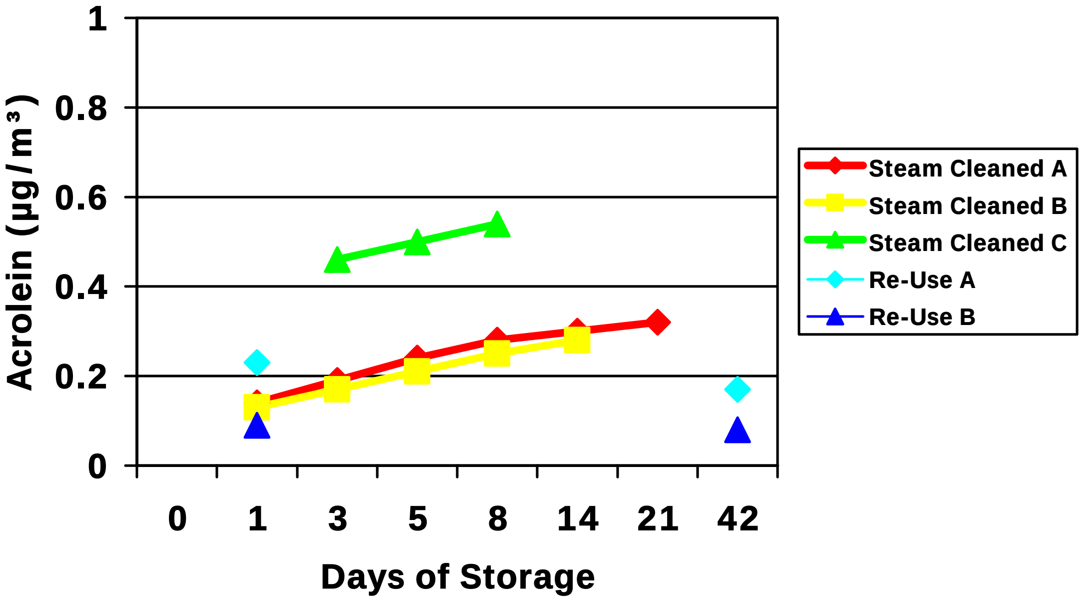


Figure 9. Artificial formation of acrolein in Canisters – with steam cleaning (Dann and Wang, 2007)

A previous study reported a potential artificial formation of acrolein in the canister during storage (Dann and Wang, 2007), particularly when the canister was not cleaned properly, which may result in higher acrolein concentrations in TO-15 method as seen in Figure 9. In future studies, the canister blank should always be checked.

The spatial and seasonal variations for all the data obtained by each method were also examined. Similar seasonal patterns were reported by each method for some species but not for all. For example, the results from the TO-11A method showed that the formaldehyde concentration measured at the background site was higher in summer than in other seasons, and no seasonal difference was observed for acetaldehyde or propionaldehyde. The results from PAKS showed no seasonal difference for all three compounds. For acrolein, both TO-15 and PAKS (if non-detects were replaced with 0) showed higher concentrations in summer; however, the difference measured by PAKS was not statistically significant when non-detects were replaced with a full MDL. PAKS did not detect any site differences for any aldehydes; however, the TO-15 method reported higher acrolein concentration at the commercial site. More field studies and further data analyses, such as correlation analysis of aldehydes with other pollutants and photochemical reaction modeling, are needed to help understand the discrepancies among these three sampling methods.

3. Summary

The PAKS method (DNSH-HPLC/fluorescence) is easily deployable and does not need power. The method appears to be a sensitive sampling method for the measurement of some aldehydes with acceptable method precision for formaldehyde (30%) and good precision for acrolein (13%). The field blank concentrations for formaldehyde, acetaldehyde, and propionaldehyde were large compared to the TO-11A method. Further investigation is needed to reduce the field blank concentrations and precision so that the method can be applied for future measurement of aldehydes in ambient air. Second, the TO-15 method may have a bias for acrolein measurement during sample storage, which requires further evaluation. Third, the method precision of the TO-11A method is very good but the collection efficiency of aldehydes for sampling time greater than 6 hours needs to be more fully evaluated. These three sampling methods need to be compared and evaluated side-by-side using a standard dynamic gas system in the laboratory as well as in the field to determine the accuracy of each method for the measurement of aldehydes.

B. Development of a Sampling & Analytical Method for the Quantification of Hexavalent Chromium in Ambient Air.

For years, scientists have been working on a reliable, reproducible method for the quantification of hexavalent chromium (Cr(VI)) in ambient air. USEPA has contracted with Eastern Research Group (ERG) to develop a method which is based on the California Air Resources Board (CARB) Method 039. However, the recovery of Cr(VI) in ambient particulate matter and the potential interconversion between Cr(III) and Cr(VI) cannot be quantified by this method because there is no standard reference material for Cr(VI) in ambient air PM and the method can only detect Cr(VI). These factors could bias the determination of the concentration of Cr(VI) in ambient PM.

During the UCAMPP study, a pilot study was conducted with resources donated by EOHSI to develop an analytical method for the measurement of Cr(VI) in ambient air. The analytical method included collection of ambient air PM on cellulose filters pre-treated with sodium bicarbonate solution (based on the ERG method), extraction of the sampled filters with 5 mL of pH=4 nitric acid solution with sonication for 40 minutes at 60ºC, separation by IC, and detection by ICPMS. The analytical detection limit was 0.12 ppb (ng/mL), which is equivalent to 0.05 ng/m3 air concentration for a sampling volume of 24 m3. The method detection limit calculated from the field blank was 0.16 ng/m3 with the exclusion of three suspected outliers. The average difference was 23% and was determined from duplicate field samples (n=13). NIST 1648 urban particulate matter was spiked with 10 ppm Cr(VI) and Cr(III) isotope solution (53Cr-isotopically-enriched hexavalent chromium, 50Cr-isotopically-enriched trivalent chromium, purchased from Applied Isotope Technologies, Inc. 851 Stella Court, Sunnyvale, CA 94087). The isotope spikes were used to evaluate the recovery of Cr(VI) and the interconversion rate between Cr(VI) and Cr(III). Conversions from both Cr(VI) and Cr(III) were observed. The conversion of Cr(VI) to Cr(III) was found to be low (0-20%) but conversion of Cr(III) to Cr(VI) was more significant (0-40%). The recovery of Cr(VI) was >80% during lab tests for Cr(VI) spiked filters only and Cr(VI) spiked on NIST 1648 particles.

The average recovery of Cr(VI) was found lower in the field study than lab tests, i.e. 57% (n=16) for the Cr(VI) spiked on filter prior to sampling and 67% (n=56) for the Cr(VI) spiked on filter samples after sampling. These results indicated that the sampling process, particle type (aged NIST particles vs. fresh particles) can affect the recovery of Cr(VI). It should, however, be noted that filters spiked with isotope standards were exposed to ambient air for a much longer time (48 hours) than the sampling time (24 hours) due to sampling logistics described in the method section. Therefore, the Cr(VI) recovery of the before-sampling spikes may reflect the lower bound of the Cr(VI) recovery.

In this report, the Cr(VI) concentrations were not corrected for either interconversion rate or recovery rate. This is because the interconversion rate was only monitored for a small subset of the samples collected (16 samples were spiked prior to sampling and 56 samples were spiked after sampling). Moreover, the interconversion rate and recovery varied largely, and it is not clear what caused the variability based on the information collected from UCAMPP. Therefore a correction factor that can be applied to all the samples cannot be determined at this point. This issue will be investigated in two additional projects, and it is hoped that a proper correction factor can be determined. It is worth noting that the Cr(VI) concentrations reported in this study may be overestimated. We have not corrected the measured concentrations by either the recovery or interconversion rate. We could not quantify the total Cr(III) concentration in the extract because the majority of Cr(III) precipitated, which prevents the ability to correct the Cr(VI) concentration by the Cr(III)-to-Cr(VI) interconversion rate. We think that the interconversion from Cr(III) to Cr(VI) should not be significant because Cr(III) is almost insoluble in our extraction condition. On the other hand, our testing results can't prove it at this point. We will be able to further characterize the correction factor during two additional and related USEPA-funded projects that came out of UCAMPP, "Development and Optimization of a Sampling and Analytical Method to Measure Hexavalent Chromium in Ambient Air", USEPA grant # XA-97264906-1 and "Evaluation of Two Analytical Methods and Sampling Trains for the Measurement of Hexavalent Chromium in Ambient Air" USEPA grant #XA-97247301.

The study 'Development and Optimization of a Sampling and Analytical Method to Measure Hexavalent Chromium in Ambient Air" is focused on improving the method (reducing the filter blank level) of Cr(VI), further characterizing the interconversion rate and characterizing the effect of environmental conditions on Cr(VI) stability during sampling (aerosol type and composition, relative humidity, temperature, ozone, sulfur dioxide and nitrogen dioxide). This project should be completed by July 2009 and the final report is expected 90 days thereafter. The second project, "Evaluation of Two Analytical Methods and Sampling Trains for the Measurement of Hexavalent Chromium in Ambient Air," will evaluate the analytical methods that were developed by EOHSI (IC-ICPMS) and ERG, Inc (IC-UV), and two or three sampling trains, one developed by New York State and Clarkson University (NYS sampler) and two developed by ERG, Inc (the NATTS sampler). This project recently got underway and the work should be complete by summer 2012 with the final report due 90 days thereafter.

VIII. COMPOUNDS OF INTEREST TO USEPA

In the Request for Applications, the USEPA identified specific air toxics as part of a series of parameters that were to be addressed in the grant application. These requirements were to ensure a congruous database to better characterize air toxics and for long term analyses. The following section provides a brief overview and information related to the specific air toxics relative to UCAMPP that were not specifically discussed elsewhere in this report.

A. Beryllium and Compounds

This compound is not able to be measured by X-ray fluorescence so no data are available for this project. However, beryllium did appear in the emissions inventory, listed by St. Joseph's Hospital as a permitted compound. The closest monitor (M site) to St. Joseph's Hospital is about 6,000 feet away. The other two monitors are 6300 ft away (C site) and 9500 ft away (I site). Since X-ray fluorescence cannot measure beryllium, it is unknown if it poses any health risk in the Paterson area.

B. 1,2-Dichloropropane (Propylene dichloride)

This VOC was not specifically listed in the emissions inventory and is not a target compound using any of the UCAMPP methods.

C. Cadmium and Compounds

Cadmium compounds were listed in the emissions inventory but all measured concentrations were ND at all Paterson sites. Interestingly, cadmium was detected 3.8% of the time at the background site. The cancer risk-based concentration is less than the MDL by an order of magnitude, $2.4\text{x}10^{-4}$ $\mu g/m^3$ and $7.3\text{x}10^{-3}$ $\mu g/m^3$, respectively so it is unknown as to whether cadmium poses a cancer risk. The noncancer health based concentration is 0.02 $\mu g/m^3$ so cadmium does not appear to pose a noncancer health risk.

D. Lead and Compounds

Lead was detected 98% of the time above the MDL for all sites combined. However, there was no short or long term health risk associated with the measured levels of lead in Paterson or at the background site.

During site visits, it was observed that there were two lead emitting facilities in close proximity to each other. At one facility, the amount of lead that was reported to be processed in 2005 was 3,720,848 lbs which did not appear to coincide with their reported air emissions (0.49 lbs lead/year). This information was relayed to Bureau of Technical Services and Enforcement and it was decided that a stack test was warranted. The facility passed the first stack test but was retested because production was not at the appropriate level during the first test. This facility was retested and passed.

The other facility lead emitter was required by USEPA to undergo stack testing to comply with the NESHAP requirements. The facility passed its stack test. Both of these facilities are visited by NJDEP enforcement staff at least one time every five years.

E. Manganese and Compounds

Although manganese was detected 100% of the time at all locations, there was no health risk associated with concentrations of manganese measured during UCAMPP.

F. Dichloromethane

Dichloromethane was above the MDL for 98% of samples for all sites combined. The annual averages for the different monitoring locations were up to one order of magnitude below the cancer risk-based concentration, 0.33 to 1.3 μg/m^3 vs. 2.1 μg/m^3 respectively and were much lower than the noncancer risk-based and short-term noncancer risk based concentrations of 400 and 14,000 μg/m^3, respectively. Based on the comparison of the health benchmark to the MDL, dichloromethane did not present any risk.

G. Nickel and Compounds

Nickel was detected 71% of the time for all sites combined. There is a health benchmark for nickel subsulfide, however nickel subsulfide is produced from nickel refineries and the manufacture of lithium batteries, neither of which are in our emissions inventory. Nickel refinery dust also has a health benchmark but there are no nickel refineries in the emissions inventory. Cancer risk was not calculated for the nickel measured in the PM_{10} in Paterson since it is highly unlikely to have been produced by any of the source types mentioned above.

The long-term noncancer reference concentration for nickel and nickel compounds is 0.05 μg/m^3 and the short-term noncancer reference concentration is 6 μg/m^3. The annual average concentrations for the Paterson sites ranged from 0.00195 to 0.00209 μg/m^3 and the background site was 0.00078 μg/m^3, all of which are all well below both reference concentrations.

H. Trichloroethylene

Trichloroethylene was detected 43% of the time for all sites combined. The annual averages were 1 to 2 orders of magnitude less than the health benchmark.

I. Vinyl Chloride

Vinyl Chloride was only detected 14% of the time for all sites combined.

IX. MODELING

A. Evaluation of NATA 2002 Using Monitoring Data

In the original National Air Toxics Monitoring Program - Community Assessment - Request for Applications, Solicitation #OAR-EMAD-03-08, USEPA specified air toxics of interest s previously discussed in this report. This section of the report compares the annual averages of some of those compounds to the NATA 2002 modeled annual averages for the applicable census tracts.

Propylene dichloride was not monitored during UCAMPP. Cadmium and vinyl chloride had too many NDs to calculate an annual average, as per UCAMPP data handling protocols.

For the most part, the monitored values exceeded the modeled values for the compounds that were chosen for this comparison.

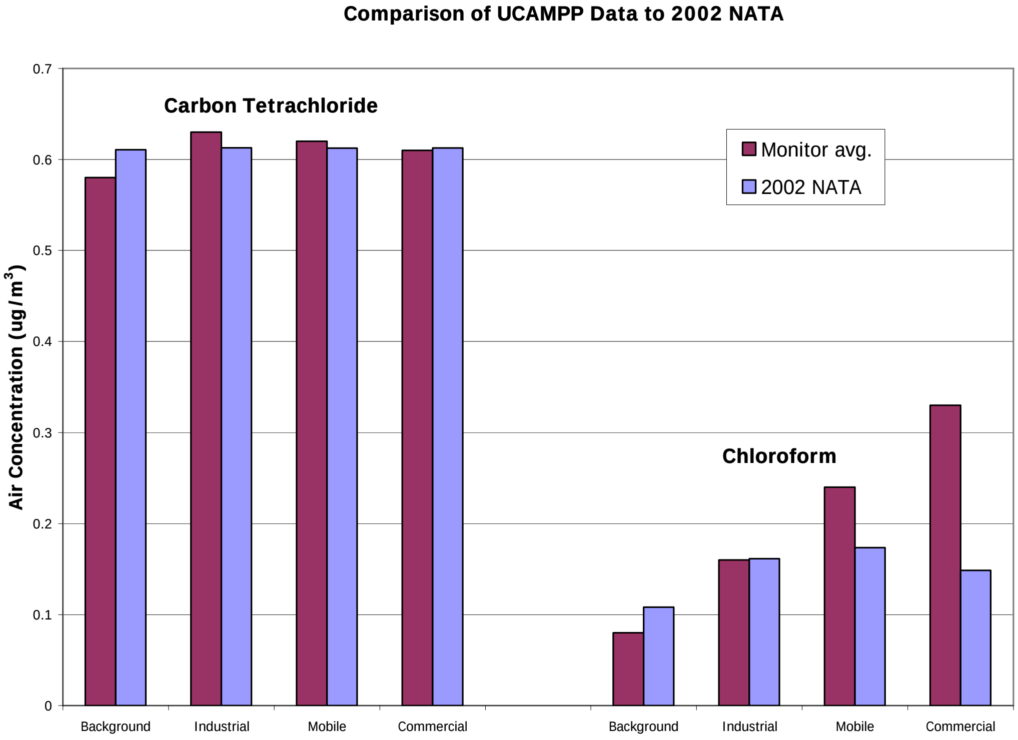
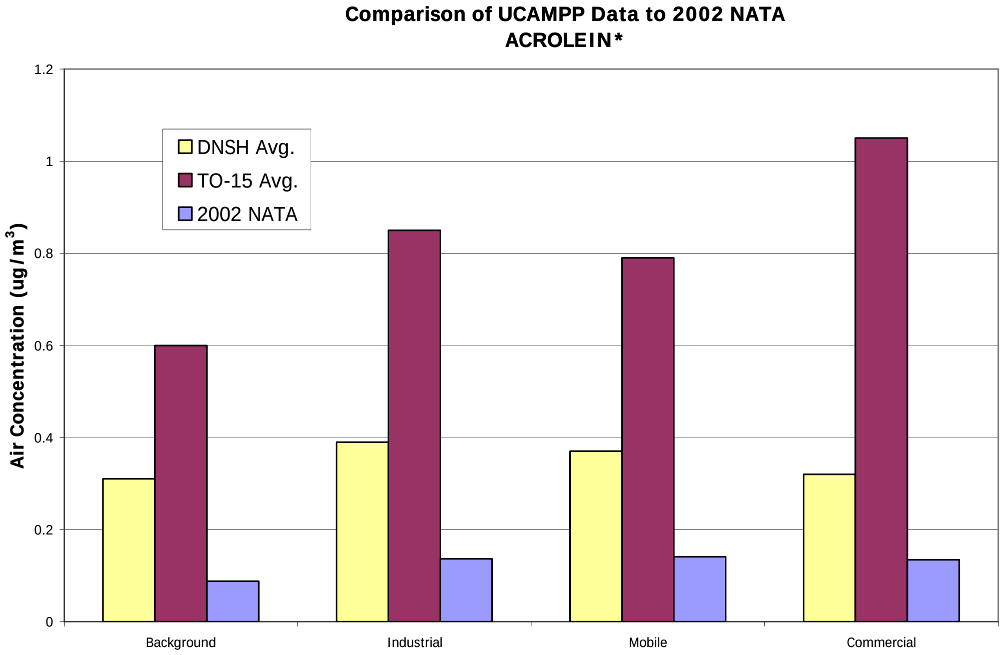


Figure 10: Annual average of monitored values and NATA for carbon tetrachloride and chloroform.

As can be seen in Figure 10, carbon tetrachloride exhibited excellent agreement between the annual averages that were monitored and modeled. This would be expected because carbon tetrachloride is rarely emitted these days, and it has a very long half-life in the atmosphere (i.e., it does not break down readily and lasts a long time in the atmosphere). It appears from the comparison of chloroform that there may be an unknown or unaccounted source located near the C site. However, the other sites agree very well.



* Includes comparison of DNSH method and TO-15 method.

Figure 11: Annual average of NATA and monitored values for acrolein by TO-15 and DNSH (i.e., the PAKS method)

Figure 11 compares the annual averages for acrolein quantified by two different sampling and analytical methods and NATA modeled data. The DNSH method had much better precision than TO-15 for acrolein. It appears that NATA may be underestimating acrolein, which is not surprising, considering that acrolein is not only a mobile source air toxic but is formed photochemically**,** (ATSDR, 2007). NATA's emission estimates for mobile sources are more uncertain than for stationary sources. It is also observed that annual averages obtained by TO-15 are 2 to 4 times greater than those obtained by the DNSH/PAKS method.

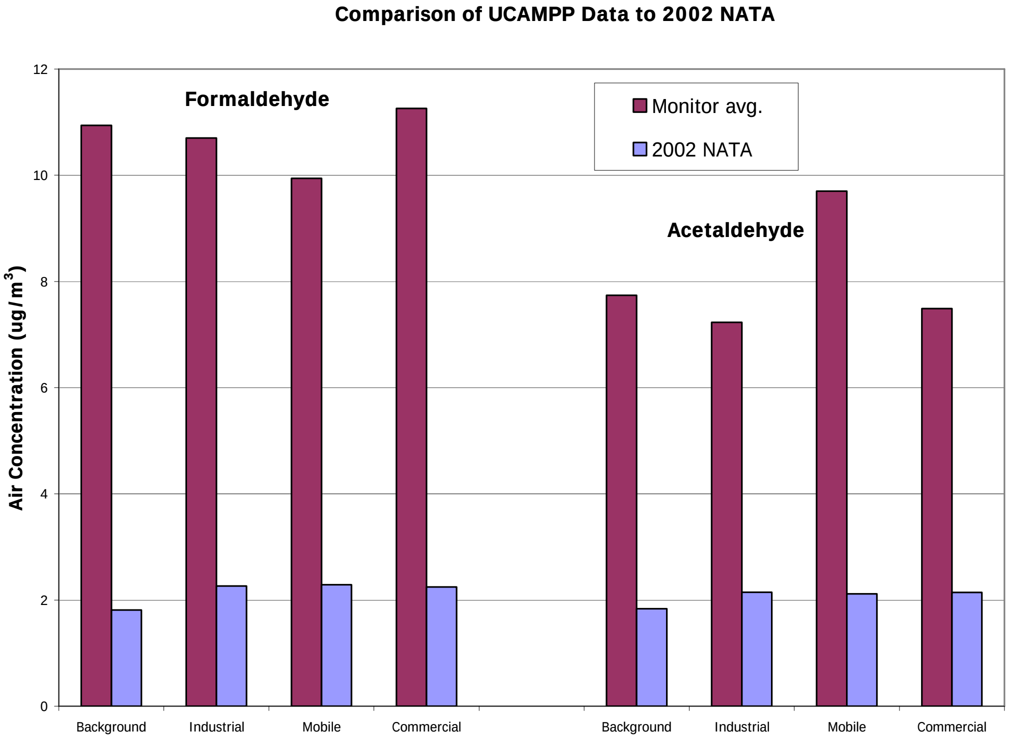


Figure 12: Annual average of monitored values and NATA for formaldehyde and acetaldehyde

The monitored values for formaldehyde and acetaldehyde are from the DNSH method and are much greater than the NATA modeled values. This was expected as both compounds are mobile source air toxics and photochemically generated. In addition, the comparison between the DNSH method and DNPH method at the background site indicates that the DNSH method most likely overestimates formaldehyde and acetaldehyde concentrations.

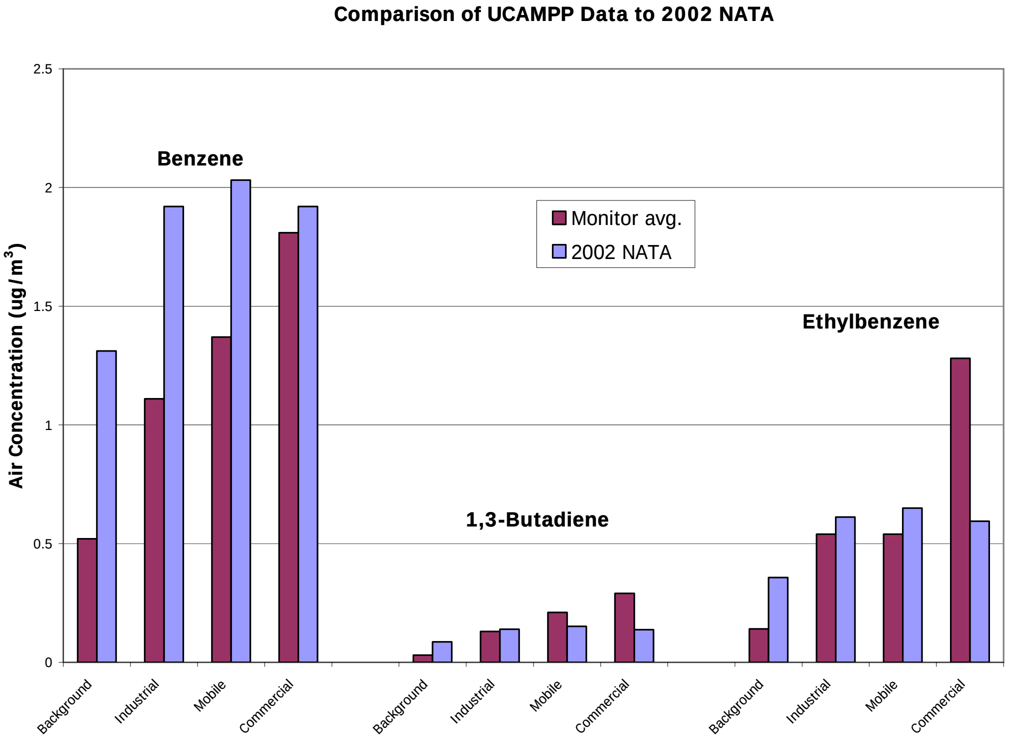


Figure 13: Annual average of monitored values and NATA for formaldehyde and acetaldehyde

Figure 13 displays the annual average of three additional mobile source air toxics and their concentrations as reported in NATA 2002. There is much better agreement between these monitored and modeled values, probably because none of these chemicals are photochemically generated. They are mostly emitted directly from the combustion of fuel.

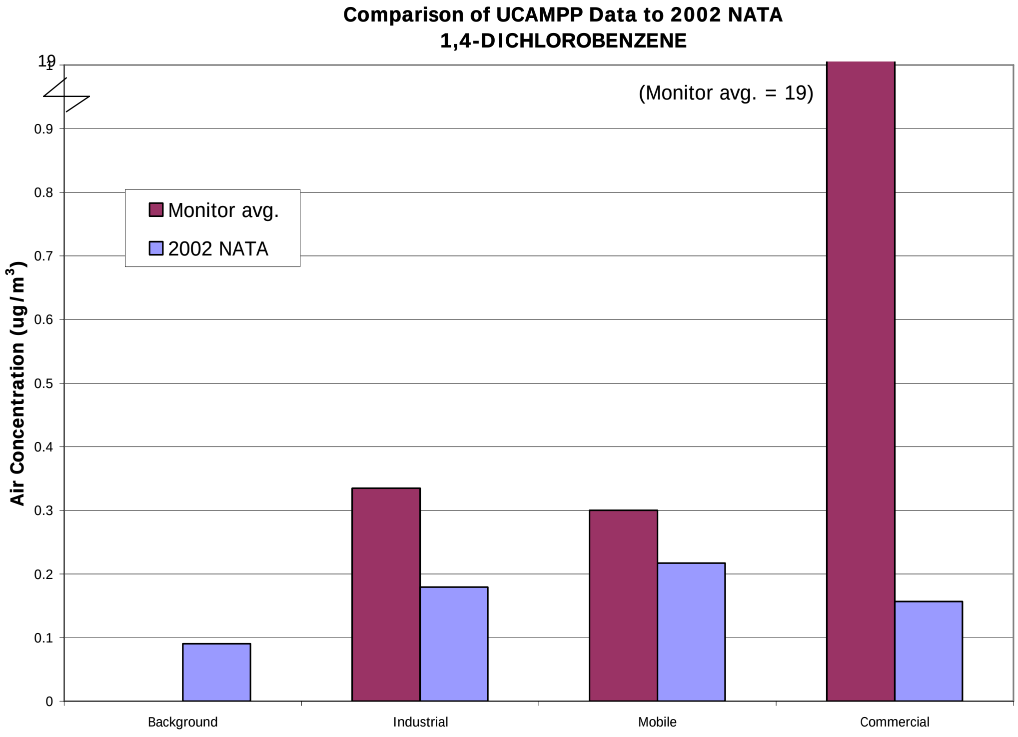


Figure 14: Annual average of monitored values and NATA for 1,4- dichlorobenzene (i.e., p-dichlorobenzene)

For all the sites except C, the agreement between NATA and the monitored values was reasonable for p-dichlorobenzene. Something out of the ordinary occurred during the fall of 2006 which resulted in very high concentrations of p-dichlorobenzene, up to three orders of magnitude above the usual concentrations (~0.2 vs. ~200 ug/m^3). NJDEP enforcement is working with local and county health departments and the investigation into this episode is ongoing. NJDEP applied for funds from USEPA to do an additional year of monitoring at and around the commercial site to determine if this is an ongoing issue or was an isolated event. The project period is expected to be from spring of 2010 through fall of 2011.

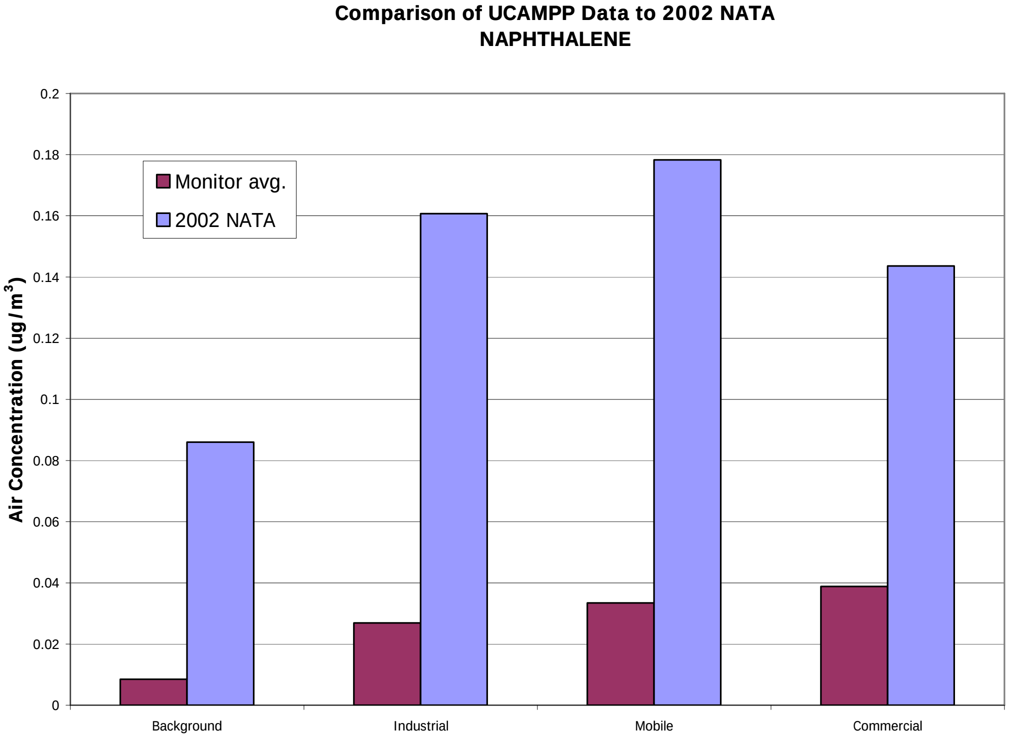


Figure 15: Annual average of monitored values and NATA for naphthalene

For naphthalene, there was poor agreement between the monitored and modeled values, with the modeled values being much greater (by an order of magnitude). One may speculate that most of the naphthalene had already broken down into other compounds due to its short half-life in the atmosphere (1 day). This discrepancy could also have to do with the way NATA estimates naphthalene concentrations. Also, there could have been a change in source emissions from 2002 to 2006.

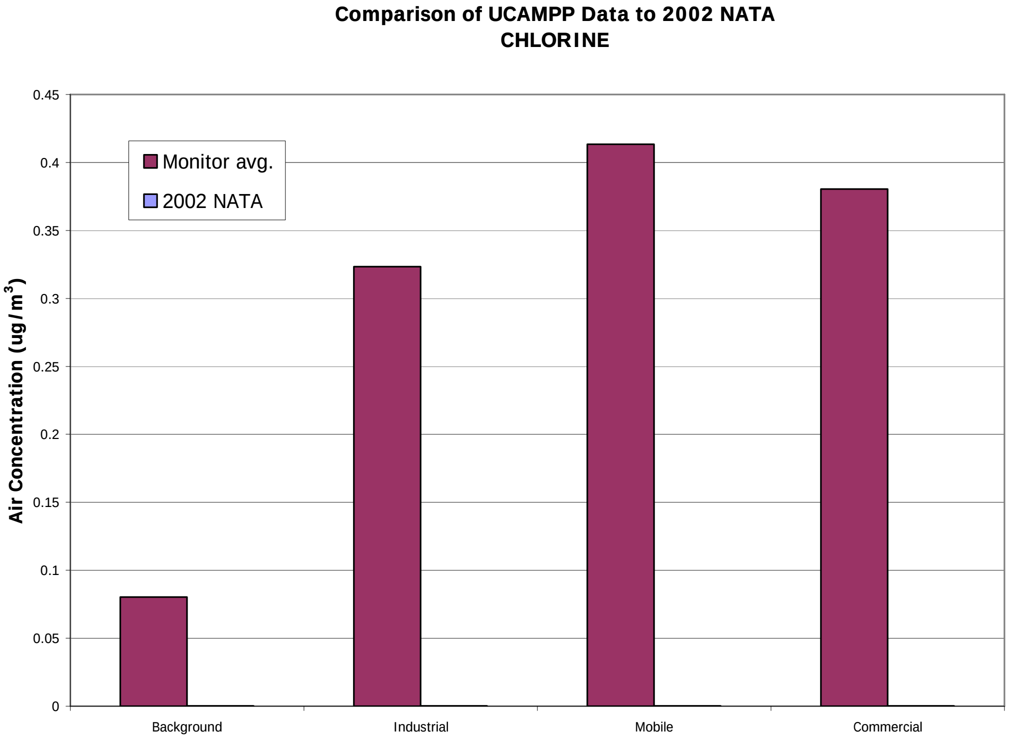


Figure 16: Annual average of monitored values and NATA for chlorine

As can be seen in Figure 16, the chlorine concentrations estimated by NATA are three orders of magnitude less than the monitored values, e.g., at the mobile site, the NATA concentration is 2.13×10^{-4} ug/m^3 vs. the monitored value of 4.13×10^{-1} ug/m^3. Chlorine is a disinfectant and is used to treat drinking water. It is also used in the manufacture of numerous items such as paper products, plastics, dyes, textiles, medicines, antiseptics, insecticides, solvents and paints. This discrepancy could also have to do with the way NATA estimates chlorine concentrations. Also, there could have been a change in source emissions from 2002 to 2006.

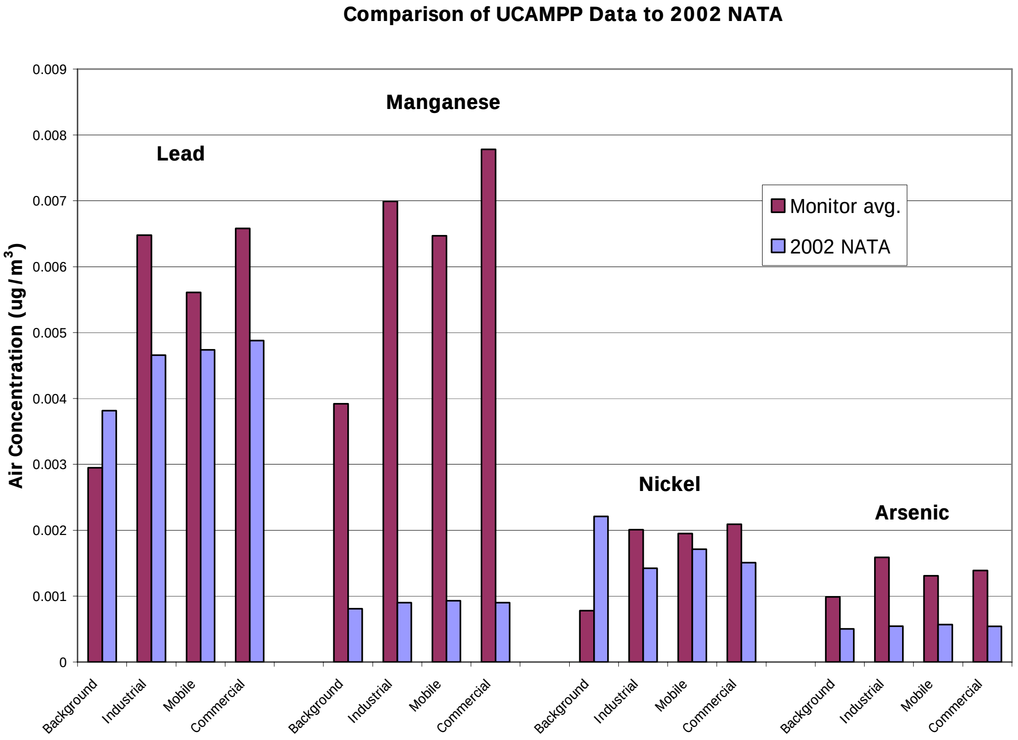


Figure 17: Annual average of monitored values and NATA for four selected metals

Of the four metals that are compared here, nickel had the best and manganese had the worst agreement between the monitored and NATA values. Differences could be due to changes in emission sources between 2002 and 2006, the way that NATA estimates concentrations, or the limitations of mobile source emissions estimation and modeling.

B. Evaluation of CALPUFF Using Monitoring Data

Dispersion Model

The dispersion modeling and the emission inventory data collected for model input is an important aspect of the UCAMPP study. The modeled concentrations are the result of dispersion modeling. This chapter provides an overview of the model, setup, key inputs, and the modeled output concentrations.

Monitoring Program and Modeling Period

Three air toxics monitors were deployed in Paterson in late 2005, collecting samples every six days starting in November 2005 and ending December 2006. One of the important and interesting components of the project was the comparison of monitored data to model predictions. A minimum of one year of monitoring is necessary to capture the varying emissions and meteorology for a full cycle of seasons, and to ensure a minimum of a year of modeled concentrations for the evaluation of lifetime exposures and risk (which is usually calculated for a 70-year lifetime, based on an annual average concentration).

Model Selection

In order to compare the model and monitored concentrations, it is better to choose a model that can make use of real-time meteorological data. Other model selection factors are the ability of the model to run during low wind speeds (less than 2 mph) when stagnant conditions can lead to the build-up of pollutants, the characteristics of the emission sources (especially for the area and mobile sources), the spatial resolution of the modeled concentrations, and the available computer resources. Despite the advantage of using real-time meteorological data, the model selection is hampered by the lack of detail in the emissions inventory, which would preclude using an airshed model. For the UCAMPP study the model domain is relatively small, and there was a need to report modeled concentrations at a high resolution.

The CALPUFF model was chosen because of its ability to predict high-resolution concentrations at near-source locations, and its ability to use concurrent three-dimensional wind fields for 2006 that could characterize the terrain surrounding Paterson.

CALPUFF Model

CALPUFF is a non-steady-state Gaussian puff model. This terminology is explained below. It is a USEPA-approved model for sources over 50 km from the study area. Although the modeling domain is less than 50km, CALPUFF can also be used at shorter distances and possesses advantages over AERMOD in this particular application. The wind fields used by CALPUFF vary spatially and temporally over the modeling domain and, in this case, incorporate multiple Rapid Update Cycle (RUC) profiles and local terrain features. CALPUFF'S ability to use real time RUC data is particularly significant for this project because it enabled the model to use similar types of windfields that influenced the monitored observations. In distinction from a plume model such as AERMOD, emissions are represented by a continuous series of puffs that wander individually across the modeling domain in response to the varying wind directions and speeds within the three-dimensional wind fields. CALPUFF is capable of handling a variety of emission sources – mobile, area and point sources all being important. The wind fields used by CALPUFF are generated by the meteorological model CALMET, discussed below.

Modeling Domain

The modeling domain is 33 x 26 km and is located in northeastern New Jersey and includes parts of Passaic, Bergen and Essex counties. The Universe Transverse Mercator (UTM) coordinates of the southwestern corner of the domain are 551000 meters east and 4516000 meters north. **Figure 1** shows the modeling domain and the air quality study area.

CALPUFF Modeling Data and Parameters

The main elements and data input requirements for this application of CALPUFF are the meteorological wind fields prepared within CALMET, the emissions inventory, CALPUFF modeling parameters and the receptor network across the air quality study area. These elements are described below.

CALMET Model

For the UCAMPP study, CALMET version 5.53 was used as a diagnostic model that incorporated the RUC data (soundings from the surface to upper levels) and geophysical data such as land use to generate the wind fields to be used by CALPUFF. CALMET produces a gridded, hourly-varying, three-dimensional wind field. A grid resolution of 150m was chosen to accommodate land use changes while allowing a reasonable processing time. Six vertical layers were chosen at 0-20m, 20-50m, 50-100m, 100-500m, 500-2000m, and 2000-3300m.

Use of Rapid Update Cycle (RUC) Data

Although CALMET is capable of generating three-dimensional wind fields from a set of surface and upper air observations, such fields lack dynamic consistency. USEPA encourages the use of meteorological fields from a prognostic model as first guess fields. Meteorological fields from Mesoscale Model 5 (MM5) are frequently used as a source of first guess fields for CALMET, but another source of prognostic modeling data that has not been as widely considered within the air quality modeling community is the real-time modeling systems from the National Center for Environmental Predictions (NCEP). NCEP is heavily involved in National Weather Service forecast operations through its use of a suite of models. An integral step in the process is the preparation of the initial fields which involves the development of a three-dimensional gridded analysis of the state of the atmosphere. This process involves using an assimilation system to blend the most recent observational data with first-guess fields from previous runs. Of particular interest here is the RUC system which is used to provide short-term forecasts. The RUC cycle is unique since it produces analyses every hour through a process known as continuous assimilation, whereby one-hour forecast fields are corrected based on real-time data collected by Nation Oceanic Atmospheric Administration (NOAA). These corrected fields serve as the starting point for the CALMET analysis described here. The locations of the RUC data points closest to Paterson are shown in Figure 18. The ambient monitoring sites are shown in Figure 19.

Geophysical Data

Geophysical data is used by CALMET to adjust the observed meteorological data and extend the data to produce wind fields that cover the entire domain. The geophysical data includes land use and terrain elevations. Differences in land use between urban and rural in this case allows the model to adjust flows to reflect mixing and turbulence effects near the surface, and to characterize the vertical mixing that varies with rising air masses from different levels of surface heating.

Terrain Elevations

The terrain data were derived from the United States Geological Survey (USGS) digital elevation model (DEM) with 30-meter horizontal resolution. These elevation data were used as inputs to CALMET, and as elevations for the receptors used in CALPUFF. Figure 18 shows the terrain of northern New Jersey with distinct topographical features to the northwest of Paterson. Figure 19 shows the location of the monitors.

Figure 18:

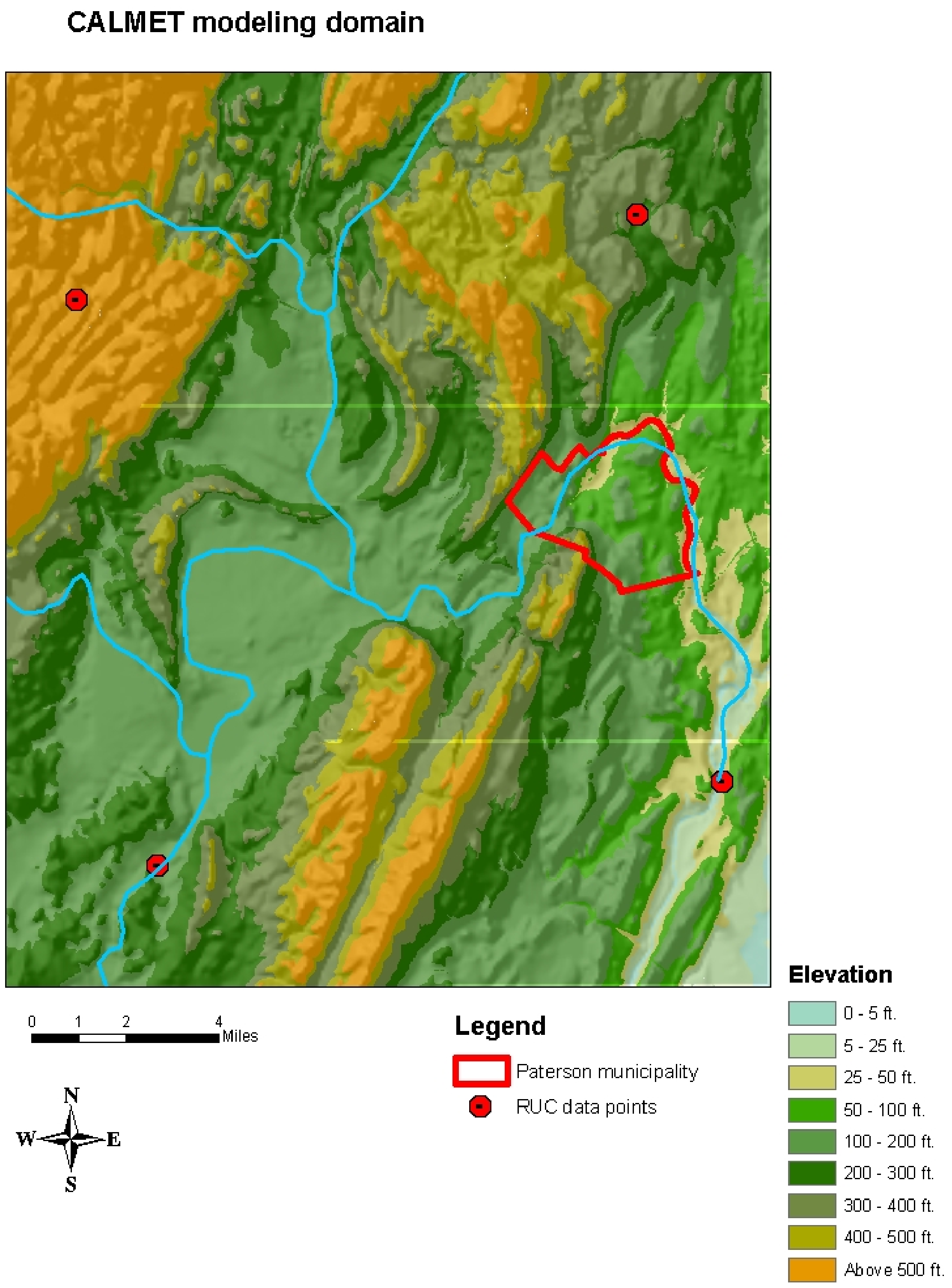

CALMET modeling domain
0
1
2
4
Miles
N
W
E
S
Legend
Paterson municipality
RUC data points
Elevation
0 - 5 ft.
5 - 25 ft.
25 - 50 ft.
50 - 100 ft.
100 - 200 ft.
200 - 300 ft.
300 - 400 ft.
400 - 500 ft.
Above 500 ft.

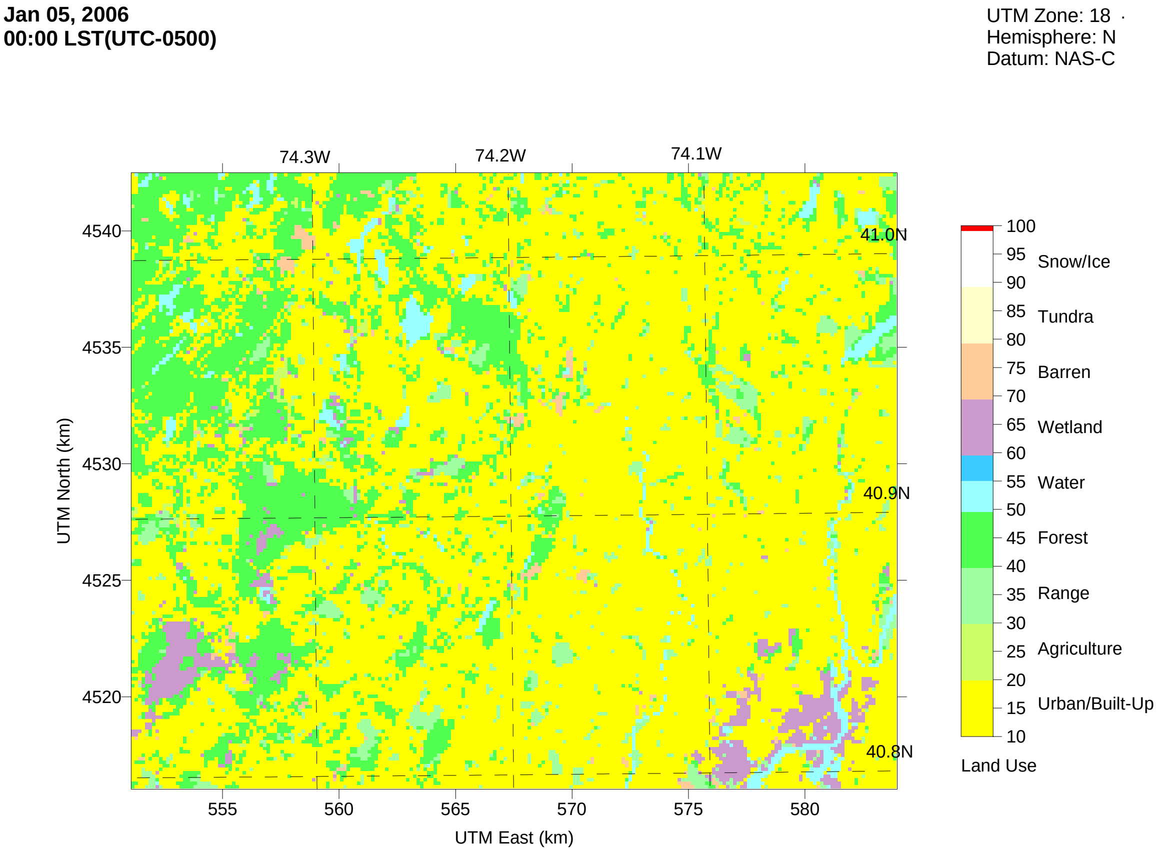
Figure 19:


Location of air quality monitors in Paterson
I - Monitor
C - Monitor
M - Monitor
I-80
I-80
N
W
E
S
Miles
0
0.25
0.5
1
Legend
Monitors
Local roads
Interstate
State roads
County roads

Land use

The land use data was taken from NJDEP's Geographic Information System (GIS) database. It is based on land use land cover (LULC) data originally developed in 1986 from aerial photography at a scale of 1:24,000. Since then there have been two revisions due to improved resolution and increases in the number of LULC categories. The 2002 LULC data used 1-ft. pixel imagery at a scale of 1:2400 and was used for this analysis. A representation showing the spatial extent of the different land use categories in the UCAMPP area are shown in Figure 20.

Figure 20: Land use classifications across the Paterson modeling domain



CALMET Modeling Options

The parameter settings in CALMET are complex. Examples of the more important parameters are described below.

Use of MM5-equivalent wind field output as input.

A source of prognostic modeling data that has not been as widely considered within the air quality modeling community are the real-time modeling systems from the National Center for Environmental Predictions (NCEP). Of particular interest is the Rapid Update Cycle (RUC) system used to provide frequently updated short term forecasts. The RUC cycle is unique among the NCEP forecast systems in that analyses are produced every hour and the gridded prognostic wind field model output fields can be used as input to the diagnostic wind field model.

- **The maximum radius of influence over land within the surface layer is 100 km.**

The influence of the surface observations is limited to 100 km from each site.

- **Minimum and maximum mixing heights are 100 and 3200 m, respectively.**

These values were chosen as realistically representing conditions in the Paterson area.
An example of a wind field is shown in Figure 21 (May 13, 2006). The arrows represent the direction of the wind as indicated and the length of the arrow represents wind speed. For this particular hour it is possible to see stronger southwesterly winds to the south of Paterson, which is in contrast to the northeastern corner where winds were more stagnant. This figure illustrates the advantage of using a model such a CALPUFF that incorporates a spatially varying wind field; if a model such as AERMOD had been chosen uniform winds across the domain would have been depicted/used.

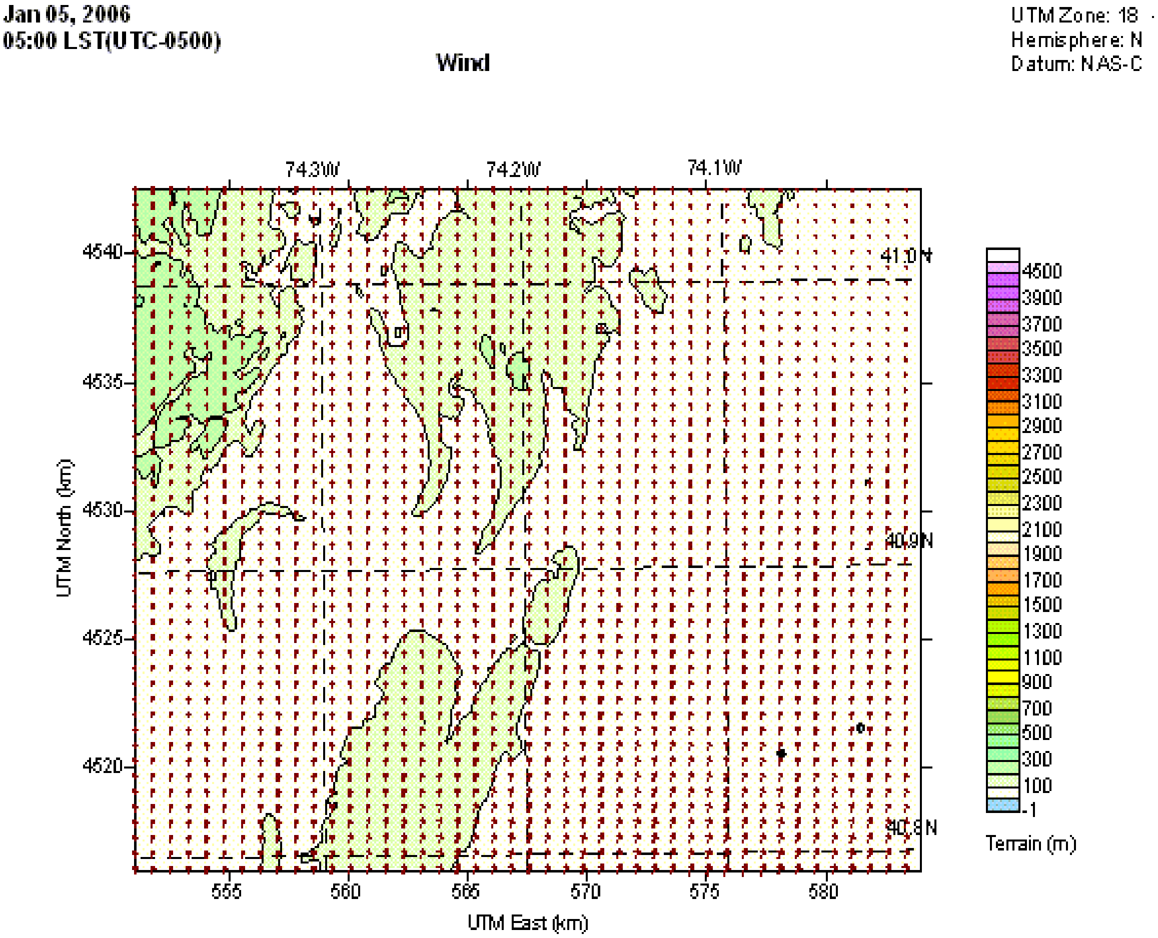
Emissions: Source Categories

It was important to assess the relative emission contributions of different source categories since this potentially could aid in the development of risk reduction strategies. The source categories modeled in CALPUFF were 1) industrial point sources 2) area sources 3) on-road mobile sources.

Emission Preparation for CALPUFF Input

Mobile emissions from local roads and highways were modeled in CALPUFF as area sources. The parameters include emission height above the surface, and sigma z and sigma y. Sigma z is a measurement of the initial vertical dispersion as a result of emissions. For example, many of the road segments are entered as area sources in CALPUFF covering segments of each roadway. These sources have a release height of 0.3m (reflecting the height of an exhaust tailpipe) but an effective initial vertical dispersion of 5m. This translates into a center of emission release at 0.3m but vertically dispersing up to 5.3m. Sigma y represents the same concept but in the horizontal plane. Point sources have distinct emissions parameters for each source. These are stack height, diameter, temperature of the emitted pollutant, and exit velocity.

Figure 21: An example of a CALMET wind field (May 13, 2006)



Model Receptors

The CALPUFF model predicts pollutant concentrations at a series of points or model receptors, which are established within the modeling domain as inputs. Due to model run-time restrictions these were spaced every 150m. Additional model receptors were placed alongside the UCAMPP monitors to enable model-to-monitor comparisons which are part of the model evaluation process.

There are a total of 2907 receptors across the model domain. Figure 22 shows their position with respect to the city of Paterson, major roadways and waterways in the region, the three downtown monitors, and all point sources modeled with CALPUFF.

Dispersion Modeling Results

Background Concentrations

The model-predicted concentrations are reported with and without background concentrations. Background values were obtained from the background (Chester, NJ) monitoring site. Table 6 shows the annual average concentrations of toxic air pollutants relevant for this study. Figure 23 shows the annual cycle of benzene concentrations at Chester in 2006.

Table 6: Background air toxic concentrations at Chester (relevant to the dispersion modeling in this section)

Pollutant	Annual Average Conc. (µg/m^3)
Benzene	0.52
Toluene	0.70
Ethylbenzene	0.14
Formaldehyde (PAKS)	10.94
Hexavalent Chromium	0.00023
Arsenic	0.00099
Lead	0.00295
PM_{10}	11.29
p-Dichlorobenzene	Non-Detect

Figure 22: Receptors and Major Roads

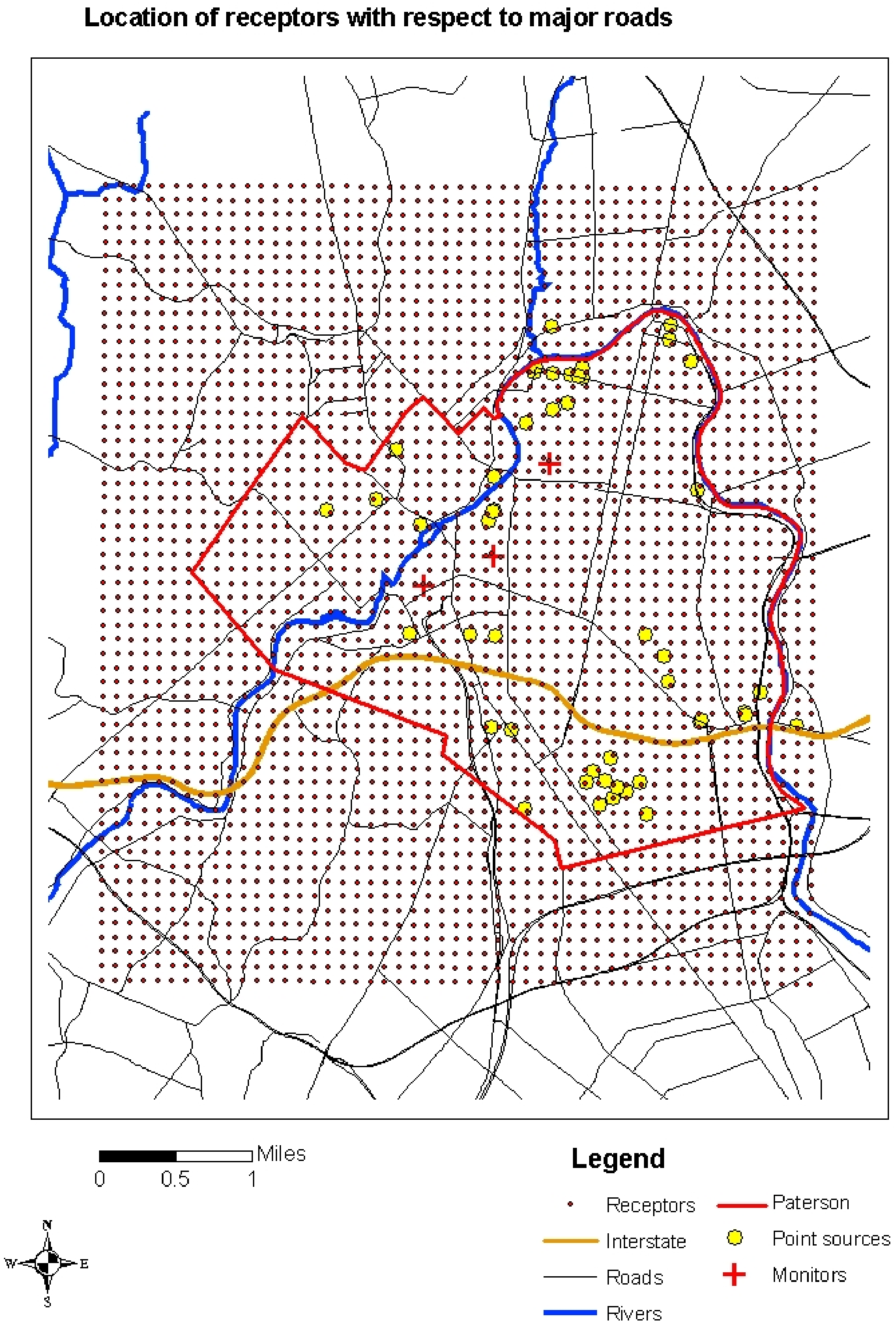
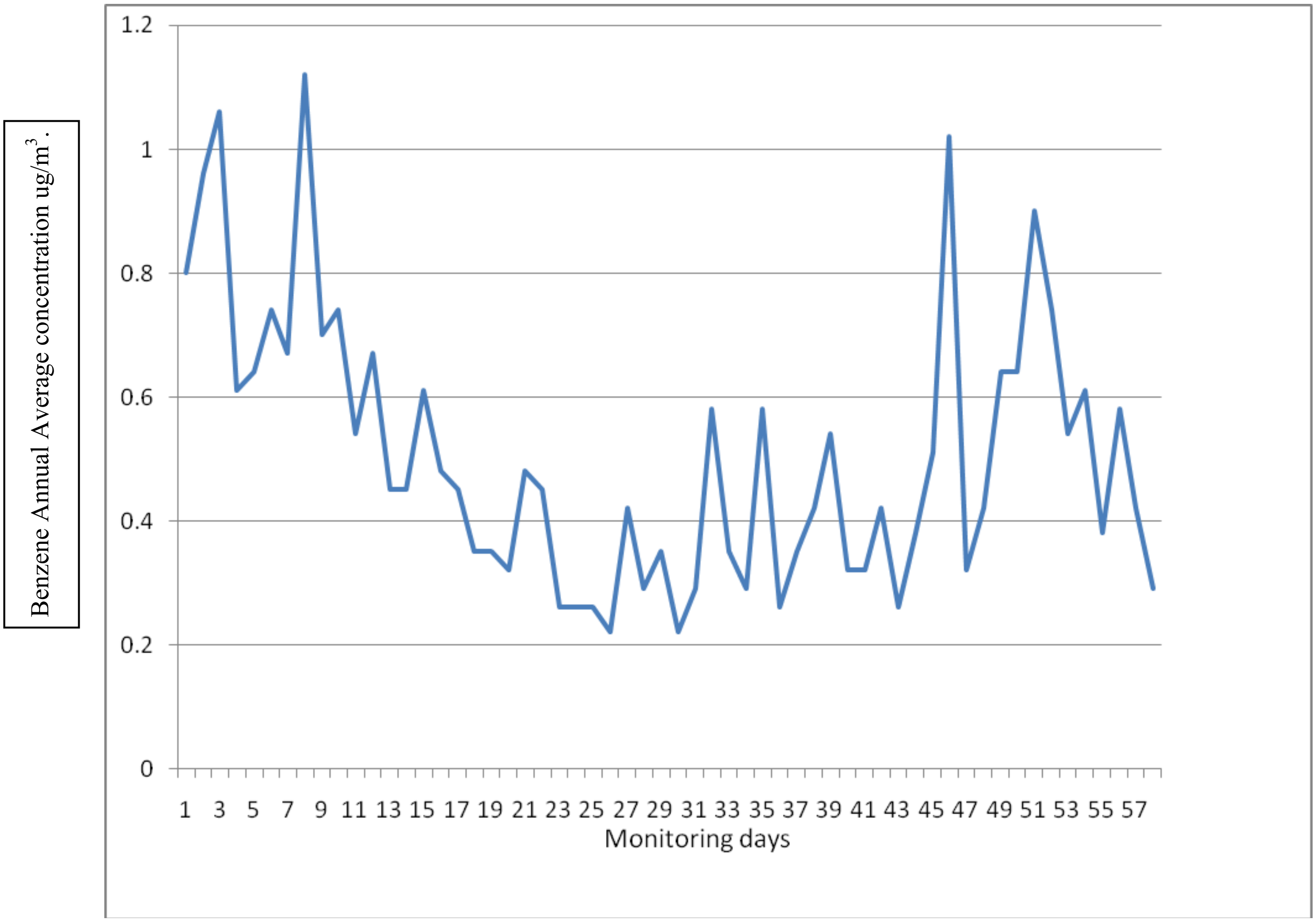


Figure 23: Benzene Concentrations Recorded at the Background Site (Chester, NJ) (2006).



Concentration Predictions

CALPUFF concentration predictions are illustrated by the spatial distribution of pollutant concentrations as isopleth plots of predicted concentration, and also by comparing these predictions to NATA values. The isopleth plots not only show the predicted concentrations at a resolution of 150 m across the city of Paterson, but also show the location of the three air quality monitors.

The plots shown here are grouped as follows: mobile-source dominated and a selection of air toxics (VOCs and metals). The selected air toxics can be divided primarily into mobile and area sources, with a few point sources. The mobile source group includes benzene, toluene, ethylbenzene and formaldehyde. The area source group includes hexavalent chromium and arsenic. The point source group consists of lead and PM_{10}.

Mobile-Source Pollutants: Benzene, Toluene, Ethylbenzene and Formaldehyde

The mobile source pollutants emanate mostly from Interstate 80 (I-80) to the south. The first plot shows predicted benzene concentrations (Figure 24). This shows areas of higher benzene (over 125 $\mu g/m^3$) concentrated along I-80, whereas most of the city of Paterson has low concentrations (below 75 ug/m^3). These plots of predicted pollutant concentration show the impact of both point source and mobile source emissions on the surrounding community and at the three monitors. Predicted concentrations of ethylbenzene (Figure 25) also emphasize the dominance of I-80 emissions in the Paterson study area. Predicted concentrations in the vicinity of the monitors are low for both pollutants. The predicted annual concentration for formaldehyde (Figure 26) also shows a mobile source contribution, particularly to the west of the city. The predicted annual concentrations for toluene (Figure 27) emphasize the presence of point source emissions over Paterson as well as mobile sources along I-80. These four plots of air toxics in the mobile source group show the same general characteristics, with a line of high concentrations along the I-80 corridor especially at the junction with Highway 20, as well as high concentrations along Union Boulevard.

Figure 24: Benzene

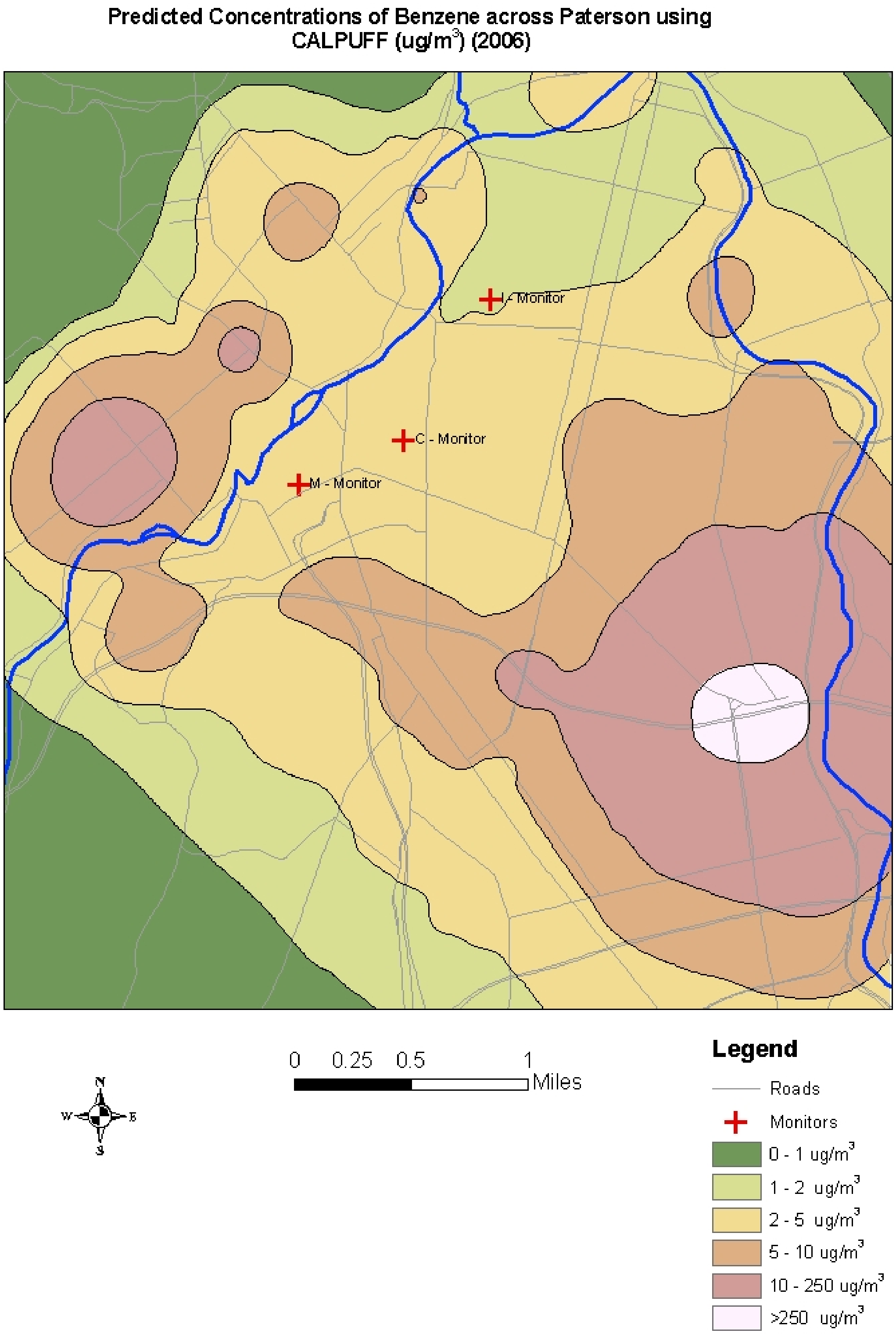


Figure 25: Ethylbenzene

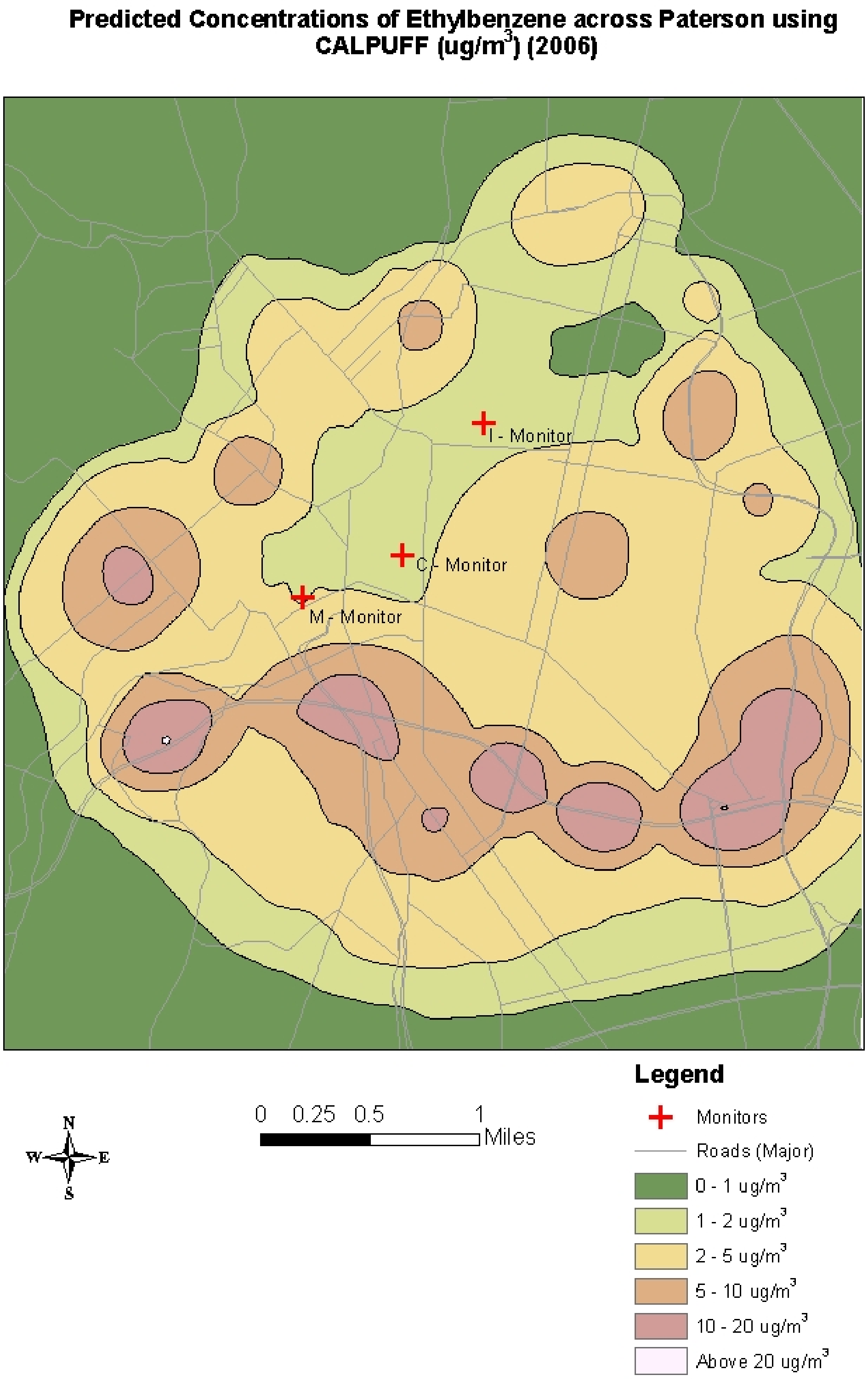


Figure 26:
Formaldehyde

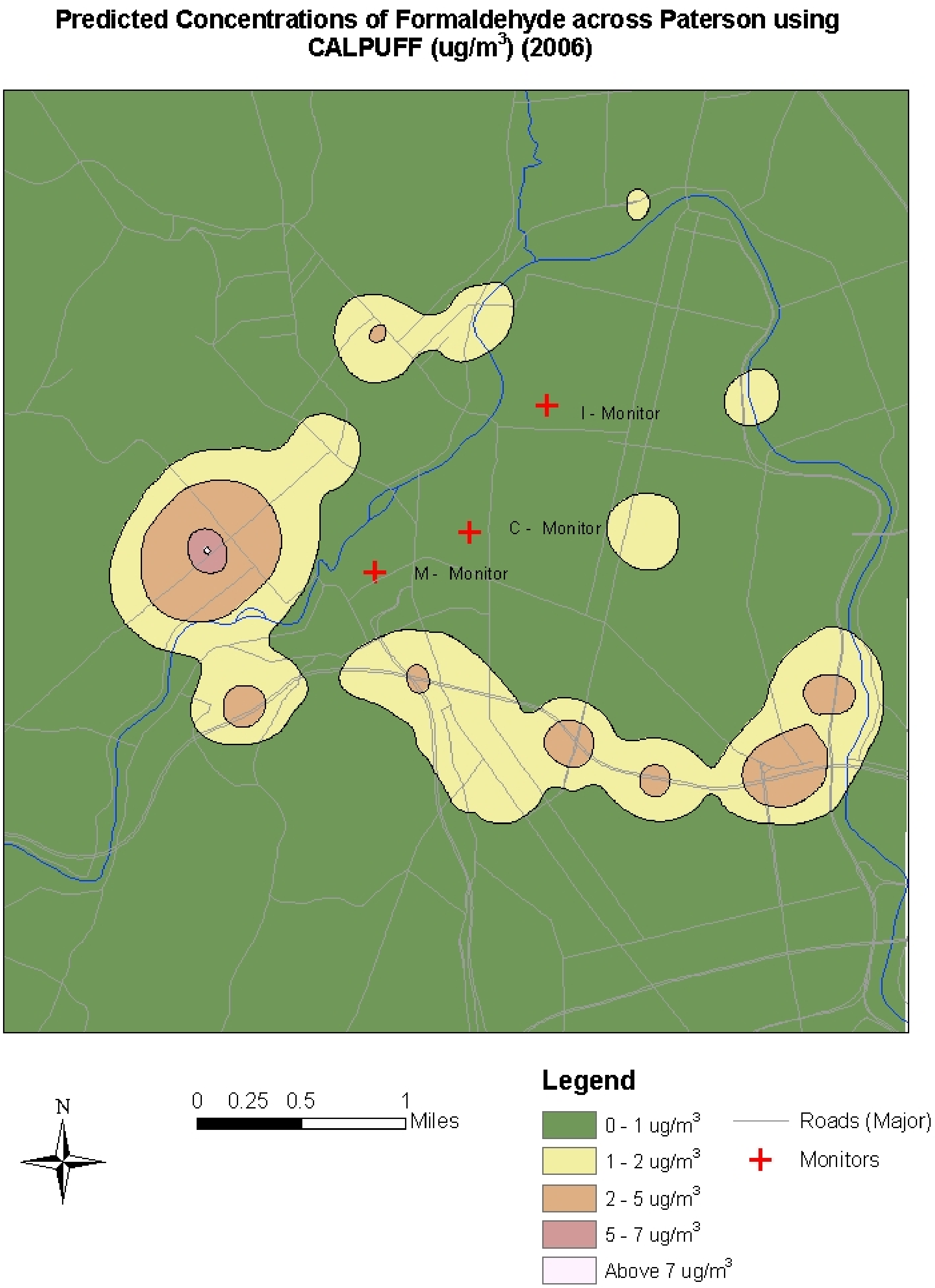
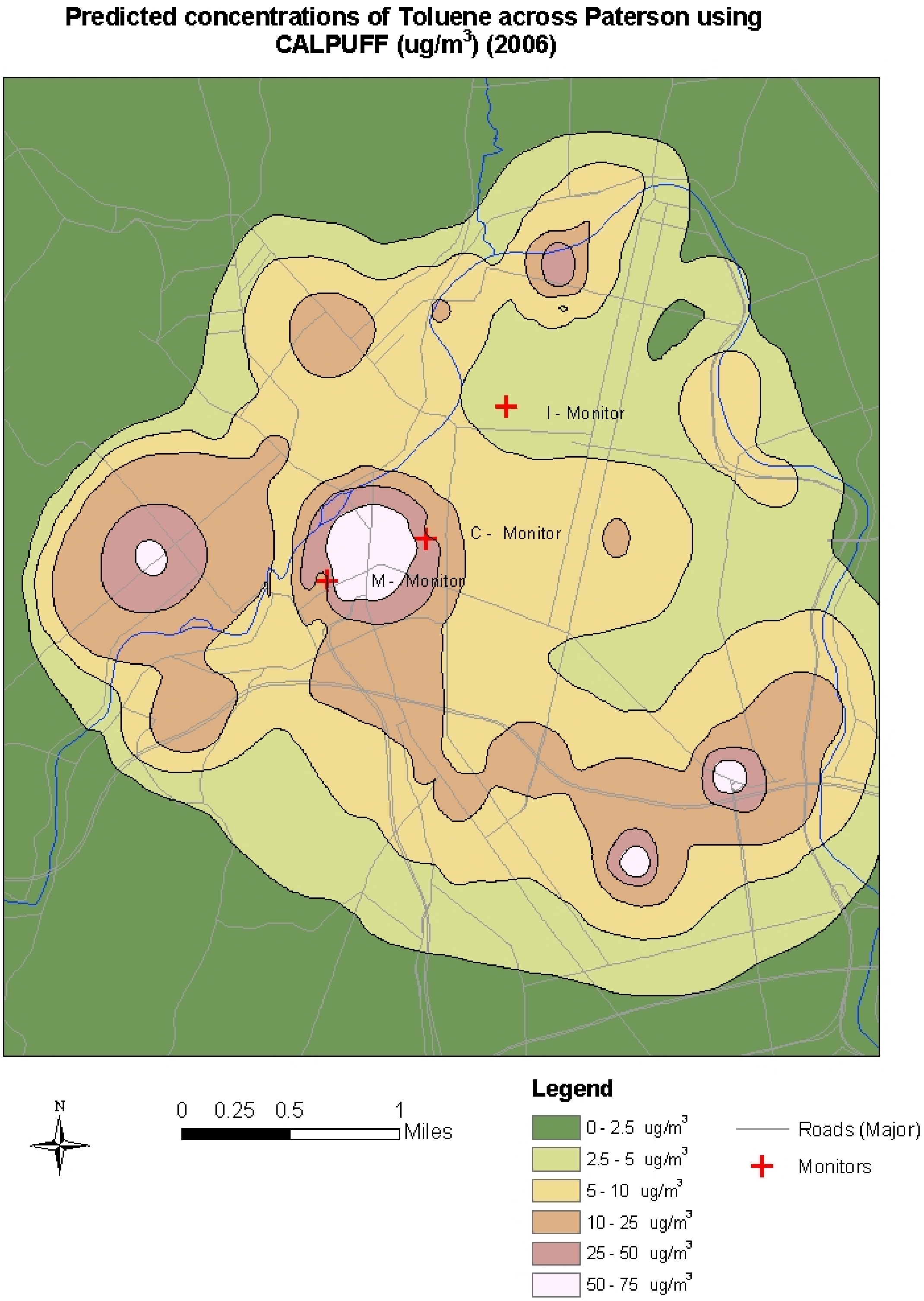


Figure 27: Toluene



Area and Point Source Pollutants: Hexavalent Chromium, Arsenic, Lead, PM_{10} and p-Dichlorobenzene

The impacts of these pollutants are characterized by the distribution of point source emissions across the city and therefore may have limited impact. The isopleth plots are shown in Figures 28 to 32. Figure 28 shows the predicted concentrations of hexavalent chromium with the highest concentrations in downtown Paterson. Figure 29 shows that the maximum predicted arsenic concentrations occur along the I-80 corridor to the south. Maximum predicted lead concentrations show peak values in the area of known point sources (southeastern part of Paterson), these being dominated by one source which only reported its permit allowable emission rates (Figure 30). Figure 31 shows PM_{10} concentrations across the city with a major focus on I-80 and other major highways. p-Dichlorobenzene emissions are dominated by two point sources to the east (Figure 32) with little impact upon the downtown monitors. The highest concentrations are in the east and each monitor is close to the 0.0001 ug/m^3 contour.

Figure 28: Hexavalent Chromium

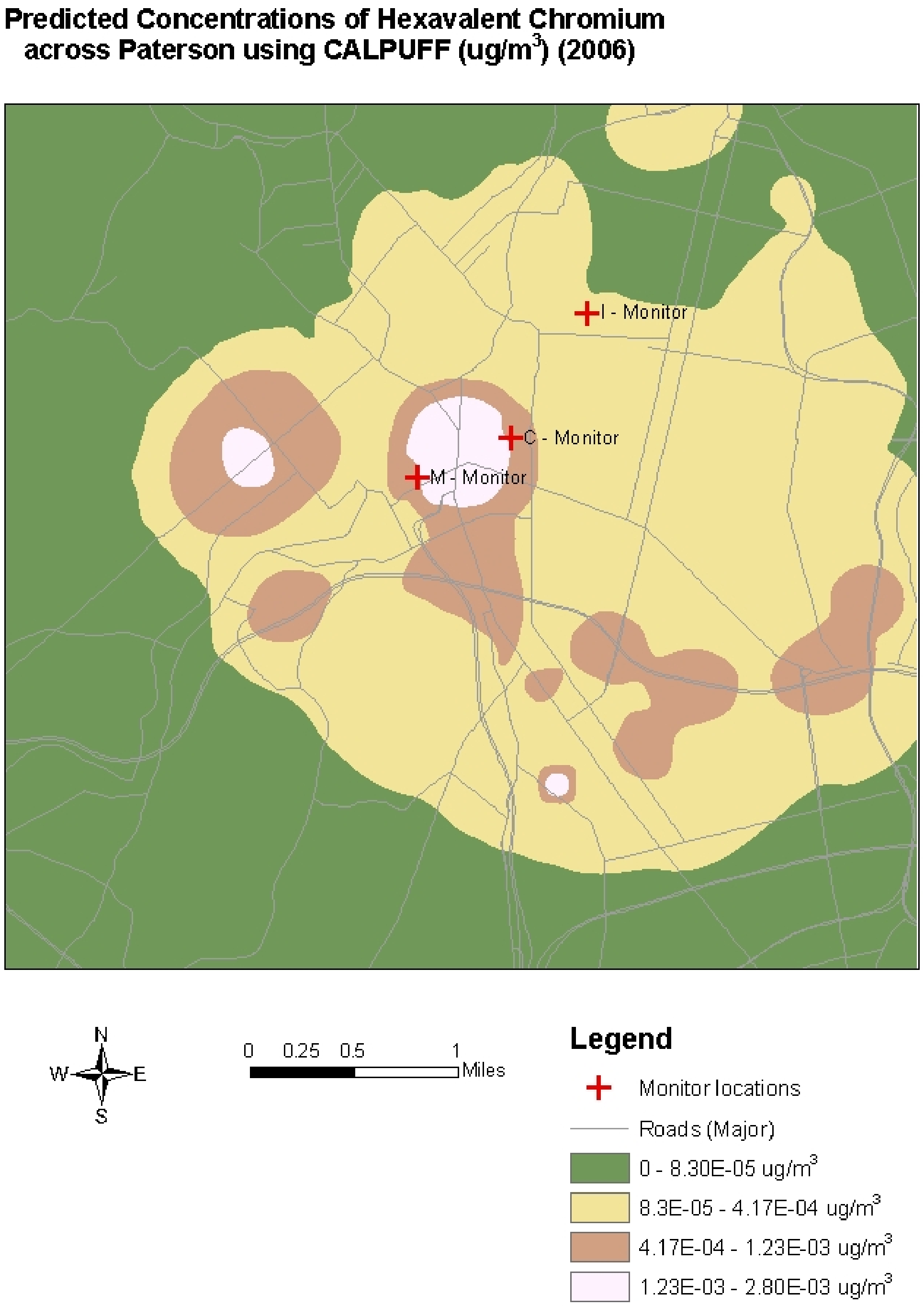


Figure 29: Arsenic

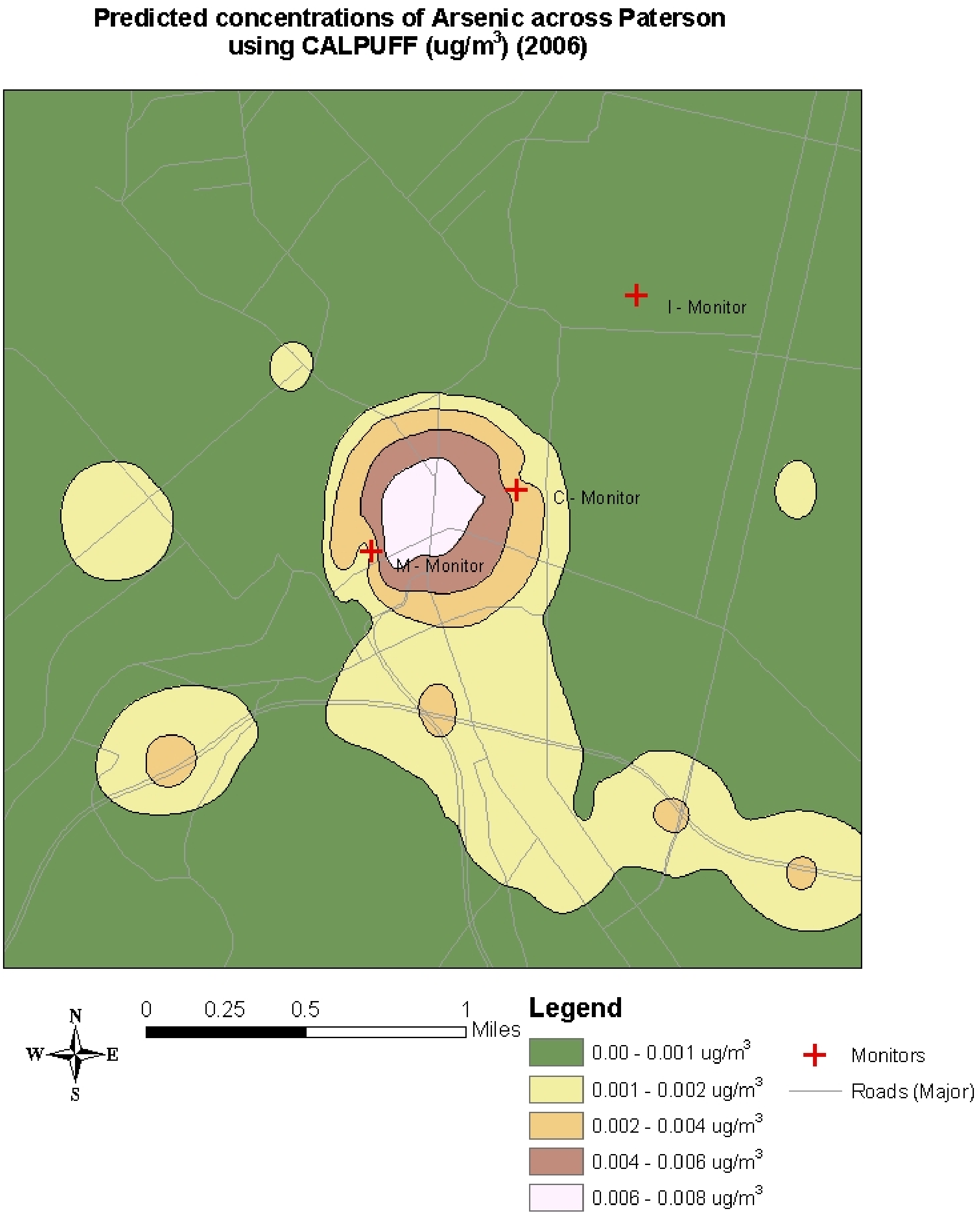


Figure 30: Lead

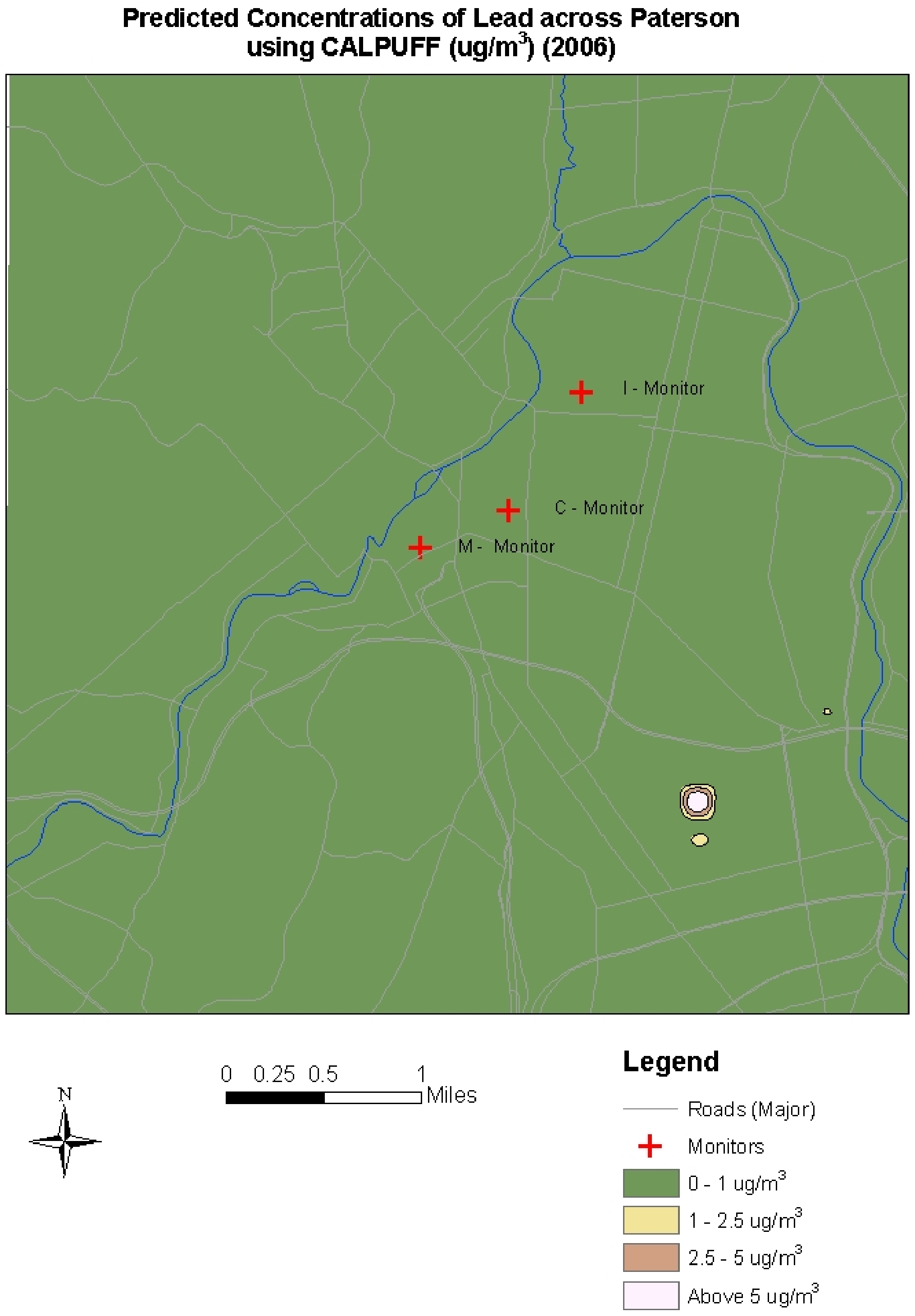


Figure 31: PM_{10}

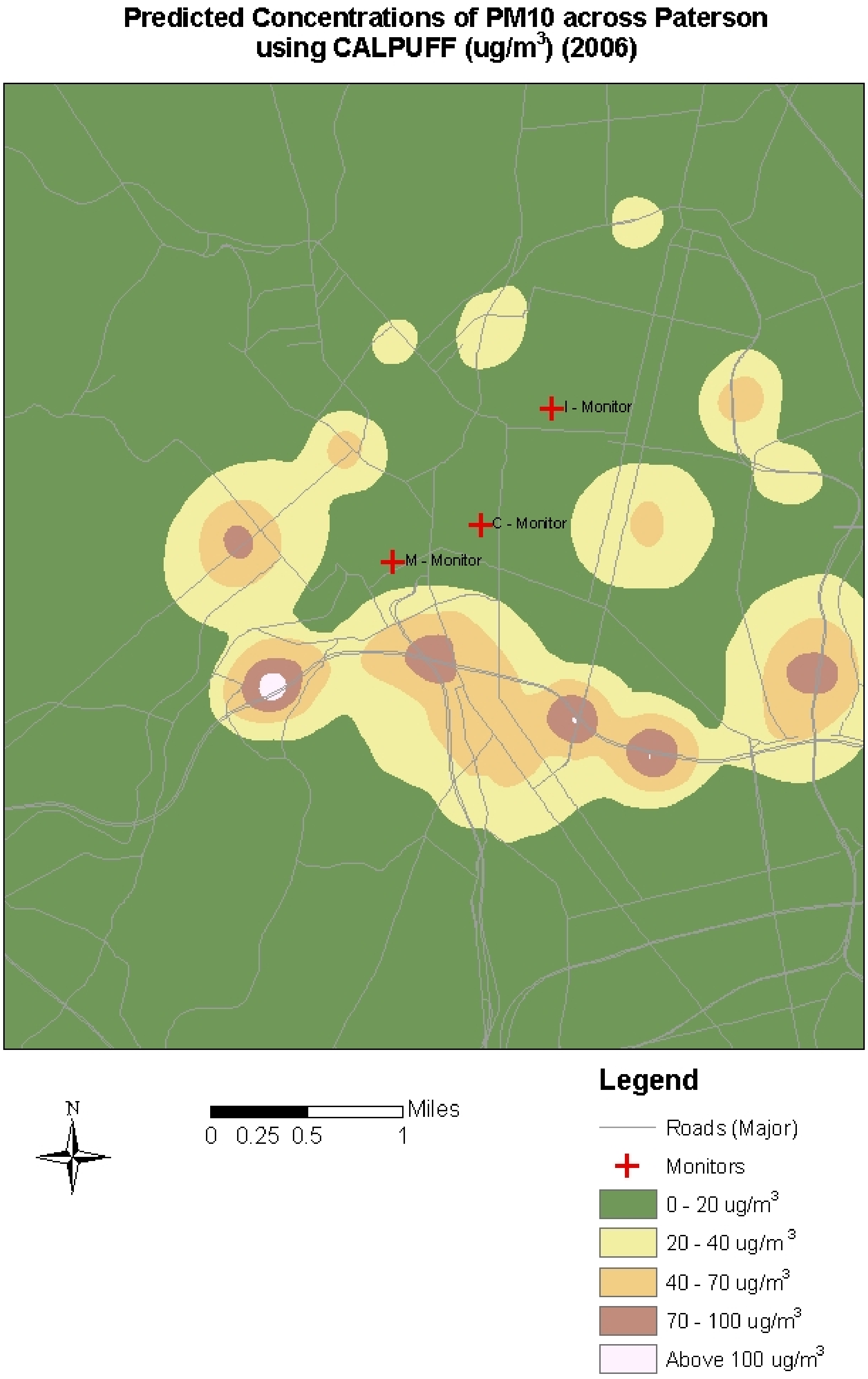
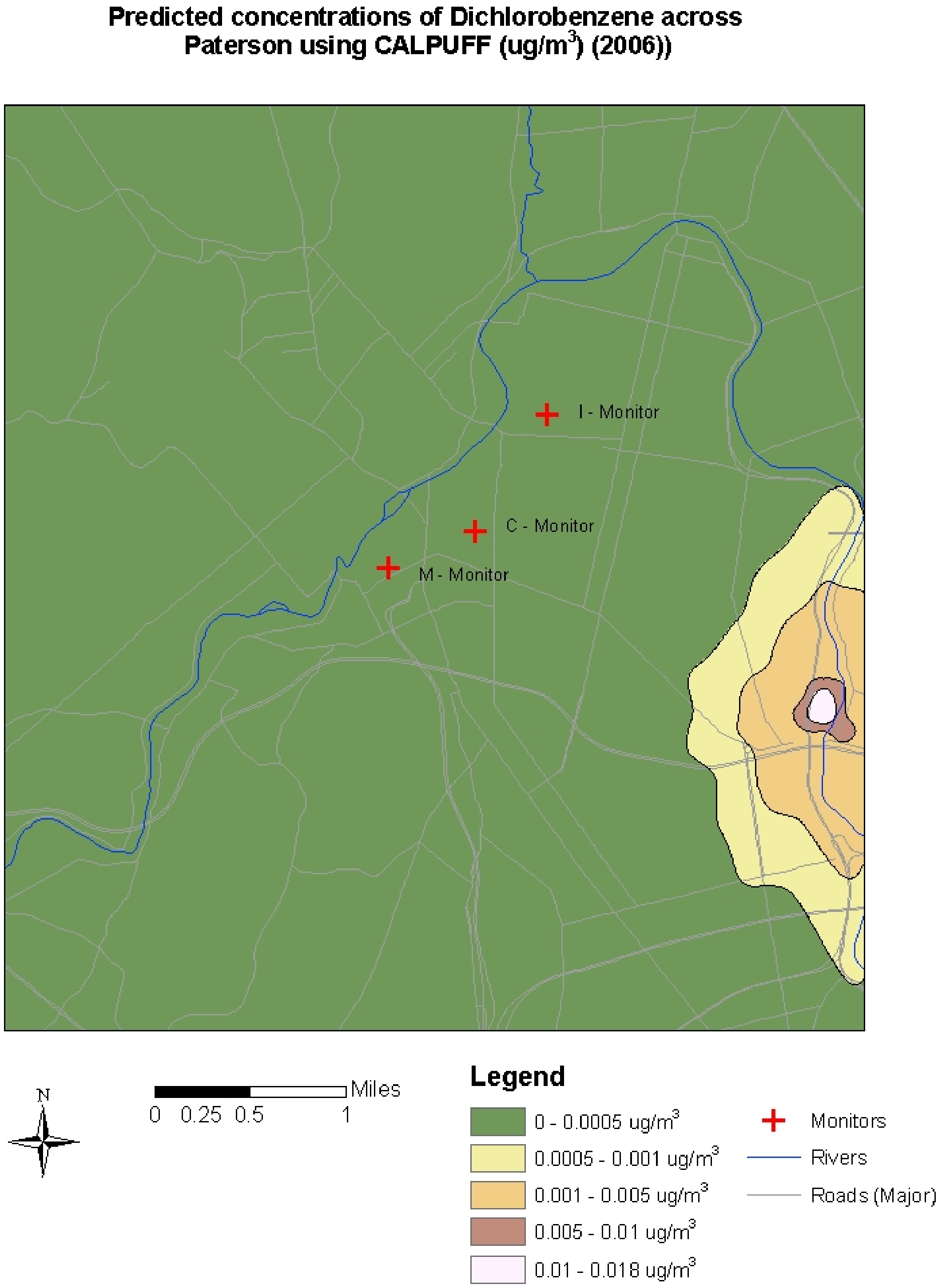


Figure 32: p-Dichlorobenzene



Model-to-Monitor Evaluation of Results

The 2006 monitored values made it possible to compare the initial set of modeled concentrations predicted by the CALPUFF measurements from the same year. This step was extremely valuable in highlighting deficiencies in the data inputs or in the model. The model-to-monitor evaluation resulted in reassessment and in some cases revision of some emissions estimates prior to the final model runs. The primary objective in doing the monitor-to-model evaluation was to determine the accuracy of the model, although factors such as monitor height or emission inventory could complicate such a comparison.

Graphic Evaluation of Model-to-Monitor Results

For each pollutant considered in the modeling section, a box plot was constructed to show how modeled annual predictions compared to the range of monitored values recorded throughout 2006 at each of the three monitors. The figures below (Figures 33 to 41) show the model-to-monitor evaluation for each pollutant and monitor. The box plots show observations above the median but below the 3rd quartile (Q3; in gray) and observations below the median but above the 1st quartile (Q1; in green). The whiskers on either side of this box represent the range in values beyond these quartiles but not outliers (the minimum range equals 1.5 x Q3-Q1; the maximum range equals 1.5 x Q3-Q1). The 'x' represents an outlier within the observations and the red square represents the annual modeled prediction.

Model Performance

It is widely accepted that if the model predictions are within a factor of two of the observed values then they are considered reasonable (EPA, 2001). There are many uncertainties involved with the model prediction of air pollutants, including the representativeness of the source emissions and meteorological data, the presence or absence of key chemical reactions, as well as the suitability of the model to the local terrain. In general, the results show that CALPUFF performed very well in most cases, although some pollutants were difficult to model accurately due to a lack of detail in the emissions inventory. Model predictions, monitored values, and predictions made in the 2002 NATA study are also provided. The comparison with NATA is made noting that the two predictions used different dispersion models and represent two different years.

Metals

Arsenic, Chromium (VI) and lead were modeled in the UCAMPP study. In general, the model tended to over predict the monitored values which, due to the location of the stationary sources, could indicate that the mobile source emission estimates are too high.

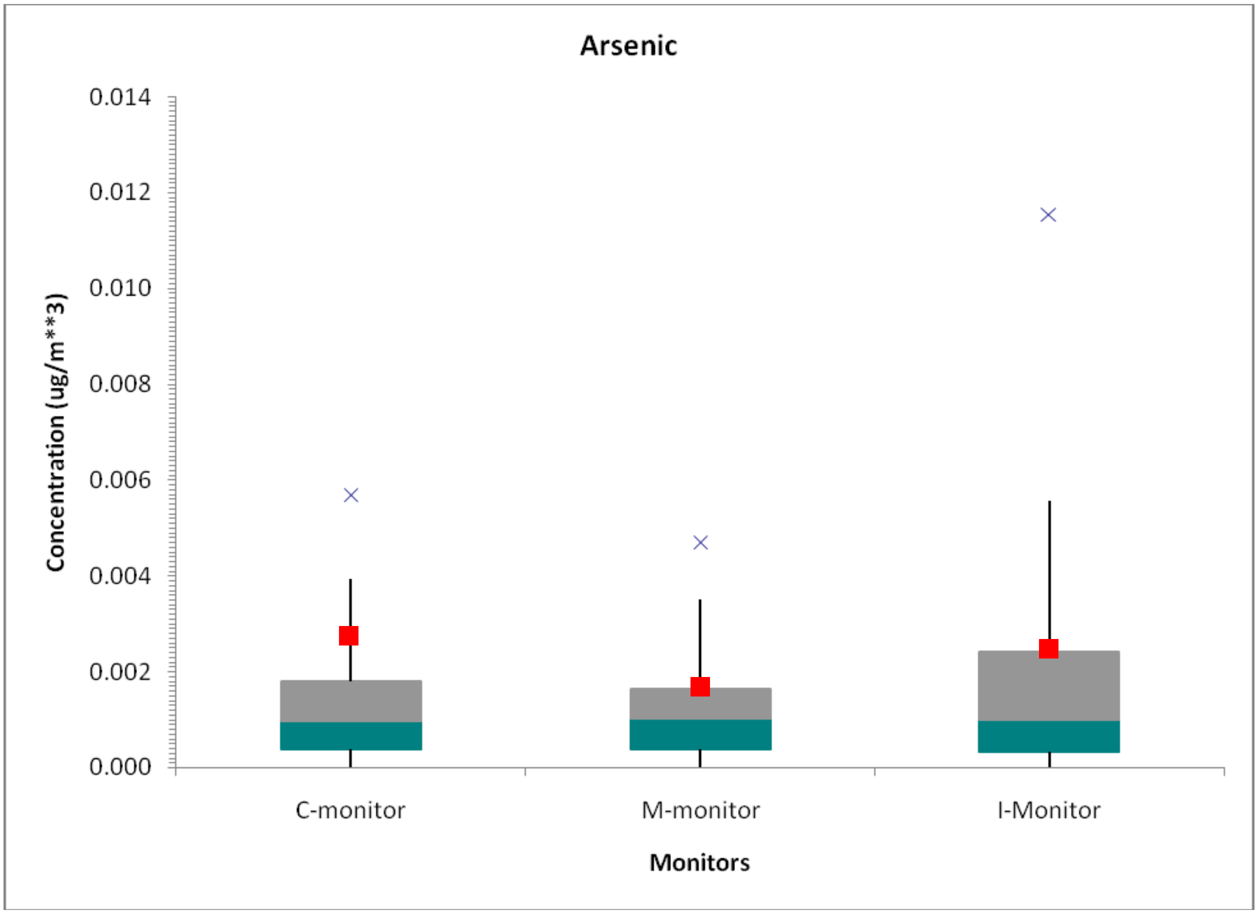
Arsenic

Model-to-monitor ratios from three Paterson monitors generally showed good agreement with CALPUFF, only over predicting observations by a factor of two (Table 7). Table 7 shows the maximum predicted arsenic concentration compared to observations. The predicted value is given with background. This represents the combined effect of the arsenic sources plus background levels and thereby representing a value that can be directly compared to the observed value. Arsenic sources are dominated by background mobile source emissions. Annual measured values ranged from 1.3E-03 to 1.6E-03 µg/m^3. Model-to-monitor ratios ranged from 2.1 to 2.7 (the nearer the value to 1.0 the better the model prediction). Figure 33 shows a box

Table 7: Maximum Predicted Annual Arsenic Concentrations Compared to Observations at Three Paterson Monitors

Monitor	Observed ($\mu g/m^3$)	Predicted (including background)* ($\mu g/m^3$)	Model-to-monitor ratio	NATA 2002 (census tract) ($\mu g/m^3$)
Mobile	1.31E-03	2.72E-03	2.1	2.15E-04
Commercial	1.39E-03	3.79E-03	2.7	1.86E-04
Industrial	1.59E-03	3.53E-03	2.2	1.90E-04

Figure 33: Model-to-Monitor Comparison for Arsenic



Key: The box represents the distance between the 1st and 3rd quartiles (the line between the gray and green boxes is the median). The whiskers show the highest and lowest data points or 1.5 times the box (Q3-Q1). Outlier points are marked x and are those that are greater than 1.5 times (Q3 -Q1). The model annual prediction of arsenic at each particular monitor is shown with a red square.

and whisker plot of the monitored values together with the annual model prediction. This shows that the model slightly overpredicts the observations but is otherwise a good match.

Hexavalent Chromium

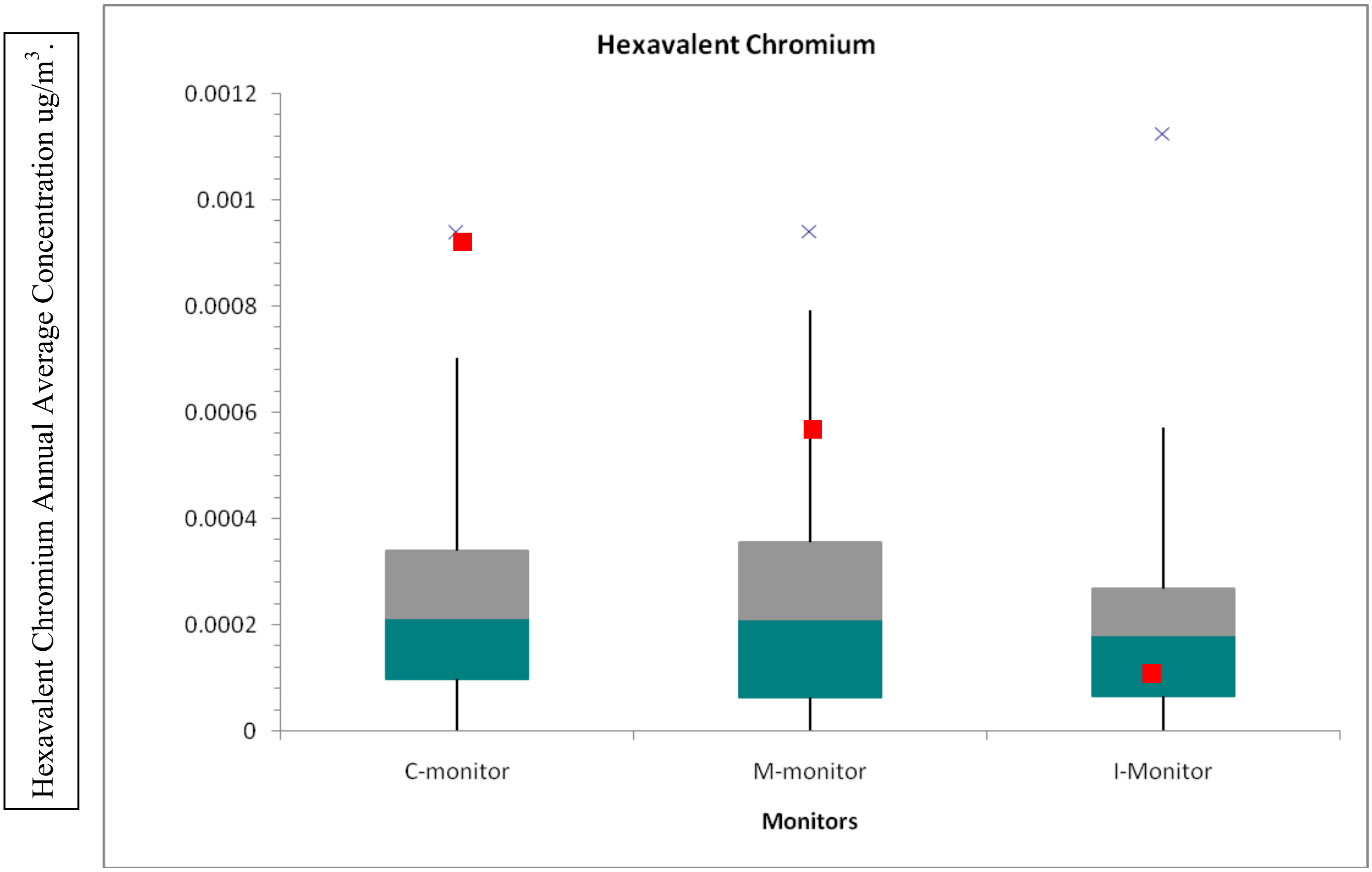
Sources include three metal processing facilities as well as highway emissions. Measured values ranged from 2.4E-04 to 2.6E-04 µg/m^3. Model-to-monitor ratios ranged from 1.3 to 4.5. Table 8 shows the difference between modeled and monitored chromium (VI) concentrations. The CALPUFF predictions are higher than observed particularly in the downtown section but are still within an acceptable range. Figure 34 graphically shows that the model over predicts at the C site, slightly less so at M-monitor whereas the prediction at I-monitor is very good.

Table 8: Maximum Predicted Annual Hexavalent Chromium Concentrations Compared to Observations at Three Paterson Monitors

Monitor	Observed (µg/m^3)	Predicted (including background*) (µg/m^3)	Model-to-monitor ratio	NATA 2002 (census tract) (µg/m^3)
Mobile	2.5 E-04	8.10E-04	3.2	5.06E-04
Commercial	2.6 E-04	1.16E-03	4.5	4.95E-04
Industrial	2.4 E-04	3.17E-04	1.3	5.58E-04

* Background values were not reliable indicators of prevailing concentrations in Paterson

Figure 34: Model-to-Monitor Comparison for Hexavalent Chromium



Key: The box represents the distance between the 1st and 3rd quartiles (the line between the gray and green boxes is the median). The whiskers show the highest and lowest data points or 1.5 times the box (Q3-Q1). Outlier points are marked x and are those that are greater than 1.5 times (Q3 -Q1). The model annual prediction of hexavalent chromium at each particular monitor is shown with a red square.

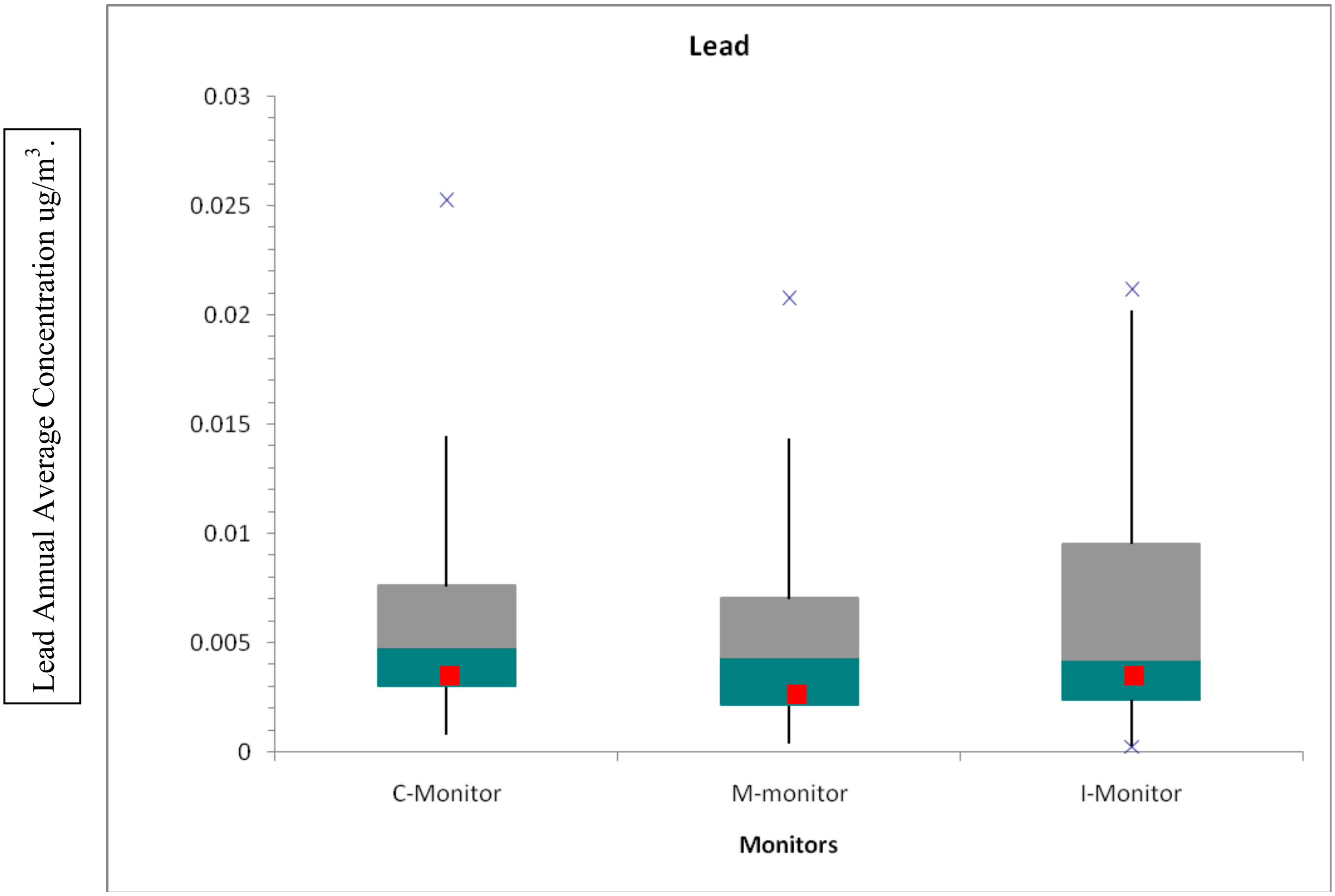
Lead

Model-to-monitor ratios from three Paterson monitors show an excellent match for lead. CALPUFF predictions were almost exactly the same as values observed at the monitors, with model-to-monitor ratios of 0.9 to 1.0 (Table 9). Measured values ranged from 0.005 to 0.006 µg/m^3 and were at some distance from the sources, all of which were industrial. Lead was released by several stationary sources with fugitive emissions. Definition of the area source boundaries within CALPUFF was determined to be critical for the accurate prediction of impacts, yet these parameters are notoriously difficult to quantify. Figure 35 shows that the model slightly under predicts observations.

Table 9: Maximum Predicted Annual Lead Concentrations Compared to Observations at Three Paterson Monitors

Monitor	Observed (µg/m³)	Predicted (including background)* (µg/m³)	Model-to-monitor ratio	NATA 2002 (census tract) (µg/m³)
Mobile	0.0056	0.0059	1.0	0.003
Commercial	0.0066	0.0063	0.9	0.004
Industrial	0.0065	0.0062	0.9	0.004

Figure 35: Model-to-Monitor Comparison for Lead



Key: The box represents the distance between the 1st and 3rd quartiles (the line between the gray and green boxes is the median). The whiskers show the highest and lowest data points or 1.5 times the box (Q3-Q1). Outlier points are marked x and are those that are greater than 1.5 times (Q3 -Q1). The model annual prediction of lead at each particular monitor is shown with a red square.

Volatile Organic Compounds

The VOCs that were modeled were benzene, ethylbenzene and toluene.

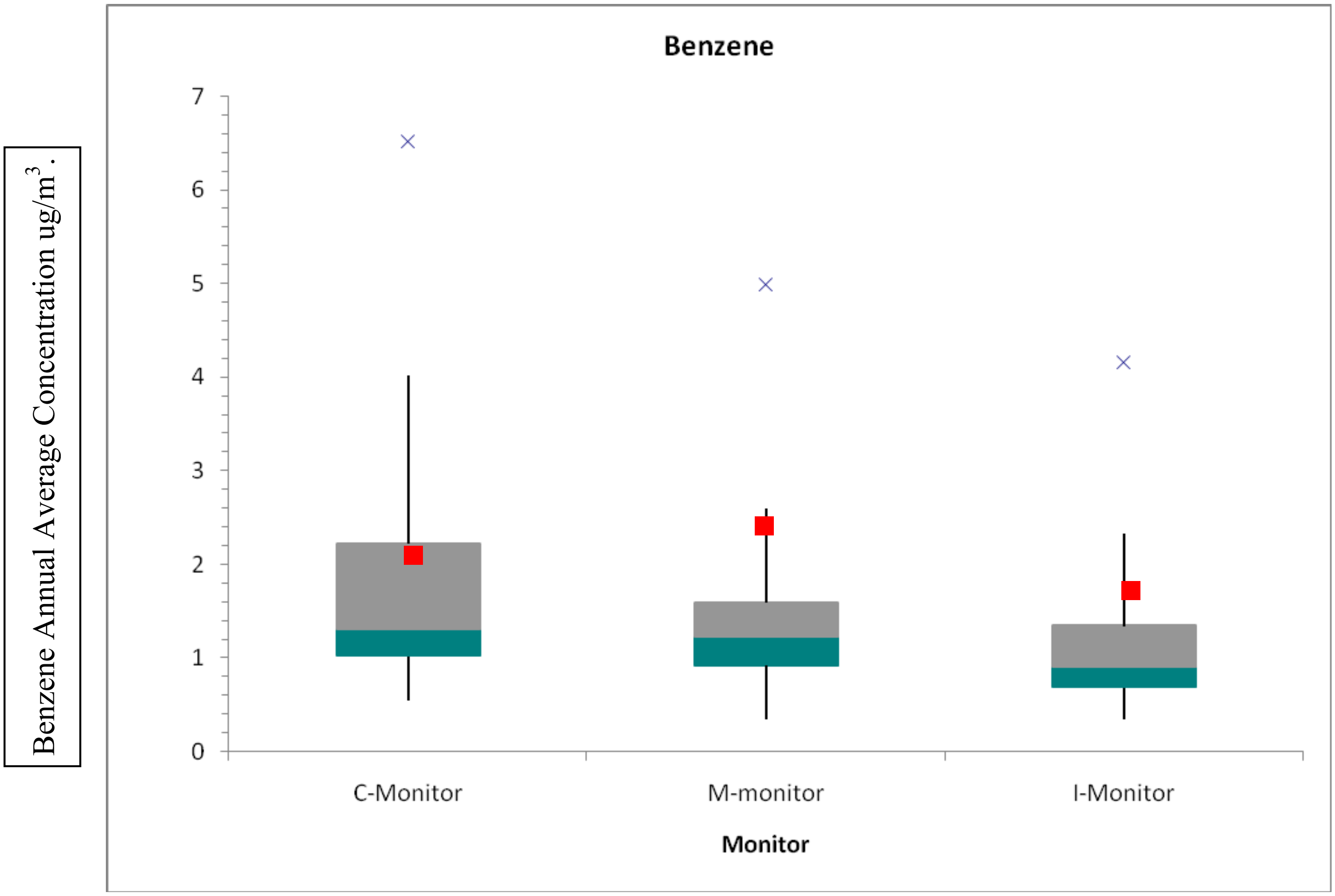
Benzene

The predicted annual concentrations at the three monitors are given in Table 10 and are also compared to the most recent NATA predictions (2002). Model-to-monitor ratios from the three Paterson monitors generally show good model performance. Emission sources are area, stationary and mobile in nature. Measured values ranged from 1.1 to 1.8 µg/m^3. Figure 36 shows in graphic form the performance of the model when compared to all monitor observations. The annual CALPUFF predictions all over predict the observations but remain acceptable. Model-to-monitor ratios ranged from 1.5 to 2.1.

Table 10: Maximum Predicted Annual Benzene Concentrations Compared to Observations at Three Paterson Monitors

Monitor	Observed (µg/m^3)	Predicted (including background)* (µg/m^3)	Model-to-monitor ratio	NATA 2002 (census tract) (µg/m^3)
Mobile	1.4	2.9	2.1	1.48
Commercial	1.8	2.7	1.5	1.38
Industrial	1.1	2.3	2.1	1.38

Figure 36: Model-to-Monitor Comparison for Benzene



Key: The box represents the distance between the 1st and 3rd quartiles (the line between the gray and green boxes is the median). The whiskers show the highest and lowest data points or 1.5 times the box (Q3-Q1). Outlier points are marked x and are those that are greater than 1.5 times (Q3 -Q1). The model annual prediction of benzene at each particular monitor is shown with a red square.

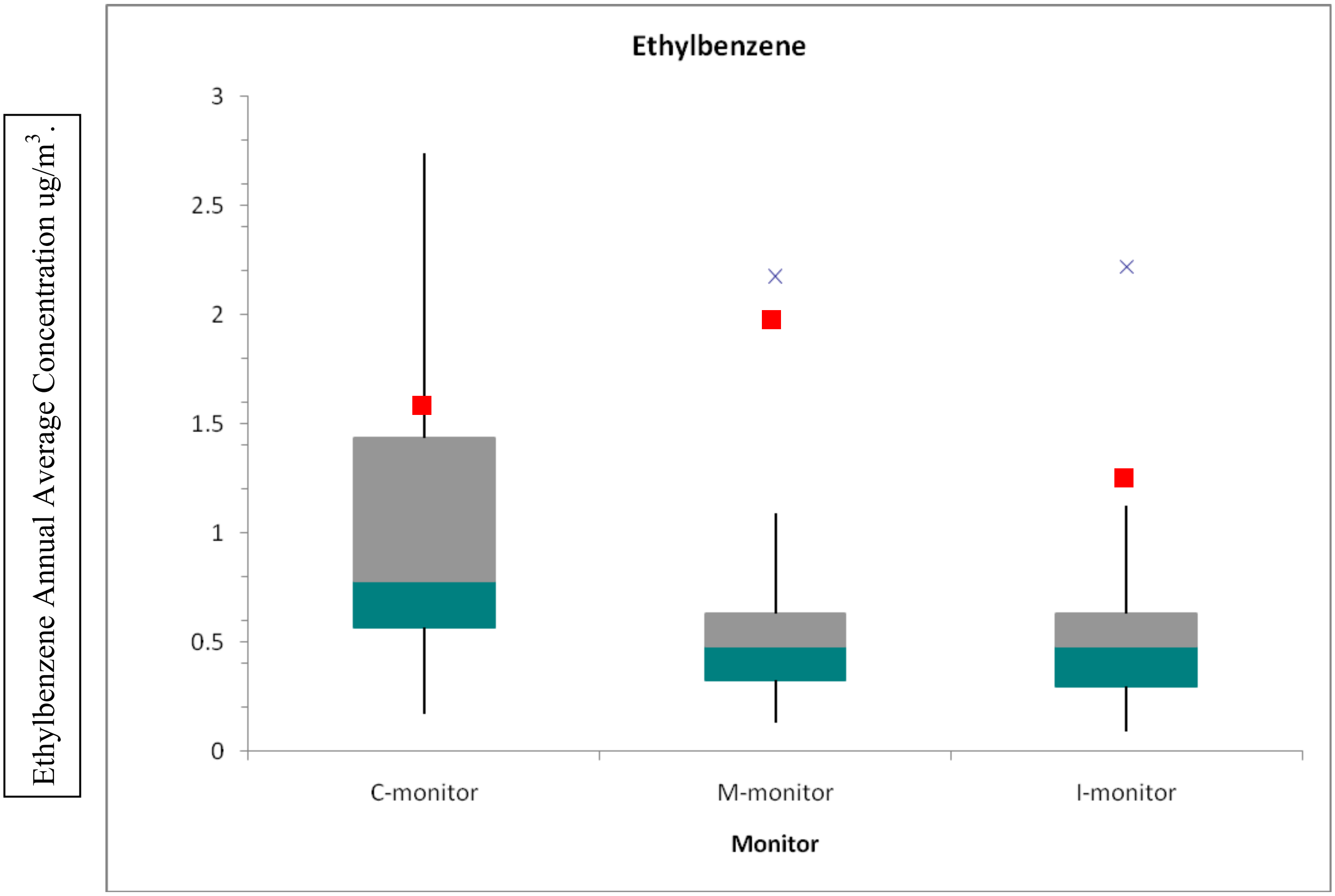
Ethylbenzene

For ethylbenzene, model-to-monitor ratios from three Paterson monitors generally showed a good correlation with observed values (Table 11), with ratios ranging from 1.2 to 3.6. Sources are a mixture of area, stationary and mobile emissions. Measured values ranged from 0.5 to 1.3 µg/m^3 although the downtown monitors were not consistent. Figure 37 shows graphically the model-to-monitor comparison indicating that the model over predicts but within reasonable limits.

Table 11: Maximum Predicted Annual Ethylbenzene Concentrations Compared to Observations at Three Paterson Monitors

Monitor	Observed (µg/m^3)	Predicted (including background)* (µg/m^3)	Model-to-monitor ratio	NATA 2002 (census tract) (µg/m^3)
Mobile	0.54	1.97	3.6	0.65
Commercial	1.28	1.59	1.2	0.59
Industrial	0.54	1.28	2.4	0.61

Figure 37: Model-to-Monitor Comparison for Ethylbenzene



Key: The box represents the distance between the 1st and 3rd quartiles (the line between the gray and green boxes is the median). The whiskers show the highest and lowest data points or 1.5 times the box (Q3-Q1). Outlier points are marked x and are those that are greater than 1.5 times (Q3 -Q1). However, the outlier for the C monitor is not shown since it skews the graphic (C-monitor upper outlier is 9.04 ug/m^3). The model annual prediction of ethylbenzene at each particular monitor is shown with a red square.

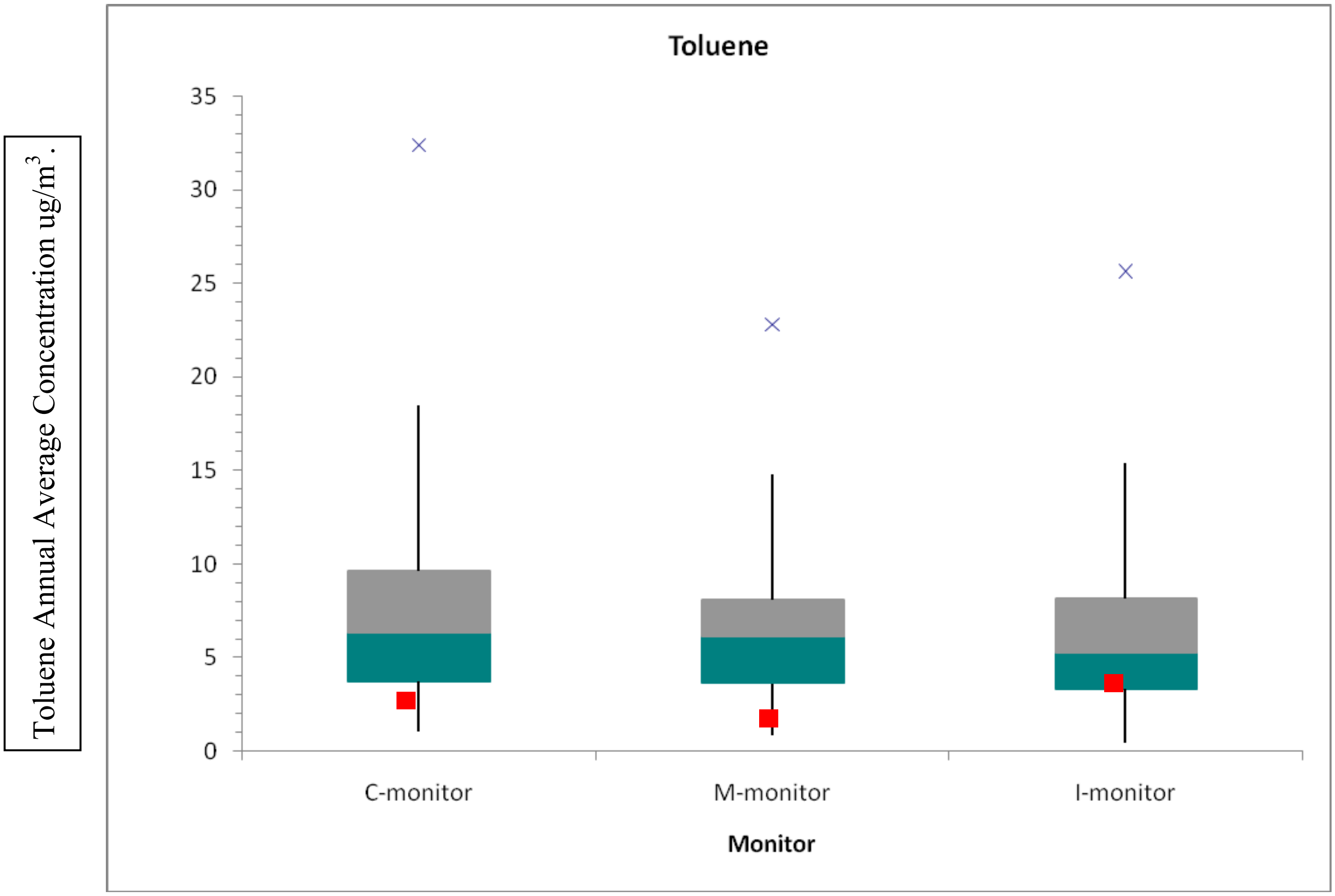
Toluene

Model-to-monitor ratios for three Paterson monitors generally show a consistent under prediction of observed values for toluene. The model-to-monitor ratios ranged from 0.3 to 0.7, with the observations being more than twice the predicted values. Emissions are from numerous stationary sources across the city as well as from area and mobile sources. Measured values ranged from 6.5 to 8.0 µg/m^3. Table 12 shows that the model under predicts at all three monitors, perhaps indicating that the mobile source component of the model needs adjustment or that there is an unknown source of toluene in Paterson. Figure 38 shows that the model under predicts the monitored observations but are within the range of observations.

Table 12: Maximum Predicted Annual Toluene Concentrations Compared to Observations at Three Paterson Monitors

Monitor	Observed (µg/m^3)	Predicted (including background)* (µg/m^3)	Model-to-monitor ratio	NATA 2002 (census tract) (µg/m^3)
Mobile	8.07	2.59	0.3	5.13
Commercial	7.98	3.60	0.5	4.60
Industrial	6.46	4.38	0.7	5.19

Figure 38: Model-to-Monitor Comparison for Toluene



Key: The box represents the distance between the 1st and 3rd quartiles (the line between the gray and green boxes is the median). The whiskers show the highest and lowest data points or 1.5 times the box (Q3-Q1). Outlier points are marked x and are those that are greater than 1.5 times (Q3 -Q1). The model annual prediction of toluene at each particular monitor is shown with a red square.

Carbonyls

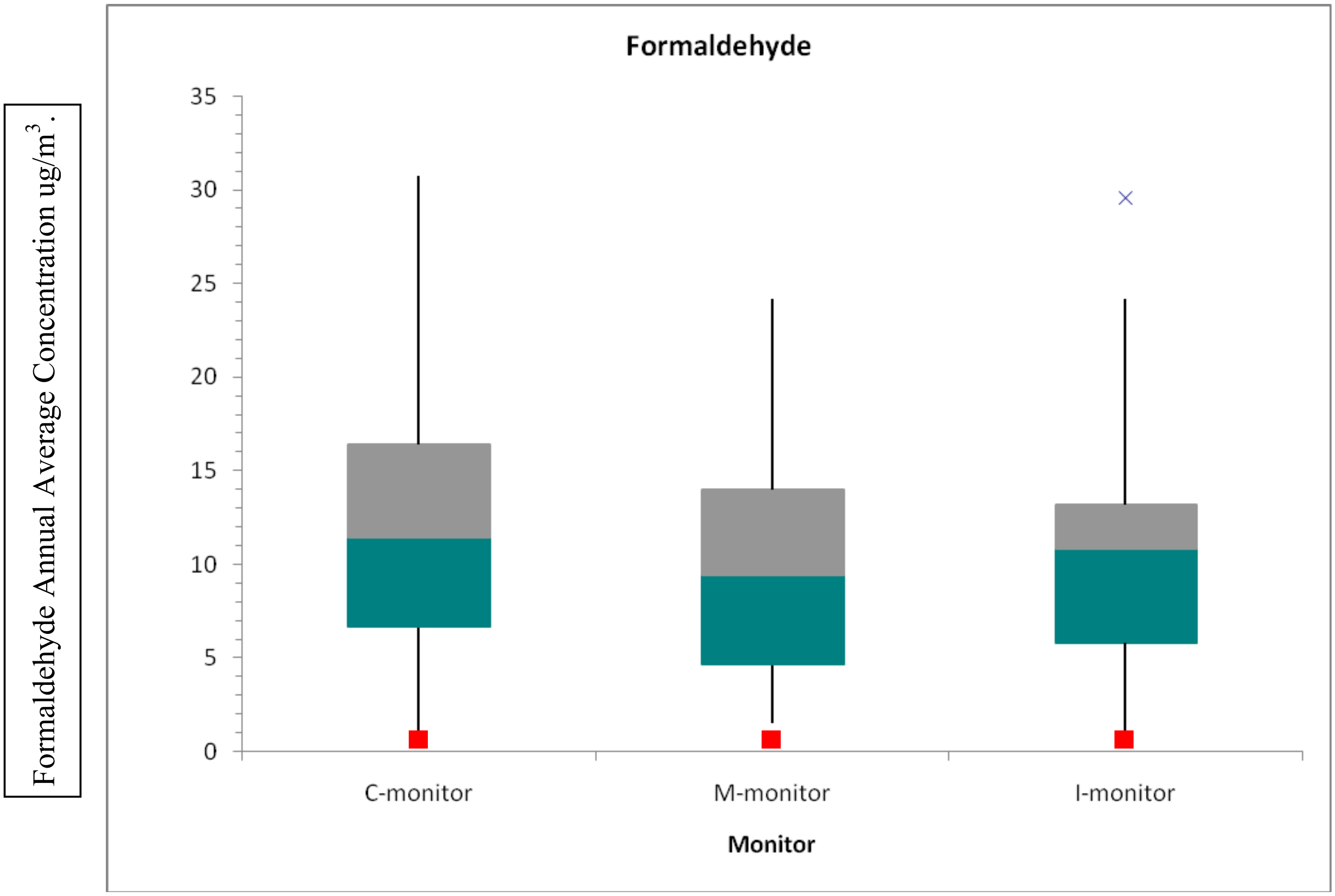
Formaldehyde

Model-to-monitor ratios from three Paterson monitors generally showed excellent agreement between predicted and observed values despite not accounting for pollutant transformation in the CALPUFF modeling. However, approximately 96% of predicted values were accounted for by background concentrations which were not included in the CALPUFF model boundary conditions. Formaldehyde is clearly a regional air pollutant that local risk reduction strategies cannot address. Annual averages from the monitoring data ranged from 9.9 to 11.2 µg/m^3. Table 13 shows an excellent agreement with observed values albeit with less spatial variation than shown in the observed values. The main sources of formaldehyde are mobile; there are only two stationary sources in Paterson. Figure 39 shows that without background concentrations the model consistently under predicts the monitors. This may be due to an inaccurate emission inventory or because the model is lacking a mechanism for secondary formation of formaldehyde, or because in this study, it was found that the PAKS method may have overestimated concentrations of formaldehyde.

Table 13: Maximum Predicted Annual Formaldehyde Concentrations (PAKS) Compared to Observations at Three Paterson Monitors and 2002 NATA Predictions

Monitor	Observed (µg/m^3)	Predicted (including background)* (µg/m^3)	Model-to-monitor ratio	NATA 2002 (census tract) (µg/m^3)
Mobile	9.94	11.37	1.1	1.04
Commercial	11.26	11.24	1.0	0.99
Industrial	10.70	11.20	1.1	1.01

Figure 39: Model-to-Monitor Comparison for Formaldehyde



Key: The box represents the distance between the 1st and 3rd quartiles (the line between the gray and green boxes is the median). The whiskers show the highest and lowest data points or 1.5 times the box (Q3-Q1). Outlier points are marked x and are those that are greater than 1.5 times (Q3 -Q1). The model annual prediction of formaldehyde at each particular monitor is shown with a red square.

Particulates

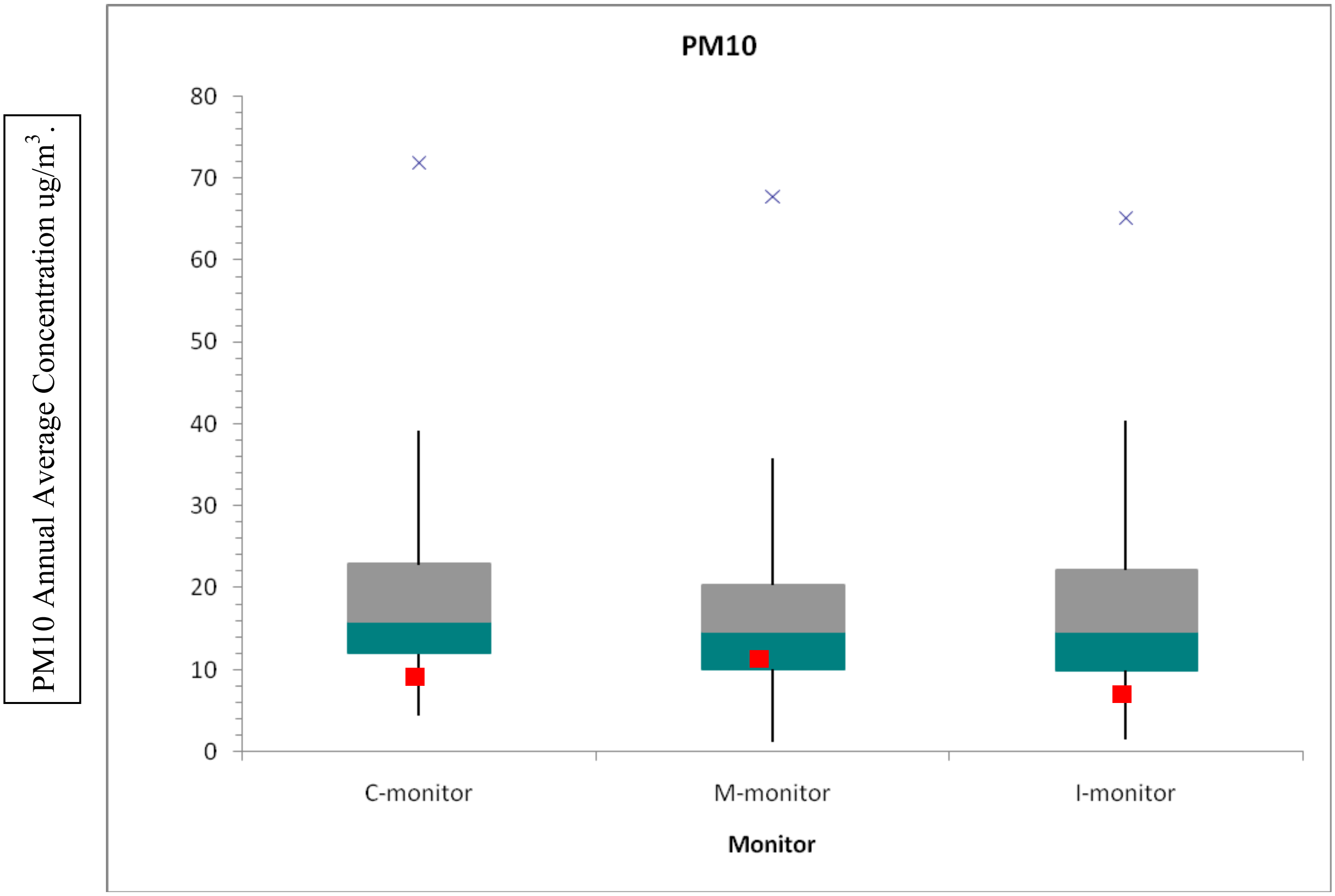
PM_{10}

Model-to-monitor ratios from the three Paterson monitors generally showed excellent agreement. Model-to-monitor ratios ranged from 1 to 1.3 (Table 14). However, as was shown with formaldehyde, a significant background level exists in Paterson. Measured values ranged from 17.1 to 19.0 µg/m^3 (no comparable values exist for NATA). PM_{10} emissions stem from a mixture of mobile and stationary sources – the latter consisting of comparatively small sources. Figure 40 shows that the model predictions are well within the range of observations for the year although it under predicted the individual observations overall.

Table 14: Maximum Predicted Annual PM_{10} Concentrations Compared to Observations at Three Paterson Monitors

Monitor	Observed (µg/m^3)	Predicted (including background)* (µg/m^3)	Model-to-monitor ratio
Mobile	17.5	22.0	1.3
Commercial	19.0	19.8	1.0
Industrial	17.1	17.9	1.0

Figure 40: Model-to-Monitor Comparison for PM$_{10}$



Key: The box represents the distance between the 1st and 3rd quartiles (the line between the gray and green boxes is the median). The whiskers show the highest and lowest data points or 1.5 times the box (Q3-Q1). Outlier points are marked x and are those that are greater than 1.5 times (Q3 -Q1). The model annual prediction of PM$_{10}$ at each particular monitor is shown with a red square.

Other Volatile Organic Compounds

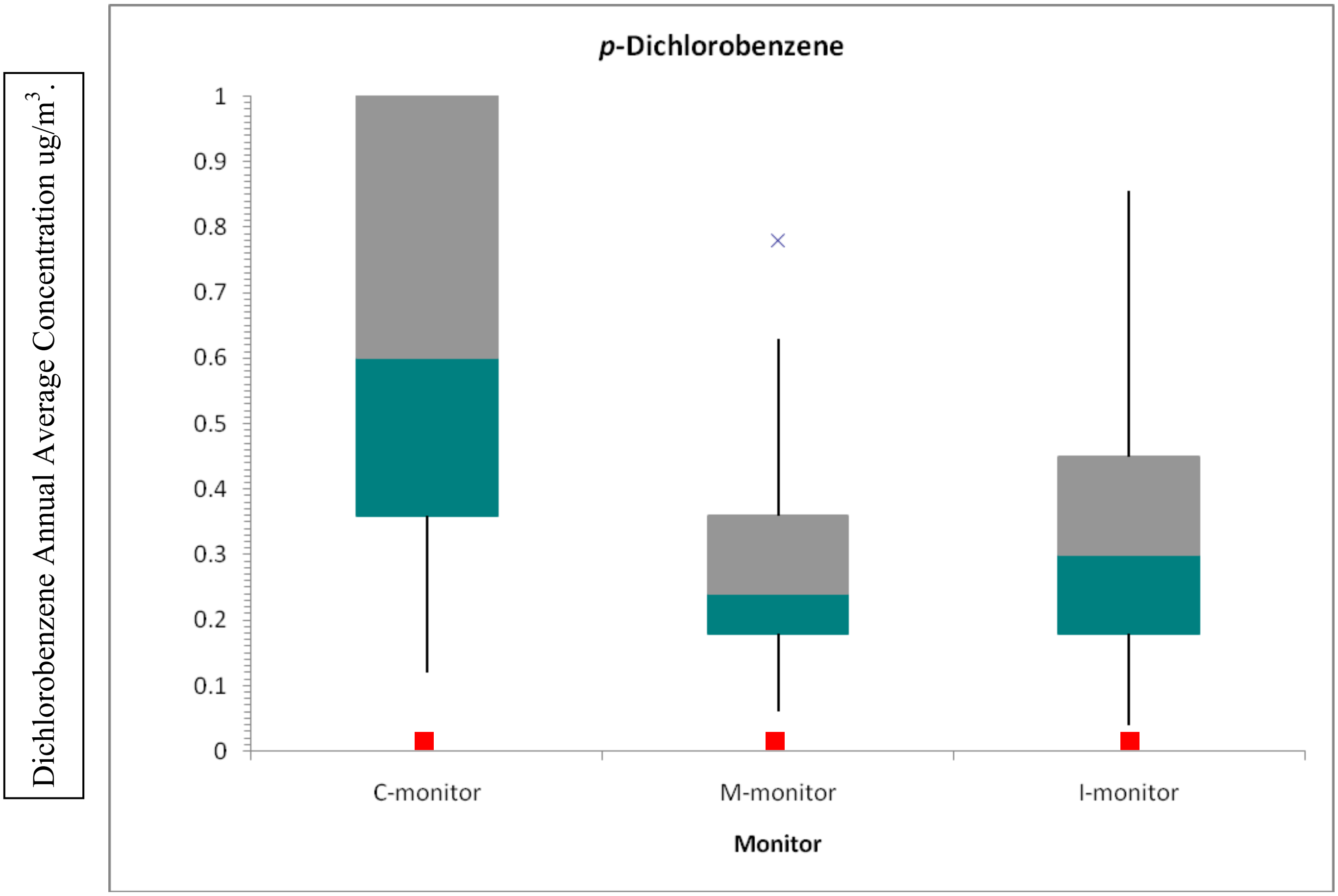
p-Dichlorobenzene

Model-to-monitor ratios for p-dichlorobenzene for the three Paterson monitors are shown in Table 15. No background concentration was used for p-dichlorobenzene since it was only detected 32% of the time at the background site. Emission sources within Paterson are two stationary sources. Measured values at Paterson showed large variation, indicating that a local source was not accounted for in the emission inventory or that there may have been a release. Figure 41 shows that the model consistently under predicted p-dichlorobenzene concentrations at the monitors. The observed annual average concentration at the C site is influenced by a few high concentrations which were measured in the fall of 2006 and is not expected to be a recurring event. The model is not able to predict production upsets or problems with emission control technology which could have caused these high concentrations. These measurements occurred only at the C site, indicating it was a localized issue.

Table 15: Maximum Predicted Annual p-Dichlorobenzene Concentrations Compared to Observations at Three Paterson Monitors

Monitor	Observed (µg/m^3)	Predicted (including background)* (µg/m^3)	Model-to-monitor ratio	NATA 2002 (census tract) (µg/m^3)
Mobile	0.30	0.05	0.1	0.17
Commercial	18.7	0.05	2.7E-03	0.11
Industrial	0.33	0.05	0.1	0.13

Figure 41: Model-to-Monitor Comparison for p-Dichlorobenzene



**** The values plotted here deliberately ignore a few extremely high values at the C monitor so as to show the more typical range of observations amongst all the monitors.**

Key: The box represents the distance between the 1st and 3rd quartiles (the line between the gray and green boxes is the median). The whiskers show the highest and lowest data points or 1.5 times the box (Q3-Q1). Outlier points are marked x and are those that are greater than 1.5 times (Q3 -Q1). The model annual prediction of p-dichlorobenzene at each particular monitor is shown with a red square.

Summary

We have analyzed the model predictions in two ways: firstly as a spatial pattern across the city of Paterson, and, secondly, by focusing on the model performance at the three monitors within the city. The spatial patterns show either the dominance of mobile or point sources (and sometimes a combination). Of the nine air toxics that have been modeled using CALPUFF, four are mobile-source dominated (benzene, ethylbenzene, toluene and formaldehyde). The isopleths for these pollutants and PM_{10} (and to a lesser extent hexavalent chromium) show high concentrations along I-80 and the adjacent major traffic corridors. The other metals that were modeled (arsenic and lead) all show more localized impacts across Paterson, reflecting their point source origins. Model to monitor results are varied. Some mobile source pollutants are over predicted, others under predicted. However, they remain approximately a factor of two of the observed values. PM_{10} concentrations are well reproduced by the model when background concentrations are included. In general, the model predicted similar concentrations at each monitor which is consistent with the measurement results.

C. Bayesian Geostatistical Modeling

One goal of the UCAMPP study is to characterize the spatial resolution and the concentration gradients of detected analytes. Mapping concentration gradients can be done using several different mathematical methods, all of which fall under the category of interpolation mapping. Commonly used methods include Euclidian interpolation, inverse distance weighted methods, spline methods, radial basis functions, and classical kriging. Unfortunately, all of the standard mapping methods requires more than three monitoring points across space to achieve minimally acceptable map accuracy. In this study the sampling coverage is limited to three stations across space. This necessitated using an advanced spatio-temporal kriging method.

The method used is called BME (spatio-temporal Bayesian Maximum Entropy kriging), and is a modern version of kriging. Measurements and trends in both space and time are mathematically integrated. The temporal density of measurement compensates for the scarcity of spatial coverage, thereby allowing the calculation of accurate mapped results.

Figures 42 through 46 are a series of maps for five monitored analytes. Each individual figure has three panels and is the mapping for a single analyte. The three panels in each map show typical contaminant concentrations for either a "low" concentration day, a "medium" concentration day or a "high" concentration day for that particular analyte. On all maps the dark blue color is at or below the current NJDEP air program health benchmark. Other colors (green, yellow, red) indicate a higher concentration.

An advantage of using the BME method is that it allows the production of companion probability variance maps. The probability variance map provides confidence information for the different regions within a mapped area. Regions with low confidence are removed from the maps presented. This is shown clearly, as the actual concentration zones show only an area approximately 1000 feet in distance from each monitoring station.

Various publications are noted in the reference section for additional background information on this very modern method for interpolation mapping.

Figure 42. Trichloroethylene (TCE)
Trichloroethylene (TCE) was evaluated using BME mapping. TCE was detected 43% of the time for all sites combined with 54 sample-days for analysis. These samples provided the required temporal density for BME mapping.

The most striking spatial pattern is that the TCE concentration gradients increased from the southwest (M site) to the northeast (I site) on the rare high concentration day. The M site consistently has the lowest concentration, the C site consistently has a midrange concentration and the I site consistently has the highest concentration of TCE. This is true regardless of the intensity of concentration level (L, M, or H) on any given day. Also notable is that the range of concentrations on a given day could vary widely among the three monitor stations.

Overall, TCE was detected in the air less than half of the time.

Tricholoethylene, ug/m^3

🟦 0 - 0.5
🟩 0.5 - 1
🟥 1.1 - 1.5

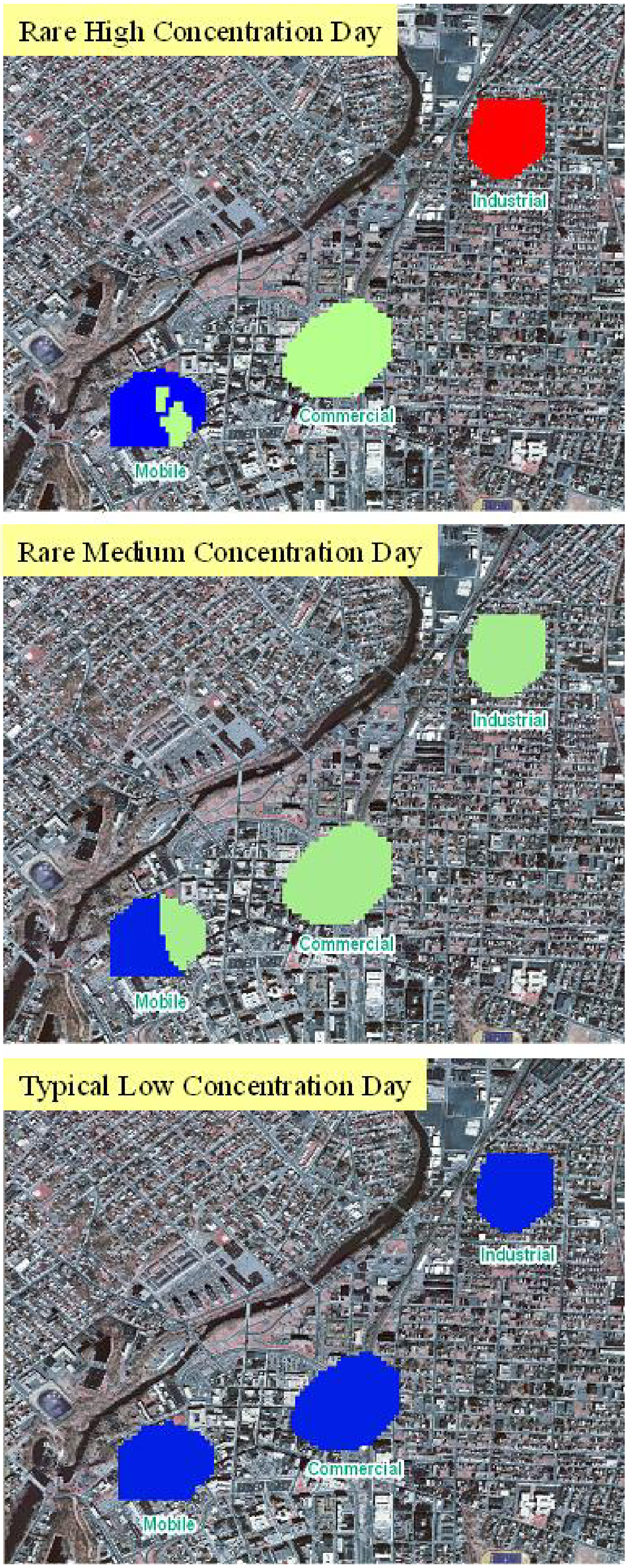
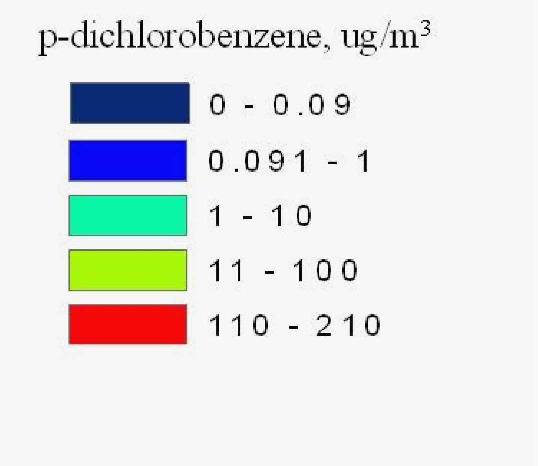


Figure 43: p-Dichlorobenzene
A different spatial pattern was found for p-dichlorobenzene.

The results for this chemical show potential cause for concern, and additional investigation may be warranted and ongoing.



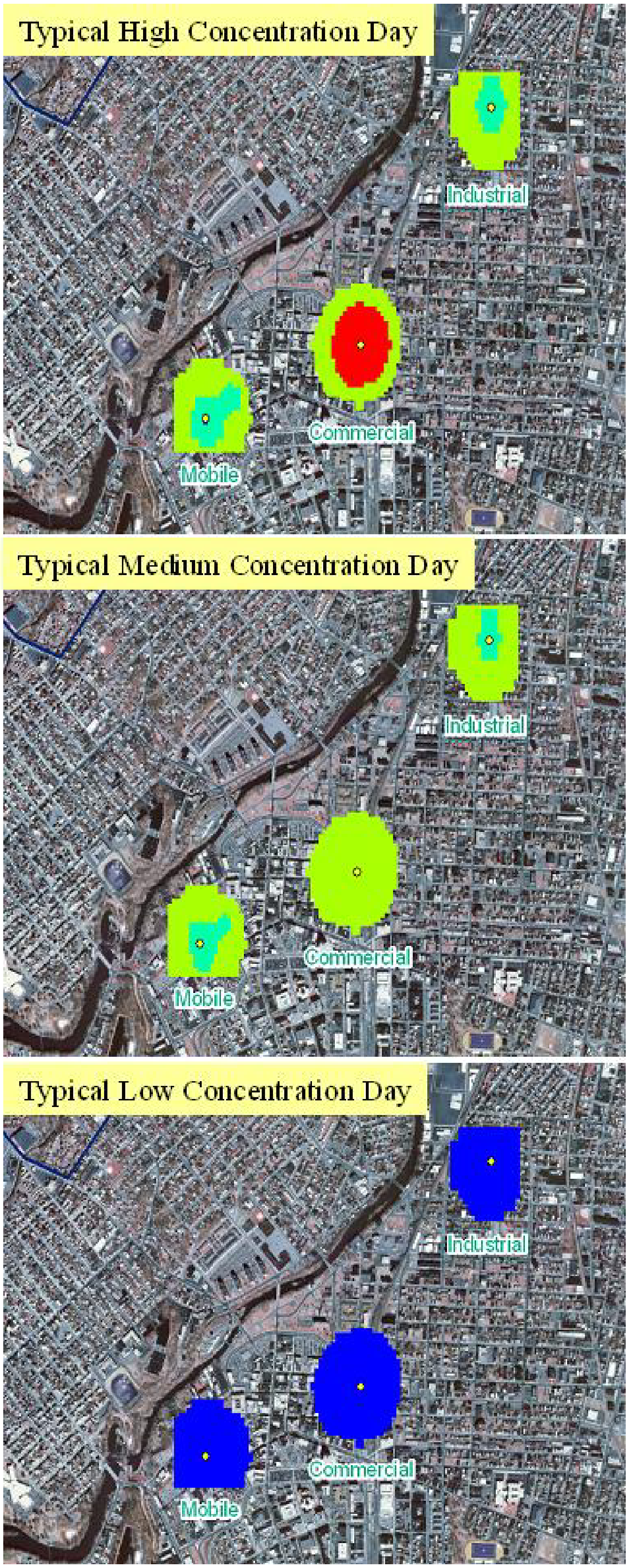
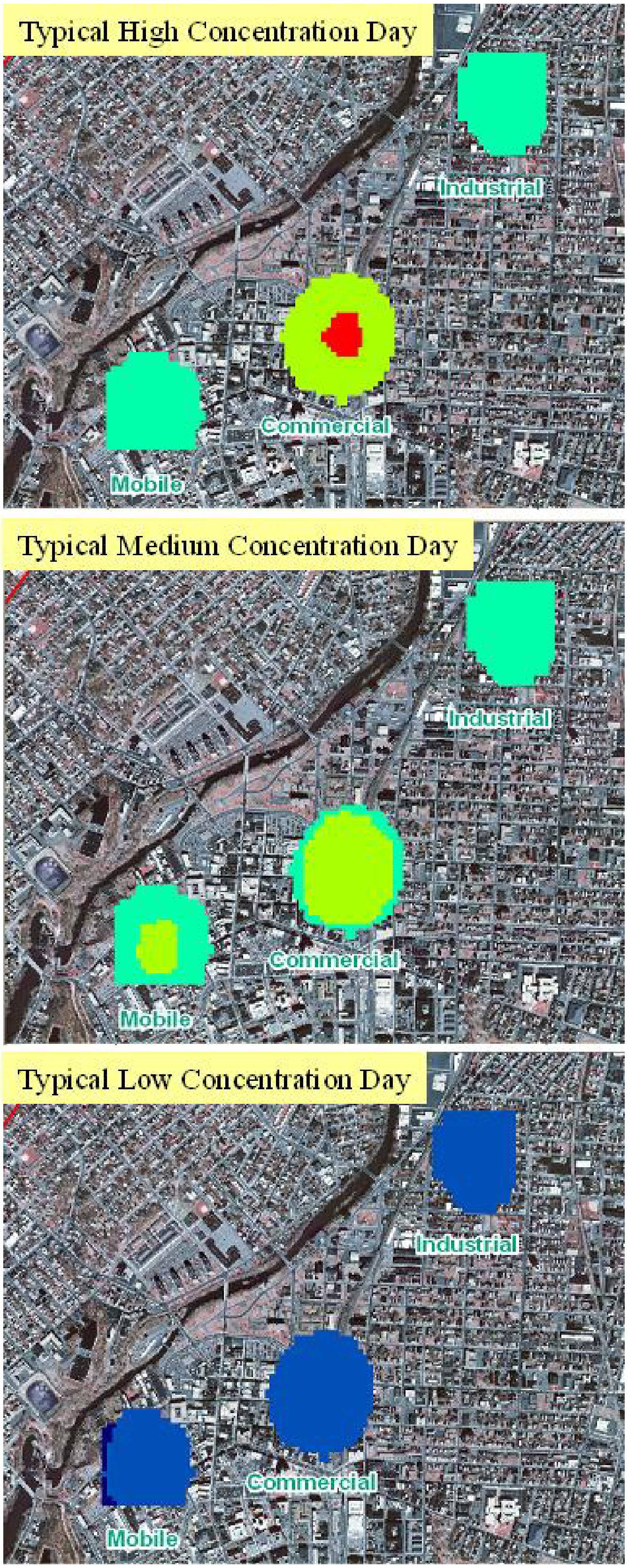


Figure 44: Dichloromethane
The highest concentration for dichloromethane on a given day shifts between the three monitoring sites, rather than being consistently tied to one station. Also, the concentration intensity is often highly localized. The concentration can be high at one station while simultaneously being low at the other stations.



Dichloromethane, ug/m^3

🟦 1.9 - 2.1
🟩 2.2 - 4
🟩 4.1 - 6
🟥 6.1 - 8

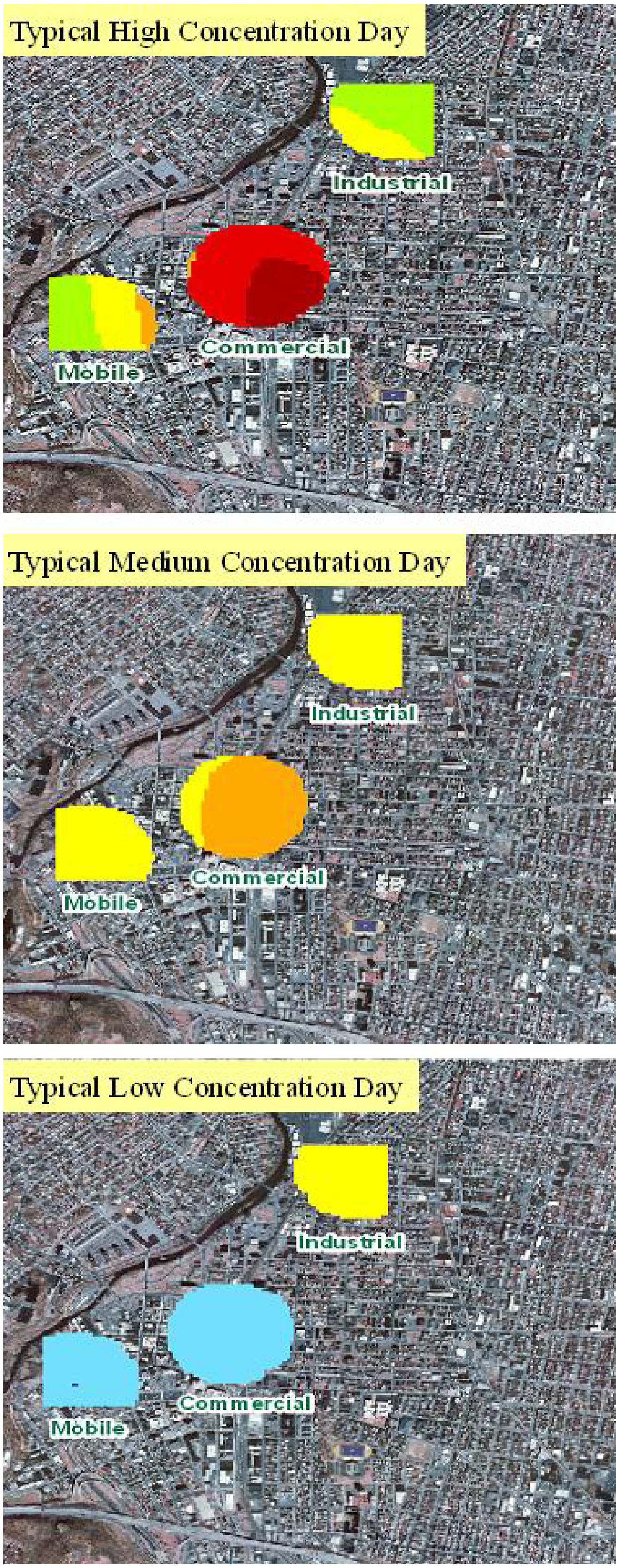
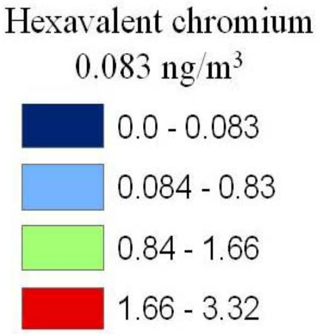


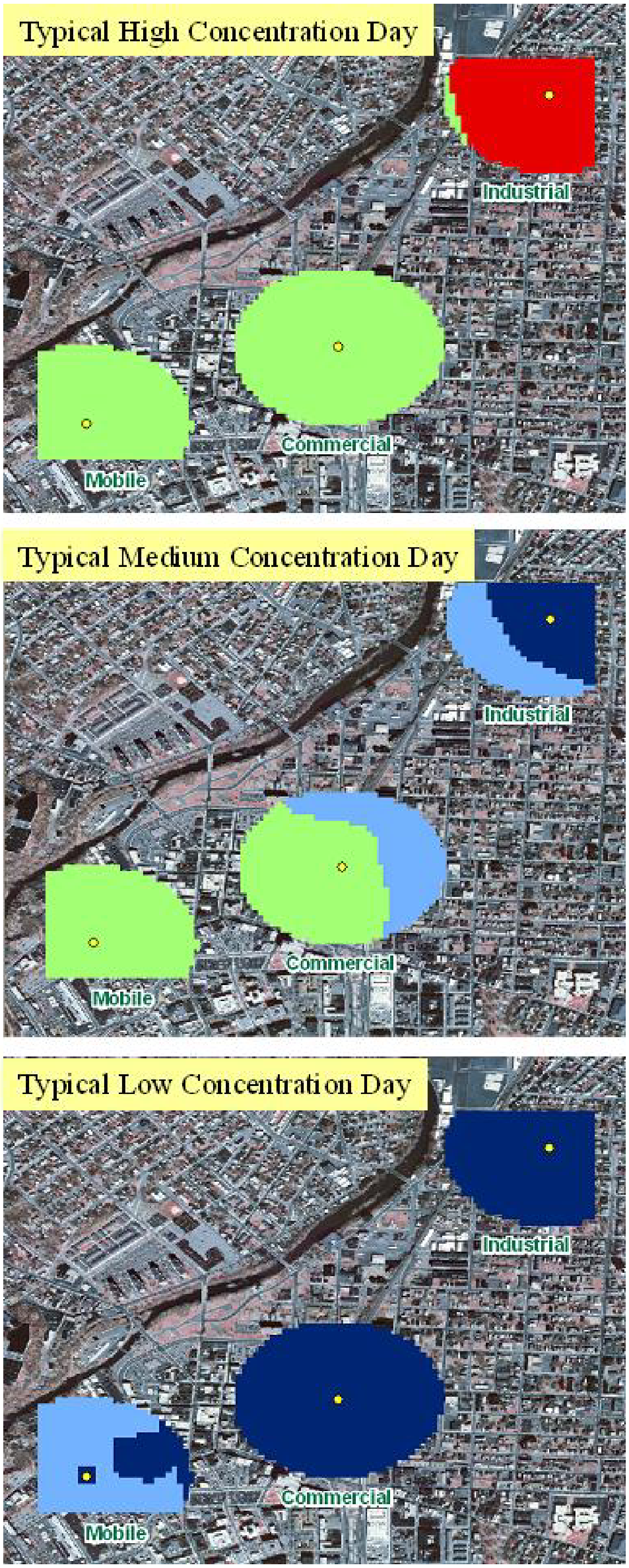
Figure 45: Tetrachloroethylene
The highest concentration of tetrachloroethylene shifted among the three monitoring sites, rather than being tied to any single station. Concentration intensity varied greatly among the three sites. No consistent concentration intensity pattern was discernible.

Tetrachloroethylene, 0.17 ug/m^3

- 🟦 0.17
- 🟦 0.18 - 1
- 🟩 1 - 2
- 🟨 2 - 3
- 🟧 3 - 4
- 🟥 4 - 5
- 🟫 5 - 6

Figure 46: Hexavalent Chromium
The highest concentration of Cr(VI) shifted among the three monitoring sites, rather than being tied to any single station. Concentration intensity varied among the three stations. No consistent concentration intensity pattern was discernible.




Typical High Concentration Day

Typical Medium Concentration Day

Typical Low Concentration Day

X. RISK ASSESSMENT

For those compounds with toxicity values, cancer and noncancer (hazard index) risk estimates were calculated using the monitored annual average concentrations. The NJDEP Air Program protocols for estimating risk were followed, and can be found on the NJDEP website at http://www.nj.gov/dep/aqpp/risk.html

For cancer risk, the unit risk factor (URF) is multiplied by the annual average of the air concentration to estimate the increased probability of contracting cancer. Only those cancer risks above 1 in a million are listed below because that is generally the health benchmark used by the NJDEP for assessing potential health risks, including the issuance of air emission permits. Non-carcinogenic risks are assessed relative to the hazard quotient (HQ). The HQ is the annual average air concentration divided by the reference concentration. If the result is less than one, no noncancer health impact is expected.

Both long term and short term noncancer risks were calculated. Long term noncancer risk (and cancer risk) assumes a lifetime of exposure which is defined as 70 years. Since monitoring occurred for only one year, the annual average was used under the assumption that the measured values would persist for a full 70 year exposure levels.

For the calculation of short term noncancer risks, only those compounds that had a 24-hour Reference Concentration (RfC) were included. 24-hour RfCs are appropriate to apply to these data since the samples were collected as 24-hour composites. The maximum 24 hr measured concentration of the applicable air toxics was used to estimate a short-term HQ.

Individual xylene (m, p, & o) concentrations were added together. When applicable, the annual average using the full MDL was used in the calculation.

No short term (24 hr) or long term (70 yr) noncancer risk was observed in Paterson or at the background site.

Table 16 provides the cancer risk for each compound posing a risk of greater than 1 in a million ($1x10^{-6}$), the NJDEP health benchmark.

Table 16: Estimated Lifetime Inhalation Cancer Risk at Monitoring Locations in Paterson and Around the State.

Air Toxic of Concern	B Site (Chester)	C Site (Paterson)	I Site (Paterson)	M Site (Paterson)	Camden	Elizabeth	New Brunswick
Arsenic (inorganic)	4.3E-06	6.0E-06	6.8E-06	5.6E-06	3.9E-06[1]	3.9E-06[1]	2.6E-06[1]
Naphthalene	2.9E-07	1.3E-06	9.1E-07	1.1E-06	n/a	n/a	n/a
1,3-Butadiene	9.0E-07	8.7E-06	3.9E-06	6.3E-06	3.9E-06	4.8E-06	1.7E-06
Benzene	4.1E-06	1.4E-05	8.7E-06	1.1E-05	9.1E-06	10E-06	5.2E-06
Carbon tetrachloride	8.7E-06	9.2E-06	9.5E-06	9.3E-06	9.2E-06	8.8E-06	9.1E-06
Chloroform	2.1E-06	7.6E-06	3.7E-06	5.5E-06	2.6E-06	2.9E-06	2.7E-06
Chloromethane (methyl chloride)	2.1E-06	2.1E-06	2.1E-06	2.1E-06	2.1E-06	2.0E-06	2.1E-06
Ethylbenzene	3.5E-07	3.2E-06	1.4E-06	1.4E-06	1.0E-06	1.3E-06	6.5E07
p-Dichlorobenzene	~0	2.1E-04[2]	3.7E-06	3.3E-06	2.3E-06	1.7E-06	8.8E-07
Tetrachloroethylene	7.7E-07	4.4E-06	4.1E-06	3.1E-06	1.9E-06	2.1E-06	1.5E-06

[1] not applicable.

[2] Please note that at the C site, there were 10 measurements over the course of 2 consecutive months, that were significantly elevated (3 measurements were 3 orders of magnitude greater than the majority of the measurements) above measurements obtained at all four site. These measurements increased the annual average concentration for the C site dramatically (19 vs. 0.3 $\mu g/m^3$) and the estimated risk.

As can be seen in Table 16, ten of the 132 air toxics that were targeted for monitoring exceeded the NJDEP health risk guideline value of 1E-06 (one-in-a-million lifetime cancer risk) in Paterson. Nine of the ten also exceeded this guideline at 1 or more of the other air toxics monitoring stations around the state. Naphthalene could not be compared statewide because comparable measurements were not made at the other locations around the state.

With the exception of the two-month elevation of p-dichlorobenzene concentrations measured at the commercial site, benzene is the major contributor to cancer risk in Paterson and at the other locations around the state, except for the background site in Chester. This is expected because a large source of benzene in ambient air is from mobile source emissions and the monitoring site in Chester is far from the road. Benzene, 1,3-butadiene and ethyl benzene are associated with the petroleum industry as well. Mobile sources are large contributors to the levels of these air toxics measured around the state.

p-Dichlorobenzene is a common chemical found in moth balls, urinal cakes and space deodorants. It is also used in the production of azo dyes and pharmaceuticals. Most emissions of carbon tetrachloride in the United States have ceased. However, because of its long atmospheric residence time (up to 100 yrs), the risk is the same at every site around the state. Tetrachloroethylene is a dry cleaning solvent and degreaser. Elevated levels are normally found in any populated area. Chloromethane is emitted from the oceans but also from rotting and burning wood. Chloroform is mainly emitted to the atmosphere from chlorinated water. Arsenic is emitted from all types of combustion, e.g., coal and wood. It is also emitted from the metallurgy industry. Naphthalene is emitted from combustion processes and motor vehicles.

Diesel particulate matter (DPM) was not measured directly during UCAMPP because there is no generally accepted air monitoring method specific to diesel emissions for use in community wide assessments. Although elemental carbon (EC) is sometimes used as a surrogate for diesel emissions, its use in general ambient monitoring would result in significantly overestimating cancer risk from exposure to DPM because EC is emitted by many nondiesel sources.

The cancer risk for acetaldehyde, formaldehyde and hexavalent chromium is not presented in this report due to high uncertainty in the measurements as new methods were being field tested during UCAMPP.

XI. RISK REDUCTION STRATEGIES.

When analysis of the data revealed the elevated p-dichlorobenzene concentrations, NJDEP proceeded to identify the source and that investigation is ongoing. At no point during the analysis of the data did the results indicate a public health threat that required immediate action. If there had been an imminent threat to public health and safety, NJDEP would have immediately notified the community.

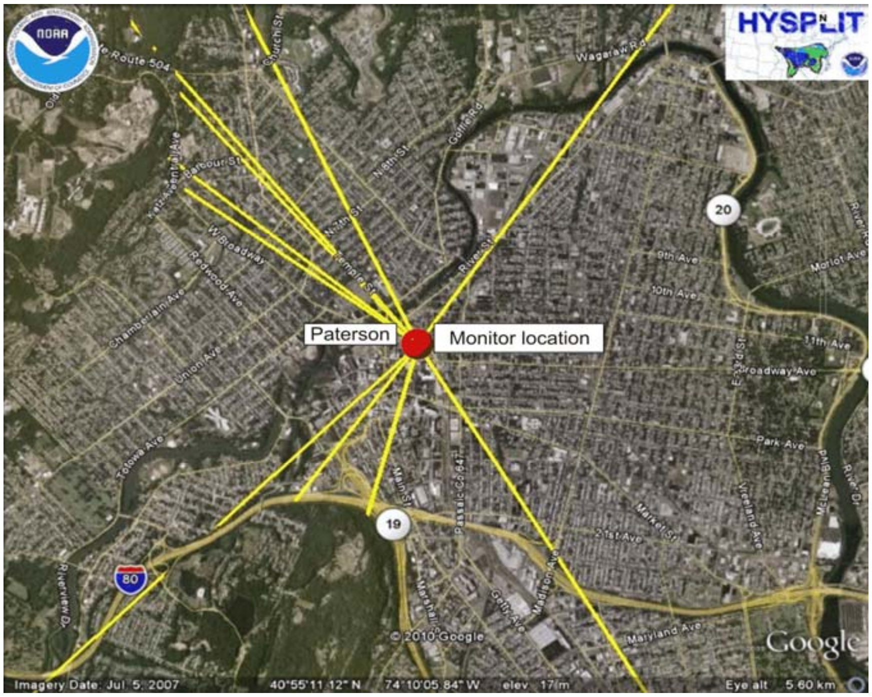


Figure 47: Hysplit model of high concentration days of p-dichlorobenzene.

Figure 47 shows modeling that was done to try and determine source location. The yellow lines on the map indicate which direction the wind was predominantly coming from on the 10 highest concentration days. The modeling does not indicate a dominant direction from which the p-dichlorobenzene may have come from. This may be partly due to the inherent limitations of the model which is more regional in nature.

The investigation by the NJDEP Enforcement Program is on-going. This investigation is not limited to sources that the NJDEP regulates. NJDEP enforcement has reached out to both the county and local health department(s) and code officials for information on potential sources. In addition, NJDEP has applied to USEPA to fund an additional year of monitoring at and around the commercial site to determine if the spike in concentration was an isolated event or not. It is anticipated that the project period will run from spring of 2010 through fall of 2011.

Risk reduction strategies during the UCAMPP monitoring period were focused on outreach and education. Specific risk reduction strategies included but were not limited to: identifying which facilities were close to residences, schools and day care; identifying which processes would benefit from a pollution prevention audit; education on anti-idling legislation, the 1-800-WARN DEP hot line, and anti-idling signs; identifying facilities that may warrant a visit from the NJDEP Enforcement Program; and identifying fleets that may be eligible for pollution control retrofits (waste haulers, bus companies); and trying to identify illegal auto body shops.

During our site visits, we found that we were able to implement some risk reduction strategies through outreach and education. At each site we visited, we gave out

information on the New Jersey anti-idling law, and two facilities bought NJDEP anti-idling signs to hang at multiple locations, both in and outside of Paterson. In addition, if the site was a hospital, painting and coating operation, electroplating or metal operation, we handed out the relevant USEPA pamphlets entitled "Reducing Air Pollution from…". We also handed out the NJDEP hotline number to report environmental incidents, abuses, and complaints in New Jersey (1-877-WARN-DEP).

During the walk-through at the hospital, the enforcement officer who accompanied the UCAMPP personnel noticed that the hospital was crushing fluorescent light bulbs, which contain mercury, in a barrel on-site. This process requires an air permit and proper maintenance and disposal of the barrel's absorbent material (e.g., carbon bed) because of the potential of mercury release. The enforcement officer notified the hospital staff of the pertinent regulations, that when the bulbs are crushed they are subject to numerous and more stringent federal and state standards than Universal Wastes (40CFR262, N.J.A.C 7:26G), such as reduced accumulation time, biennial reporting, and manifesting. (http://www.nj.gov/dep/enforcement/advisories/2005-13.pdf). The hospital decided to discontinue crushing the spent bulbs on-site and instead send them back to the manufacturer whole, thereby reducing the potential for misuse of the equipment, the release of mercury into the environment, and potential associated health effects.

The NJDEP, USEPA and local agencies have many programs that are designed to reduce concentrations of air toxics and thereby reduce the associated risk. Examples include but are not limited to; NJDEP limits the amount of air pollution industrial facilities can emit by requiring air pollution permits, record keeping, installation of air pollution control technology, and compliance inspections. For smaller sources, NJDEP has a consumer products regulation which limits certain chemicals in cleaners, paints, cosmetics, etc., emission control devices at gas stations, new restrictions on dry cleaner's emissions /equipment and requirements for proper equipment and training for auto-body shops. Air pollution from mobile sources is also reduced by anti idling legislation which limits idling by most vehicles to three minutes (see N.J.A.C. 7:27-14 and 7:27-15), requiring diesel retrofits, and inspection and maintenance requirements. USEPA has multiple programs which include cleaner motor vehicles, fuels and wood burning stoves etc. Local agencies also work to protect the health of NJ residents with such programs as banning outdoor wood boilers (OWB).

XII. MISCELLANEOUS

A. Leveraged Resources:

1. Equipment

The meteorological station which was purchased with UCAMPP funding was used in another USEPA funded grant, "Development and Optimization of a Sampling and Analytical Method to Measure Hexavalent Chromium in Ambient Air", (end date Sept 30, 2009) and will be used in another USEPA funded grant, "Development and Optimization of a Sampling and Analytical Method to Measure Hexavalent Chromium in Ambient Air" (end date July 2012). The Partisol Speciation Sampler- Model 2300 was also used in the "Development and Optimization of a Sampling and Analytical Method to Measure Hexavalent Chromium in Ambient Air" and was used to collect samples for a Ph.D. student's dissertation. Both of the hexavalent chromium projects were a direct outcome of the method development work on measuring hexavalent chromium in ambient air during UCAMPP.

2. Air Toxics Monitoring Data:

UCAMPP used data from the Chester site which was collected as part of routine and ongoing air toxics monitoring by the NJDEP. The VOC s were collected by the same method and analyzed by the same laboratory as UCAMPP (ERG, Inc.). The metals in $PM_{2.5}$ were analyzed by the same laboratory as the PM_{10} metals during UCAMPP (RTI, Inc.). This data will allow for a future comparison between metals in $PM_{2.5}$ and PM_{10}. Carbonyls were collected by a different method and analyzed by different laboratory to allow for a comparison between the existing USEPA method (TO-11A) and a new EOHSI method (PAKS). These samples are paid for by NJDEP air toxics monitoring program so UCAMPP funding was not needed.

3. NJDHSS Occupational Survey

State resources were leveraged during UCAMPP when NJDEP staff assisted the NJDHSS by delivering their occupational surveys on work related chemical exposure during UCAMPP site visits. When NJDEP staff handed out the surveys for NJDHSS, it saved state resources. This was not funded by the UCAMPP grant, NJDEP staff did it as a way to promote collaboration between the two state agencies.

B. USA Today Article

In December 2008, USA Today published a series of articles on air toxics exposures at schools around the country. Schools were ranked relative to each other, based on air concentrations estimated from modeled TRI releases.

Here are several reasons why it is inappropriate to compare the USA Today articles on "The Smokestack Effect: Toxic Air and America's Schools" to monitoring data from UCAMPP:

1. The articles did not include mobile, area or background air toxics, and there is no way to eliminate them from our monitoring data to allow direct comparison.

2. The articles provided only a ranking of the schools by percentile, based on toxicity ranking score and not the total risk.

3. The articles listed cobalt as a toxicity driver, accounting for 20% overall toxicity respectively at PS#10 in Paterson and 9% of overall toxicity at PS#2. At PS#10 and PS#2, cobalt was detected only 4% of the time. The MDL (0.5 ng/m^3) is well below the health benchmark and the RfC used by NJDEP is 5 ng/m^3.
Therefore, it appears that the assumption of significant cobalt levels by USA Today reflects a modeling inconsistency.

4. USEPA’s RSEI model used in the USA Today report uses toxicity values whose basis is unclear. They are weighted, and are therefore different from the IRIS, California, and other values used by NJDEP.

C. Paterson Survey

NJDEP, funded the “Awareness of and Exposure to Air Pollution in an Urban Environment” survey. This work was completed in 2007 in Paterson. This project it could have been done in any urban environment but the NJDEP wanted to focus resources in Paterson.

This survey aimed to identify the degree of and factors in Paterson residents' beliefs, attitudes and behaviors regarding outdoor air pollution, self-protection, and pollution reduction. This study has confirmed previous findings that official communications about air quality are only partly successful at best. The Air Quality Index and similar messages fail to reach all of those who may need this information, and do not seem relevant to those they do reach, because some residents feel they are not vulnerable to air pollution and others do not see the official data as matching their own sensory or health experiences. As a result, self-protection and pollution reduction behaviors may not occur at health- or cost-effective levels. Because definitions of air pollution and relevant cues and effects vary widely, both within the public and between citizens and officials, further progress in communication is unlikely without linking message design to more sophisticated analysis of differences in views and how these might be resolved.

XIII. CONCLUSIONS

★ The project generated a high percentage of valid field samples (i.e., 90% valid samples). %ND and precision varied by species.

★ The DNSH method for quantifying aldehydes appears to overestimate formaldehyde, acetaldehyde and propionaldehyde but appears to capture acrolein concentrations well, if precision is used to characterize the method.

★ The initial work on a method to quantify hexavalent chromium in ambient air has lead to two other projects which further develops and compares this promising method to another method currently in use.

★ Many annual averages were found to be higher in Paterson than the background site and higher on weekdays than weekends in Paterson. These air toxics include aluminum, calcium, iron, magnesium, manganese, silicon, titanium, EC, fluorine, pyrene, dichloromethane, MEK, methyl isobutyl ketone, MTBE, tetrachloroethylene, and toluene

★ Other air toxics which were higher in Paterson but did not exhibit weekday/weekend differences include bromine, chlorine, copper, lead, nickel, potassium, sodium, strontium, vanadium, zinc, zirconium, OC, PM_{10}, all measurable PAHs, 1,1,1-trichloroethane, 1,2,4-trimethylbenzene, 1,3,5-trimethylebenzene, 1,3-butadiene, acethylene, acrolein, benzene, chloroethane, chloroform, dichlorodifluoromethane, ethyl benzene, m,p-xylene, n-octane, o-xylene, p-dichlorobenzene, propylene, styrene and trichlorofluoromethane.

★One very interesting result from this study is that when there was a difference observed among the sites in Paterson, the C site was usually the highest (for copper and the following VOCs: 1,1,1-trichloroethane, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,3-butadiene, benzene, ethylbenzene, methyl isobutyl ketone, m,p-xylene, o-xylene, and p-dichlorobenzene). There is a strong mobile source signature at this site because it is located between busy intersections, had an active parking lot behind the building, and an active rail line behind that. However, these findings cannot all be explained by mobile sources. There are point and area source signatures that may be associated with other compounds such as p-dichlorobenzene and 1,1,1-trichloroethane.

★These results indicate the impact of anthropogenic activities and that urban air quality is not driven solely by mobile source air toxics but that area and point sources are important contributors. i.e., an urban footprint.

★ Of all the air toxics that were measured during UCAMPP, only carbon disulfide and acetonitrile were higher at the background site than in Paterson.

★ Many pollutants had higher concentrations in the winter than other seasons, with spring generally having the lowest. This was most likely highly influenced by meteorology (low wind speeds, low mixing heights, inversions) and source variation, e.g., combustion of fuels used for heating. There were two exceptions: hexavalent chromium and strontium were higher in the summer. It was theorized that the hexavalent chromium was higher in the summer due to photochemical processes, high heat, and humidity. However, filter contamination may have contributed as this trend was not observed in a subsequent study so more research is needed. The strontium is linked to the very high values that were measured on July 4, as strontium is used in fireworks for its bright red color.

★ The comparison of monitored values to NATA 2002 indicates that better information is needed in the emissions inventory used in the NATA modeling. For instance, for carbon tetrachloride, which is no longer emitted and has a long half-life in the atmosphere, the agreement was almost perfect, while for manganese, chlorine and naphthalene, there was very poor agreement. Ethylbenzene and p-dichlorobenzene had fairly good agreement at all sites except the C site. These are influenced by the high concentrations that were measured at the C site in the fall of 2006. Differences may have occurred simply because NATA 2002 was compared to monitoring data in 2006 and changes in sources may have occurred over that four year period.

★ The comparison of the CALPUFF model with monitoring data showed very good agreement for some compounds but not for others. In general the model tended to over predict the monitored values that, due to the location of the stationary sources, could indicate that the mobile source emission estimates are too high. p-Dichlorobenzene had very poor agreement, but that is most likely due to an “event” in the fall of 2006 when concentrations measured at the C site were very high.

★ The BME modeling exercise indicates that this model provides an interesting method of looking at the spatial distribution and concentration gradients which, if expanded upon, could assist in identifying factors such as daily source intensity. One of BME's strengths is its ability to characterize daily air quality.

★ The following compounds had cancer risks above the NJDEP air program guideline value of 1 in a million lifetime cancer risk in Paterson and at one or more of the other monitoring sites around the state; arsenic, 1,3-butadiene, benzene, carbon tetrachloride, chloroform, chloromethane, ethylbenzene, p-dichlorobenzene, and tetrachloroethylene. The risk from naphthalene marginally exceeded the guideline value at two sites in Paterson. Naphthalene could not be compared to the other three monitoring stations around the state because comparable measurements were not made there. There was no short term (24 hr) or long term (70 yr) noncancer risk.

XIV. LESSONS LEARNED

► One of the most important lessons is that the NJDEP air toxics monitoring network captures and characterizes over 90% of air quality issues in New Jersey, including urban community air quality. However, community based projects are still important to pinpoint local issues, such as the p-dichlorobenzene issue in Paterson.

► Improvements to NJDEP Emissions Databases could be accomplished by expanding current permit requirements so that facilities would have to submit stack-specific speciated VOCs and HAPs. The Emission Statement Program’s current requirement that major facilities report only 36 HAPs at the facility- wide level could be expanded to include additional air toxics (i.e., all those with risk-based toxicity values) and permit reporting thresholds need to be revised to reflect risk.

► It would have been useful to have a meteorological station at each monitoring location. This may have helped identify the source(s) associated with the high concentrations measured at the C site.

► For enforcement purposes, assessment of the data and notification of potential issues needs to be more timely, i.e., to allow for enforcement to take action more effectively and find the cause of the problem.

► Recommend completion of an emissions inventory and site visits before scoping out the monitoring plan. This would have helped to focus in on target analytes, reduce MDLs, locate the monitoring sites near potentially risky sources and conserve resources.

►Complete, at a minimum, a screening level of modeling to assist in scoping out the monitoring plan, i.e., analyte selection and monitoring location(s).

► Neighborhood drive-throughs are an effective way to identify sources that are no longer operating.

► Site visits are vital to completing a thorough and accurate emissions inventory.

► Site visits are an excellent way to implement outreach and education, and identify, communicate and implement risk reduction strategies.

► Projects of this scope require the cooperation of many program areas in a state agency, (science, statistics, air monitoring, permitting, enforcement, risk assessment, risk communication, pollution prevention, etc.).

► Urban air quality is not dominated by only mobile sources. For example, this is shown by the concentrations of tetrachloroethylene (an area source air toxic) and p-dichlorobenzene (a point source air toxic) that were measured in Paterson.

►In Paterson, the risk was in the within the same order of magnitude as other locations around the state.

XV. FUTURE WORK

It is recommended that the following analyses be done in the future, but it is acknowledged that completing this additional work will depend on available resources.

►The data from Paterson should be compared other UATMP sites around the country.

►Compare 2005 NATA results to the 2006 monitoring data from Paterson.

►Compare metal concentrations in PM_{10} to $PM_{2.5}$ obtained from the background monitoring location, i.e., Chester, NJ.

►Characterize of air toxics trends over time.

►Characterize ratios of air toxics.

►Compare the Paterson data to other measurements reported in the literature.

►Continue to use the instrumentation purchased during UCAMPP in other air monitoring projects.

►Continue to communicate results of the study to interested parties.

►Continue to improve the PAKS and hexavalent chromium methods.


No
Trespassing
PSEG


VISITOR
PARKING
TWO HOUR
LIMIT


LOU
COSTELLO
1906 • 1959
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APPENDIX I: Tables 17-20: General Information