SPATIAL AND TEMPORAL CONCENTRATIONS OF BENZENE IN TWO NORTHERN NEW ENGLAND COMMUNITIES: A MODELING VALIDATION STUDY

Local-Scale Air Toxics Ambient Monitoring Program Grant RFA OAR-EMAD-05-16

FINAL REPORT to the EPA
Vermont Air Pollution Control Division

Air Pollution Control Division (APCD)
Department of Environmental Conservation
Vermont Agency of Natural Resources

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Executive Summary

The purpose of this modeling study was to confirm sources of and to define spatial gradients and temporal differences of ambient benzene concentrations in Burlington, Vermont and its surrounding area during the period of an intensive enhancement of ambient benzene monitoring starting in June 2007 and continuing into June 2008.

A previously completed modeling study of benzene in Burlington in 1999 (*Ambient Benzene Modeling Study for Chittenden County*, July 2005), hereafter referred to as the *1999 Modeling Study Report*, demonstrated that a puff dispersion model, CALPUFF, could be a useful tool to help us estimate the spatial and temporal gradients of ambient benzene in Burlington. While the model performed reasonably well at the single monitoring location for 1999 meteorology, there was no concurrent benzene monitored data from any other site in the urban area which allowed much confidence that the model was able to adequately capture the gradients of concentration across an urban area.

In 2006, the Vermont Air Pollution Control Division (APCD) sought, and received, funding to conduct an enhanced benzene monitoring program for one year (Local-Scale Air Toxics Ambient Monitoring Program Grant RFA OAR-EMAD-05-16). One important goal of the project was to obtain a robust spatial and temporal data set of ambient benzene measurements that could be used to validate the CALPUFF modeling approach previously used in the 1999 modeling and to possibly extend the applicability of that type of modeling to other similar urban locations in northern New England.

Experience gained with the previous modeling approach for the year 1999 was invaluable for designing the grant modeling study approach. Most of the inventory development and meteorological data creation software used in the 1999 modeling study was transferrable for use in this grant modeling study. Updates to activity factors and to mobile emission factors as well as use of the current 2007 through 2008 raw meteorological parameter measurements were the primary adjustments that were made in the model data inputs. There was however a significant enhancement of the specification of the mobile on-road sources emitting benzene, based on more refined definition of the spatial locations of the road emissions and a change from an "area source" representation of the on-road emissions to a "volume source" based approach. It was interesting that this change in the on-road source representation from "area" to "volume" did not produce significantly different results at receptors specified in the study, based on sensitivity testing conducted prior to running the model in its final configuration for the full time period.

The 24-hour average impacts predicted by the CALPUFF model should not be directly compared to the Vermont health-based standard because that standard was established based on long-term exposure (70 years) to average ambient concentrations for time

periods of more than a year. The 24-hour modeled impacts shown in this report are presented to show the variation in impacts that occur over short time periods from the several source categories independently and also when all are combined. Short-term (24-hr) exposure to levels of benzene in the ambient air which are greater than the Vermont standard is not currently believed to cause the same health effects as exposure for long time periods to the same or lower ambient levels of ambient benzene.

Specific life-style habits such as smoking also influence the amount of benzene a person is exposed to over the long-term. Smoking tobacco is one of the most direct ways that long-term benzene exposure is increased, particularly for the individual smoking but also for those in the same indoor environments as smokers. A study on motor vehicle emission related exposure of humans to benzene ⁽⁷⁾ published by the U.S. Environmental Protection Agency in 1993 indicates that "active smoking of tobacco" accounts for "roughly half of total population exposure to benzene, which is over and above that from motor vehicles. Outdoor concentrations of benzene, due mainly to motor vehicles, account for roughly one-quarter of the total".

The modeling study involved several separate activities, each of which is described in the section below.

- 1. Preparation of spatially detailed (200m horizontal resolution) hourly 3-dimensional meteorological wind fields for a large portion of Chittenden County.
- 2. Identification of all local sources of benzene emissions to the ambient air and selecting the significantly emitting categories for modeling.

Five primary source groups were identified from the emission inventory work that had been conducted for the 1999 modeling study.

Group 1: on-road motor vehicles (urban-core)

Group 2: on-road motor vehicles (non urban-core)

Group 3: home-heating fuel burning

Group 4: gasoline service station activity

Group 5: large industrial sources (only 1 warranted inclusion in modeling)

These groupings allowed examination of each particular set of similar sources independent of the remaining sources. As in the 1999 modeling study, several candidate benzene source categories were not included in the 2007-2008 grant modeling study based on a reasonable understanding that their emission potential was so minimal that impacts were not significant enough to warrant the intense effort that would have been needed to estimate the emissions on an hourly basis. See the discussion identifying these categories that was contained in the 1999 Modeling Study Report cited above.

- 3. Estimation of the mass of benzene emission each source contributed in each hour during the time period being modeled from June 2007 thru June 2008. Characterization of how benzene emissions occurred were consistent with the approach used in 1999, except for the characterization of the on-road sources as mentioned above. For the grant study modeling we used volume sources of dimension 10m by 10 m square which were spaced along the road-links extracted from a GIS database. The on-road emissions of benzene were assumed to be emitted at 1 meter height with an initial sigma y of 10m and and initial sigma z of 0.5m.
- 4. An intensive monitoring program (only briefly described in Section 4) identified 13 discrete receptors, considering the specific goals of the grant study, where ambient benzene sampling of various duration and frequency was conducted on the domain which was modeled.
- 5. Modeling of all benzene emission sources for the entire year period from June 2007 to June 2008 and evaluation of modeling results at the 13 sites where monitors were located. The model performed with varying degrees of success at the receptor sites, dependant on the averaging time of the sampling method used and the location of the monitor relative to source categories.
- 6. After the evaluation confirmed that the model was performing reasonably well over the longer time frames relevant to risk assessment for human exposure to ambient benzene concentrations, a full model run of all sources was conducted using a set of 72 gridded receptors. These gridded receptor locations allowed an estimate of spatially predicted benzene concentration within the 8km by 10km urban portion of Chittenden County centered on downtown Burlington, Vermont for the entire year modeling period.

Spatial and temporal patterns of urban air contaminants in the ambient air (a general comment on what the CALPUFF modeling approach allows us to conclude from this modeling study):

The magnitude of the annual total emissions from a source type throughout the domain is not an absolute indicator of which source type actually causes the highest impact of ambient benzene measured at all locations in the domain. The actual air quality at any location is a result of these emissions being dispersed and transported from their sources to the receptors (measurement locations). Modeling the emission and the dispersion and transport of the benzene to all parts of the domain in the 1999 study indicated that although emissions from motor vehicles traveling on roadways generally determine the overall benzene concentration patterns (because the roadways are fairly uniformly distributed across the domain), hot-spots of even higher concentration on average could

exist in close proximity to gasoline service stations and other point sources of benzene emission.

The short-term variability of concentration impacts relative to distance from specific source categories tends to be more difficult to replicate than the long-term average concentrations in the domain. This is because the uncertainty of an emission rate estimated during any short time period is much higher than the uncertainty of an estimated long-term average emission rate. The process of modeling the emission sources of benzene involves taking a relatively well estimated annual emission total and allocating these emissions to hourly rates through application of differences in daily, weekly or monthly activity and diurnal patterns of activity. In this grant study, the ability of the model to reproduce measured hourly ambient benzene concentrations in the vicinity of one specific gasoline station was seen to be problematic. The characterization of evaporative benzene emissions temporally and quantitatively from the activities associated with gasoline marketing was not as successful as was the characterization of on-road tailpipe emissions of benzene for this study.

Diurnal patterns of on-road vehicles tended to be more accurately known than the diurnal potential for evaporative emission from gasoline marketing at gasoline stations, although several additional data collecting methodologies to try to better quantify hourly benzene evaporative emissions were employed during this study to try to overcome this. It was not feasible, given the resources that would be required, to adequately estimate the hourly emission patterns from gasoline stations that would be necessary to allow the model to better replicate reality. A surveillance camera was used to survey traffic and the activity at a gas station across the street from the main monitoring site at S. Winooski and Main Street intersection as part of the supplemental data collection methodologies. It proved too time consuming to gather the wealth of available data from the images to allow this information to improve diurnal and temporal differences in activity for other than a few short time periods in the year of modeling.

Results

Modeled Results Used to Depict Spatial Concentration Gradients:

When the modeling results from the 13 discrete receptors used in the enhanced benzene monitoring program became available for the complete year of sampling, the evaluation of the performance of the CALPUFF model at the receptors was found to be reasonable, but not quite as good as we had hoped, especially for certain receptor locations as described above. Nevertheless, the results were good enough to proceed with a gridded set of receptors that could be used to interpolate gradients of benzene concentration and show these spatial gradients over the domain of the modeling. A full set of hourly benzene concentration impacts at 72 receptors in an 8 x 9 grid, covering the central portion of the urban area, was produced. This set of results comprised more than 9000 hours of time

from June 20, 2007 to June 29, 2008. The hourly results were averaged for different time periods so that monthly and seasonal maps for the domain showing concentration gradient could be produced. An overall annual average map was also created.

The maps of the gradients were created in two ways. The first method, with monthly maps shown below, utilized independently developed computer code that combined the concentration prediction outputs of many runs of different source groups in the domain into one combined impact output and also generated the graphic images. Maps were also generated using ARCview software and GIS databases. The ARCview generated maps are included in Section 6 of this report.

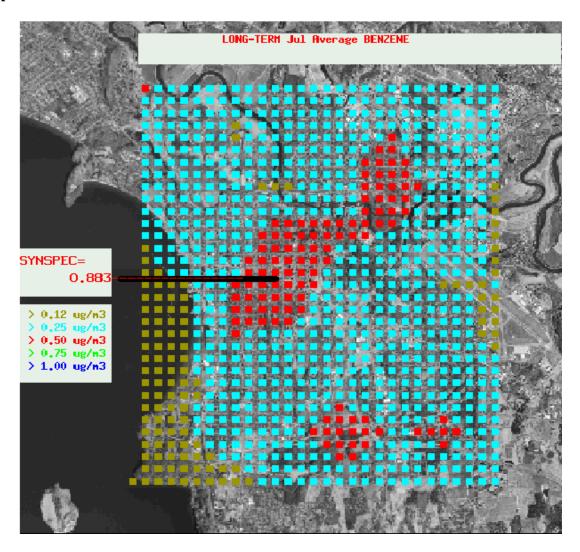
Shown on the following maps, which are relatively simplified to depict only up to five different levels of concentration over the domain, is the average benzene measured at the downtown trailer location at S. Winooski and Main St. In most cases, it is encouraging to see that the measured average long-term concentration is close to and follows the variability of the modeled long-term concentration average in the vicinity of that monitoring location.

In summary, Maps 1 thru 12 show the monthly averages for the July 2007 to June 2008 time period. For eight of the 12 months, Aug, Sep, Nov, Dec, Feb, Mar, May, and Jun the measured benzene average corresponds very closely with what the modeled isopleths map depicts for that location. The model shows an under-prediction of the actual average value measured for Jul, Oct, Jan, and Apr.

Maps 13 thru 16 show the seasonal averages for the time periods Jul-Sep, Oct-Dec, Jan-Mar, and Apr-Jun. For three of these 4 quarters the modeled predicted average agrees very closely with the measured seasonal average at the downtown trailer.

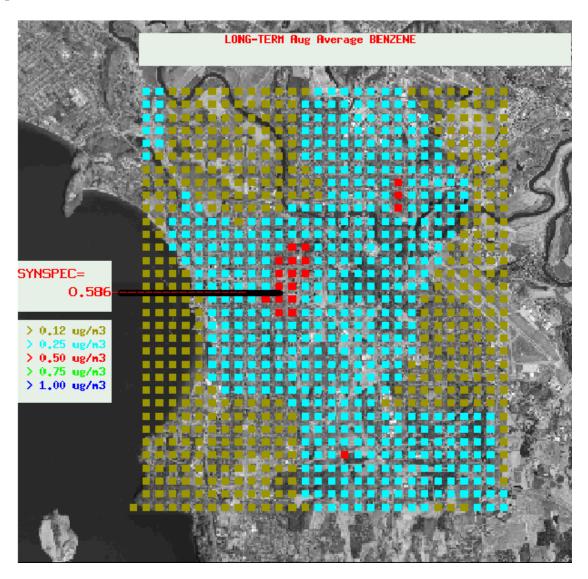
Map 17 is the overall annual average isopleth map for the domain modeled. As can be seen, the measured benzene average annual concentration at the trailer is $0.816~\mu g/m^3$ and it occurs very close to the predicted location of a portion of the domain that is modeled to be greater than $0.75~\mu g/m^3$ but less than $1.00~\mu g/m^3$ annual average.

1. JULY 2007 average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



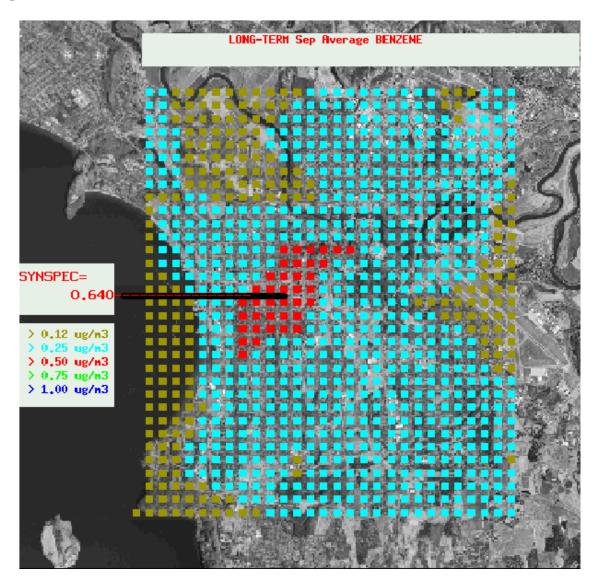
July 2007 Average Benzene ~ μg/m³

2. AUGUST 2007 average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



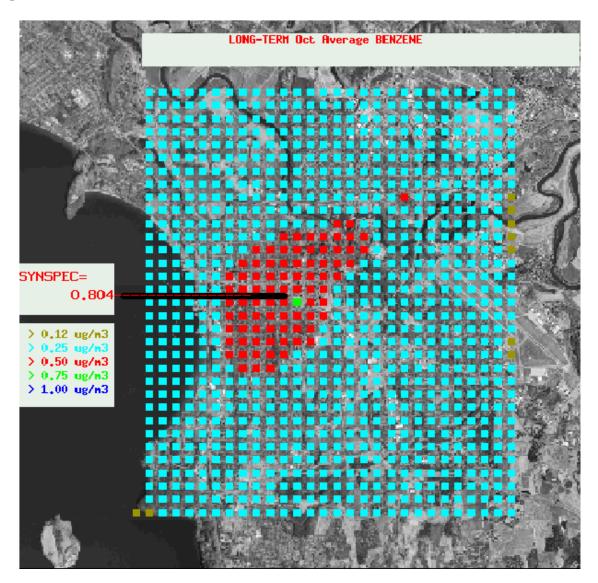
August 2007 Average Benzene ~ μg/m3

3. **SEPTEMBER 2007 average ambient benzene** (μ g/m3) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



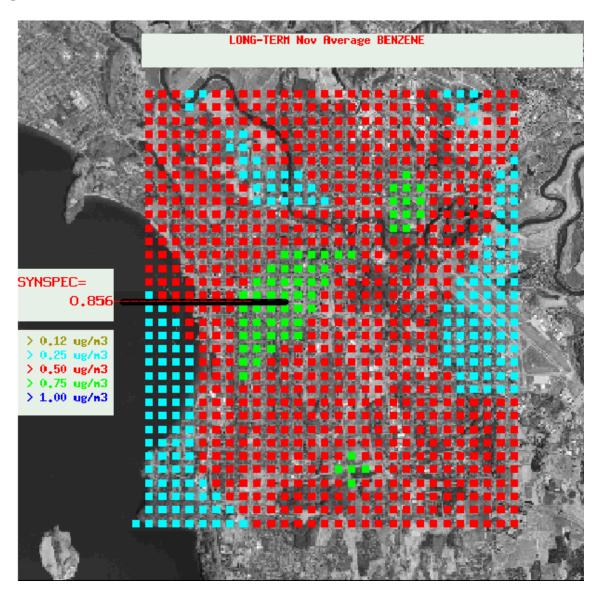
September 2007 Average Benzene ~ μg/m3

4. OCTOBER 2007 average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the $16~km \times 16~km$ portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



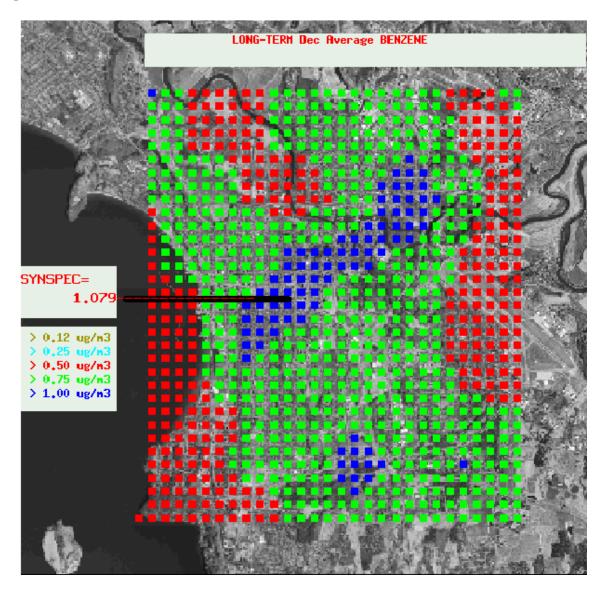
October 2007 Average Benzene ~ µg/m³

5. NOVEMBER 2007 average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



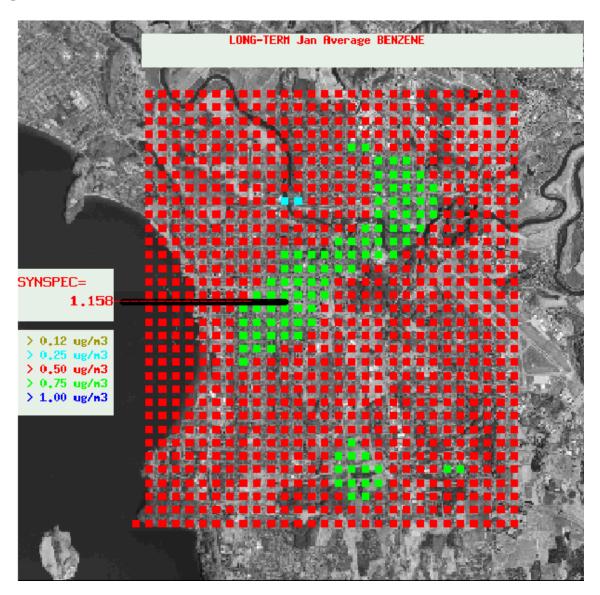
November 2007 Average Benzene ~ μg/m³

6. **DECEMBER 2007 average ambient benzene** ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



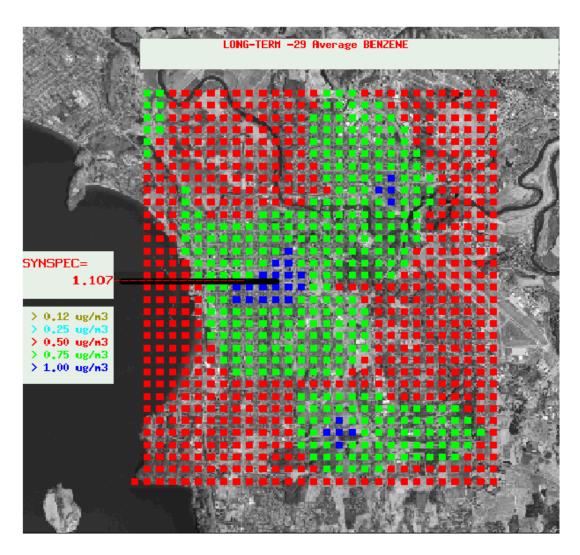
December 2007 Average Benzene ~ μg/m³

7. **JANUARY 2008 average ambient benzene** ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



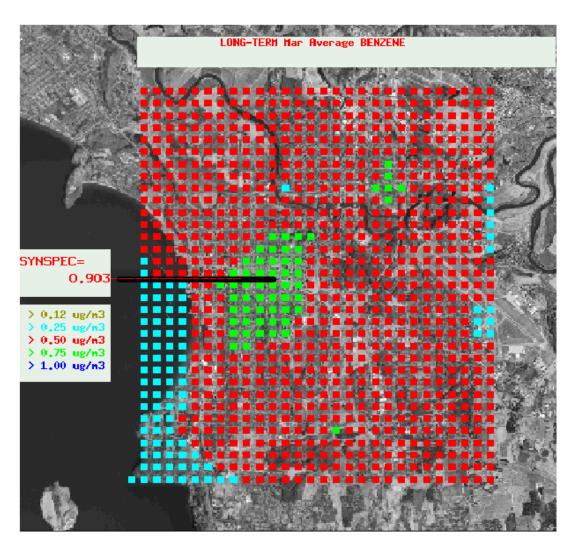
January 2008 Average Benzene ~ μg/m³

8. **FEBRUARY 2008 average ambient benzene** ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



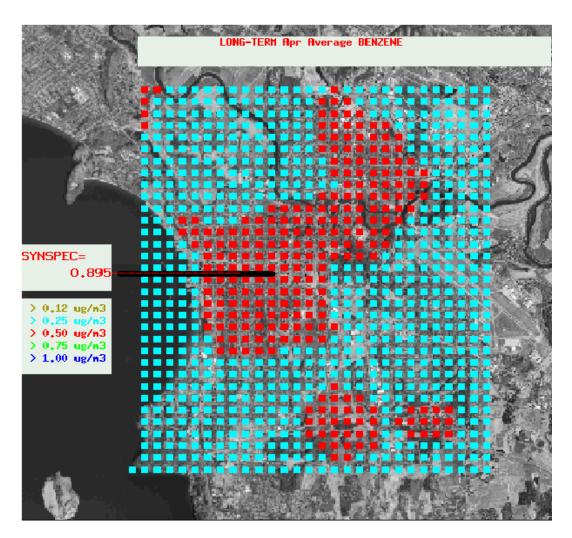
February 2008 Average Benzene ~ μg/m³

9. MARCH 2008 average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



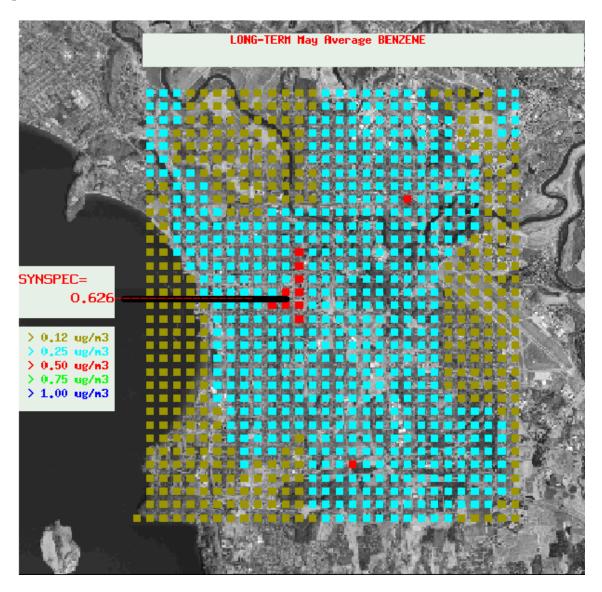
March 2008 Average Benzene ~ μg/m³

10. APRIL 2008 average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



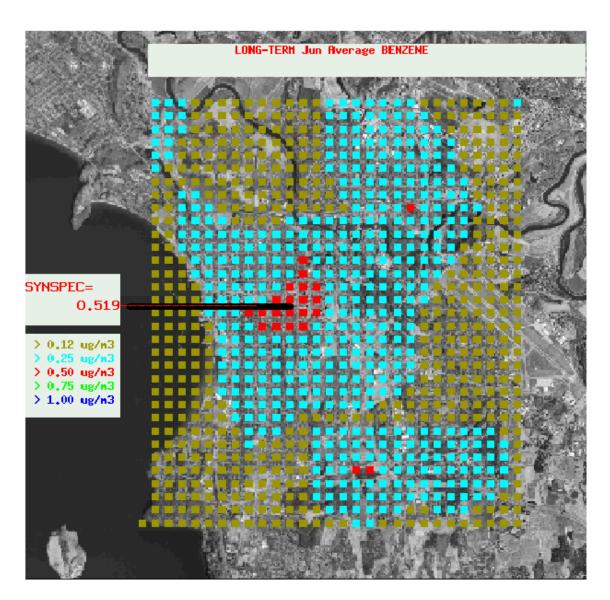
April 2008 Average Benzene ~ μg/m³

11. MAY 2008 average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



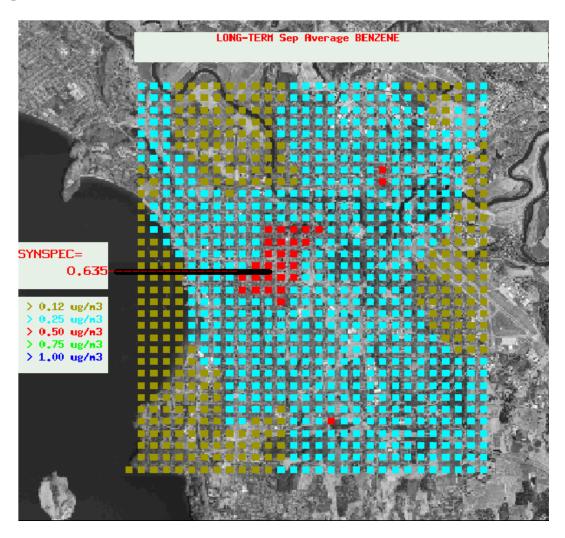
May 2008 Average Benzene ~ μg/m³

12. JUNE 2008 average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



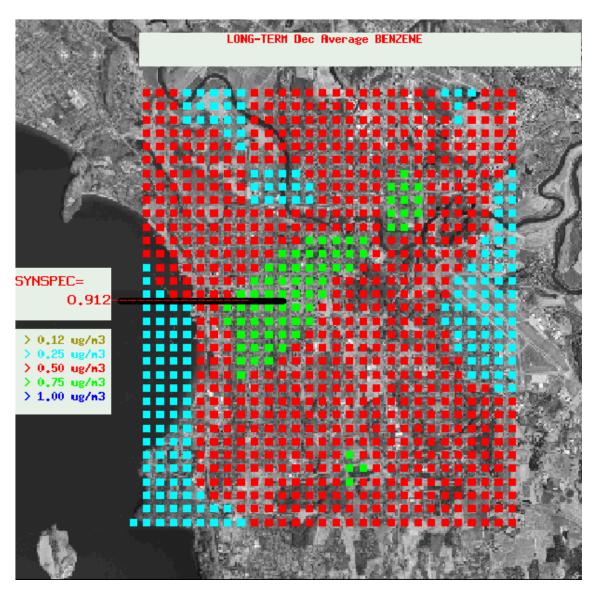
June 2008 Average Benzene ~ $\mu g/m^3$

13. JUL-SEP 2007 SUMMER average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the $16~km \times 16~km$ portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



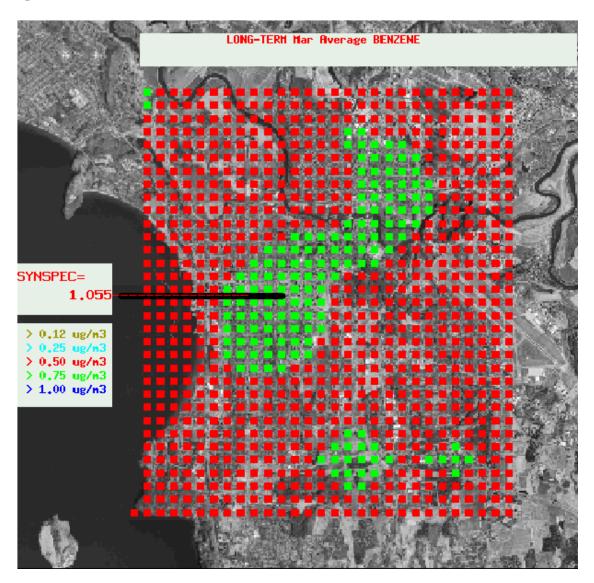
July - September 2007 SUMMER Average Benzene ~ μg/m³

14. OCT-DEC 2007 AUTUMN average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



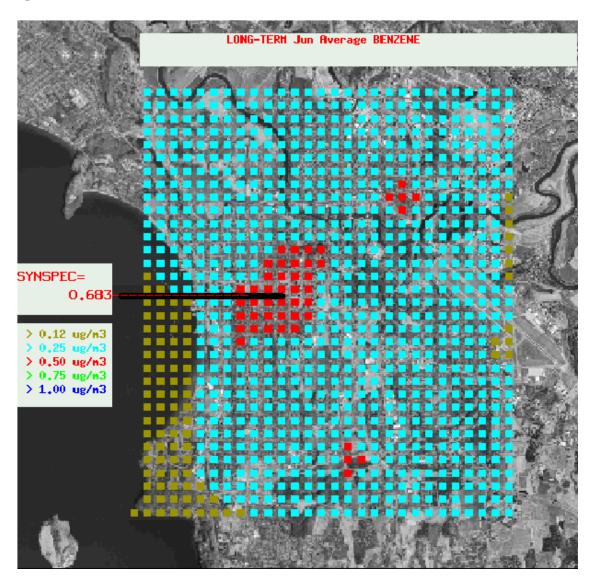
October - December 2007 AUTUMN Average Benzene ~ $\mu g/m^3$

15. JAN-MAR 2008 WINTER average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the 16 km x 16 km portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



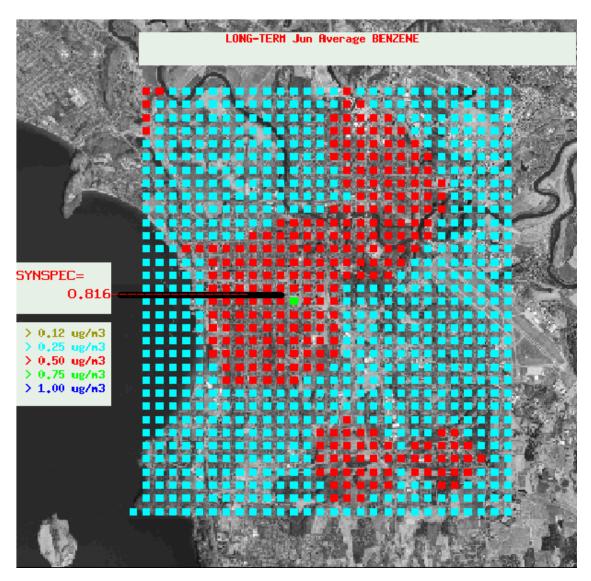
January - March 2008 WINTER Average Benzene ~ μg/m³

16. APR-JUN 2008 SPRING average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the $16~km \times 16~km$ portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



April - June 2008 SPRING Average Benzene $\sim \mu g/m^3$

17. JUN 2007-JUN 2008 ANNUAL average ambient benzene ($\mu g/m^3$) predicted by CALPUFF on the Burlington domain; all modeled sources of benzene in the $16~km \times 16~km$ portion of Chittenden County centered on downtown. The SYNSPEC Monitoring site average measurement at the downtown S. Winooski Trailer location is also shown on the map.



June 21 2007 – June 28 2008 ANNUAL Average Benzene ~ $\mu g/m^3$

Conclusions

The CALPUFF model was able to reasonability predict ambient air concentrations throughout Burlington. The model performance was improved over longer time scales. Further, the CALPUFF model was not able to capture short-term peaks in benzene concentrations, due to unexpected activities. However, using the CALPUFF model over complex terrain to estimate benzene concentrations throughout an urban community may have great utility. This modeling platform may be transferred to NH, if the modeling expertise is available.

Introduction

Long-term air quality monitoring of ambient benzene had been conducted in the urban center of Burlington (S. Winooski & Bank Street intersection) from 1993 to 2000 and from 2003 to present (S. Winooski & Main Streets). That monitoring was part of the State Air Pollution Control Division's hazardous air contaminant management program. The measurements obtained are specifically applicable to the monitor locations but are also representative of locations in the immediate vicinity of the monitors. For purposes of long-term exposure to potentially cancer causing air contaminants, it is important to be able to estimate the spatial and temporal distribution of an air contaminant like benzene throughout a city or region, not just at a point location of measurement. This current study was intended to validate a modeling tool that would allow such estimations of long-term exposure throughout the city of Burlington.

For 1999 the data indicated that the monitoring location 10 meters to the east of the S. Winooski & Bank Street intersection had ambient concentrations of benzene which exceeded the Vermont hazardous ambient air standard for benzene (0.12 μ g/m³ on an annual average basis) by roughly a factor of 20. The results of the modeling conducted for the year 1999 at this location implied that the CALPUFF modeling platform may be a useful tool in assessing how benzene concentrations are distributed throughout Burlington.

The CALPUFF model is a model that can represent the behavior of benzene emitted into the air from a variety of possible source types and can account for its dispersion and transport in the urban area. Benzene is assumed to be a relatively non-reactive component of VOC emissions that does not get removed significantly by chemical reaction in the time frames and spatial extent of the modeled dispersion and transport that occurs in a small urban area such as Burlington, Vermont. The design of the grant program monitoring network took into account the need for spatial and temporal benzene concentration data that could be used to validate the relatively simple CALPUFF modeling approach without chemical reaction removal mechanisms in the specific urban domain being examined.

Exposure To Benzene Not Limited to Ambient Air Concentrations

Exposure of an individual to benzene through the air is not solely determined by the ambient concentration levels in urban settings. Most people, especially those living and working in urban centers spend the majority of their lives in an indoor environment. Studies $^{(5),(6)}$, done mainly in Europe, have shown that indoor levels of benzene actually tend to be higher than levels measured in the ambient air of the urban centers where homes and businesses are located. For the towns in Europe studied using personal exposure samplers carried by volunteers, it was found that indoor benzene concentration levels were on average 1.5 times the ambient outdoor benzene levels, and the studies also found that people spent 59.1% of the time at home $^{(5)}$. With respect to both the indoor and the outdoor air concentrations, these studies also indicate that meteorological hourly variation and/or differences in meteorological conditions over longer time frames "strongly affects the benzene concentrations" $^{(6)}$ measured at any monitoring site.

Although Burlington, Vermont's situation may differ somewhat from that in European cities, these basic findings are likely to be generally true for urban Burlington.

Objectives

- a. Characterization of the risk and exposure to ambient benzene in Burlington
- b. Model validation

Methods

Monitoring Network Design for High Spatial and Temporal Resolution Monitoring

The design of the sampling effort for this grant work resulted from the fact that both temporal and spatial validation of the modeling effort was desired. Based on the previously completed benzene modeling study done for calendar year 1999 and dated July 2005, the APCD believed that the model was capturing the temporal variability of ambient benzene (due primarily to diurnally varying on-road source emissions) at the one location near the road for which sampling data also existed during 1999. That study had not been able to confirm (with measurements) the spatial variability of ambient benzene across the domain which was predicted by the model. It was also desirable to look at a micro portion of the entire domain in order to confirm or refute near-field modeling results due to urbanized road networks with their associated gasoline marketing activities. The 1999 modeling predicted islands of higher average benzene in the near vicinity of gasoline marketing (service stations).

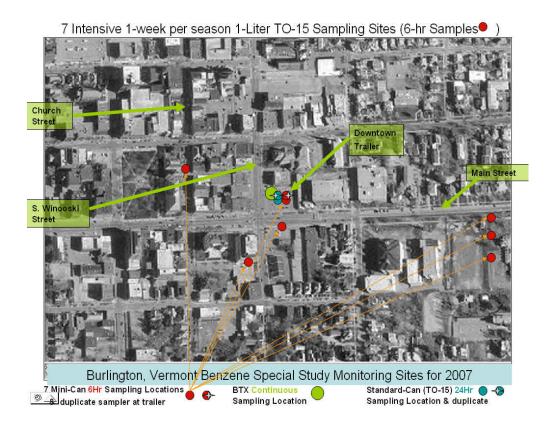
After consideration of the resource requirements for sampling benzene and the availability of two sampling technologies which might actually complement each other, the project design for sampling ambient benzene incorporated three specific components.

Component 1: Intensive 1 week long (7 days) sequential 6-hour sampling periods Four 1-week intensive sampling time periods were built into the one year time period, one in each of the seasons from June 2007 to June 2008. Under this component VOC canisters were collected at 7 locations within roughly 500 meters of the location of APCD's air monitoring station which is located in the parking lot at the intersection of Main Street and South Winooski Street. The current location of the APCD's monitoring station which has been collecting 24-hour samples in 6-liter VOC canisters every 12th day for benzene analysis by TO-15 since 2003 was also included as one of the 7 locations used to collect 6-hour canister samples. The intensive week sample collection was performed following the schedule outlined below using 3-liter VOC stainless steel canisters that were setup to collect samples for 28 consecutive 6-hr time periods during each of the 4 separate intensive sampling weeks.

The 1-week intensive sampling periods for the study were as follows:

Sunday Jul 15, 2007 to Saturday Jul 21, 2007 Sunday Oct 21, 2007 to Saturday Oct 27, 2007 Sunday Jan 13, 2008 to Saturday Jan 19, 2008 Saturday Apr 12, 2008 to Friday Apr 18, 2008 Intensive week 6-hr sampling periods are list below and were collected on Local Time, which meant that during March to November (covering spring, summer and fall intensive weeks), adjustments had to be made to model results to account for Standard Time output from the CALPUFF model.

- 1. 12 midnight to 6 am
- 2. 6 am to 12 noon
- 3. 12 noon to 6 pm
- 4. 6 pm to 12 midnight

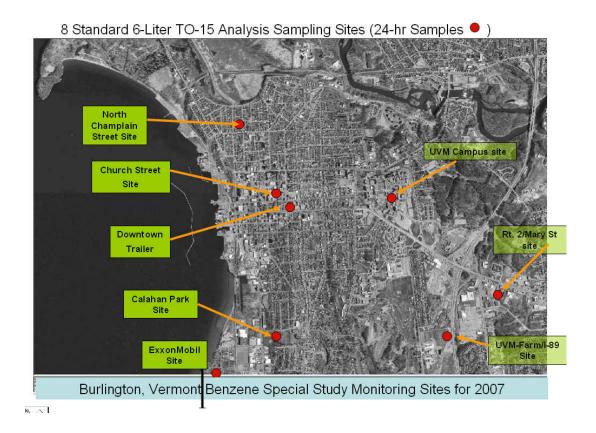


Component 2: ONSITE SEMI-CONTINUOUS MONITORING

Semi-continuous ambient benzene monitoring was performed using a Syntech Spectras GC955-series GC/PID instrument manufactured in the Netherlands by Synspec. The direct measurement analyzer was operated at the APCD's Burlington monitoring station for this grant study beginning on June 21, 2007. The instrument was operated primarily to obtain benzene data for this study. Details of the operation of this instrument may be found in the Monitoring Section of this report. In summary, this instrument provides four , 15-minute integrated samples during each hour which are averaged to obtain 1-hour benzene, toluene, xylene, and ethylbenzene ambient concentration estimates during the time period of the grant study June 20, 2007 thru June 30, 2008. CALPUFF Model predictions for each hour at the trailer site were compared to the hourly benzene measurements over the entire year period.

Component 3: EVERY 12TH DAY, 24-HR SAMPLING PERIODS

Individual 24-Hr integrated 6-liter VOC canister samples were collected every 12^{th} day at the Burlington monitoring station trailer location for TO-15 analysis was expanded into an eight site sampling network each using the same sampling technology on the same time schedule of sampling. This monitoring effort was done to allow for validation of the spatial gradients predicted by the modeling. The eight sites operated on a schedule consistent with the current national network every 12^{th} day sampling schedule. Sampling started on Monday June 11, 2007 and continued every 12th day after that until Sunday June 29, 2008. Average 24-hr benzene sampled at all eight locations was compared to model predicted 24-hour averages at these locations for the set of ~ 30 sampling days with valid data during the year.



Details of the operation of the 3 monitoring components discussed above are provided in Part 2 of this report. General quality assurance of the ambient benzene sampling data is also provided. Section 5 below utilizes the results of the ambient monitoring components which were certified by the APCD monitoring project manager and compares these ambient sample values to the modeled values predicted. Comparisons presented in Section 5 are for the most part between monitored and modeled values paired in space and time, although model results produced for a gridded receptor field have also been presented as spatial gradient maps.

Benzene CALPUFF Modeling

By obtaining continuously monitored benzene measurements from several locations within Burlington, as well as an increased number of samples collected at additional sampling sites at the same frequency as our current monitoring location, we were able to evaluate the model short-term performance at the existing downtown monitoring location (with refinements, if necessary) and increase are confidence in model performance for the entire domain.

Results

Please see Parts 1 and 2 of this report for study results.

Part 1 Ambient Benzene Modeling Study

Author

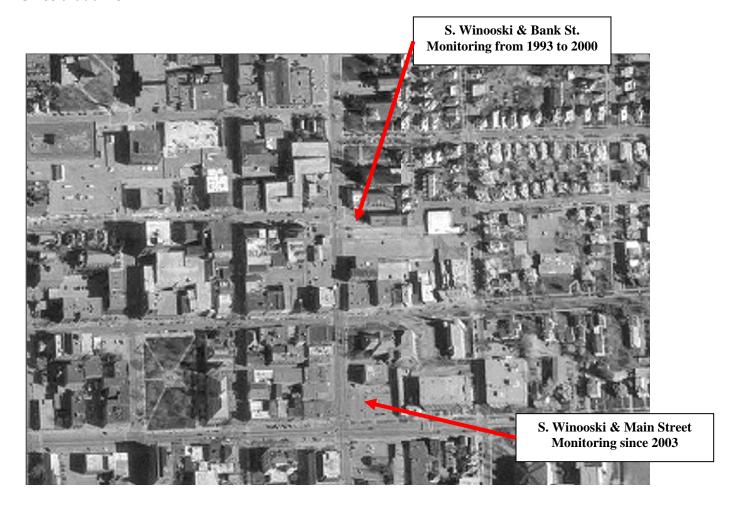
Paul Wishinski, APCD Planning Section Chief (Retired)/Project Consultant

Purpose of this Report

This report was prepared as one technical product resulting from ambient modeling activities conducted in fulfillment of objectives of a study of spatial and temporal ambient concentrations of benzene in Chittenden County for which the APCD received a federal grant from the Environmental Protection Agency in 2006. The modeling study which is the subject of this section was initiated in mid-2007, after a period of more than a year of preparatory work identifying monitoring locations and sampling methodologies to be employed. The study's goal was to establish baseline benzene concentrations and also to further validate an air quality model being used for spatial and temporal resolution of ambient benzene concentration gradients in Chittenden County, primarily the City of Burlington. The modeling portion of the study was specifically intended to spatially and temporally extend the information obtained in the monitoring effort and will be used to inform future decisions and policies of the APCD regarding control and management of benzene (and other similarly emitted HACs) in the ambient air.

Introduction

Benzene monitoring has been conducted in downtown Burlington routinely since mid-1993. The site at which the sampling was done from 1993 thru 1999 on a regular "every 12th-day" schedule was located in a parking area next to the police station opposite the intersection of Bank Street with S. Winooski Avenue (see figure below). Since mid-2000 there was a period of about three years during which benzene monitoring was suspended while a new site was established several hundred meters away in a parking area on the corner of S. Winooski Avenue and Main Streets. Monitoring for benzene on the same schedule as previously was resumed in January 2003 at the new location and has continued since that time.



In addition to these urban area monitoring sites in Burlington, benzene has also been monitored for varying coincident time periods in several other urban centers (Brattleboro, Winooski, and Rutland) as well as in Waterbury and also at the Proctor Maple Research Center in Underhill, Vermont. The Underhill site serves as a rural background type of site which is useful for evaluating relative local and regional-scale source influences, particularly with respect to the Burlington downtown sites. A report of the State Toxicological Advisory Committee dated February 1998 (1) describes in detail the data

collected from the entire hazardous air contaminant monitoring program conducted in Vermont through that time.

Meteorological Wind Fields Used in Modeling

Choice of Model and Domain:

Prior to conducting the 1999 benzene modeling study described in the appended report cited above, the Air Division Planning Section examined the appropriateness of several models for use in modeling benzene which is primarily emitted by on-road sources. It was quickly determined that EPA's Guideline on Air Quality Models did not preclude the use of a regional scale puff dispersion model called CALPUFF for the study. Although the recommended use of CALPUFF in complex terrain situations at that time was on a case-by-case basis, the fact that model evaluation against actual monitored data was included as one aspect of the study implied that the use of CALPUFF for the study would certainly be appropriate. Also the location of Burlington, which was to be the primary focus of the 1999 year modeling, is in the relatively smooth Champlain Valley making considerations due to complex terrain less important.

Several specific reasons made the choice of CALPUFF very appropriate as well as advantageous. For one thing, the other complex terrain models available at that time would not have been able to accommodate as many sources and would not have been able to account for innumerable smaller terrain features embedded in a domain of the size of Chittenden County. The CALPUFF model system is able to account for such features using a spatially and temporally varying wind-field created with a model system component called CALMET. CALPUFF is also capable of handling shoreline fumigation situations that might develop near Lake Champlain as well as capable of handling air stagnation situations that might occur.

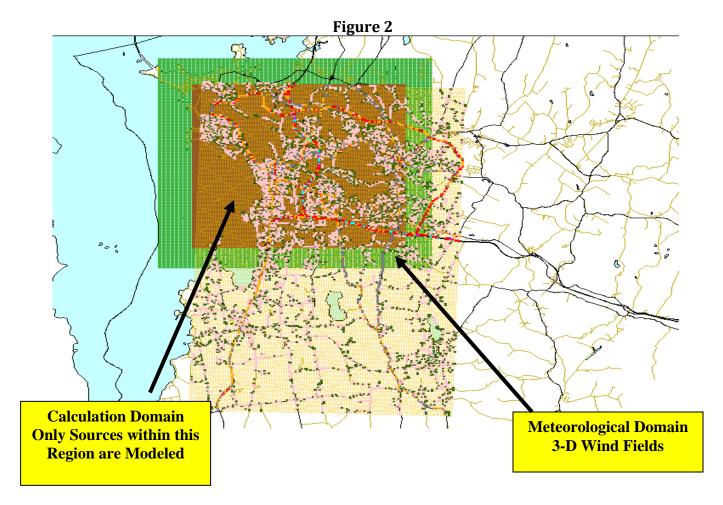
For this calendar year 2007-2008 benzene grant modeling work, the applicability of the CALPUFF model and its CALMET was considered already established and the same approach for creating meteorological wind fields on the same 16 km x 16 km domain was used as has been described in the 1999 study. Of course the appropriate raw input data for surface and upper air measurement sites was obtained for the years of interest.

Meteorology:

A meteorological field resolution at 200 meter grid spacing covering a square of 16 kilometers was used for the grant study modeling wind fields. Choices of surface meteorological measurement sites and upper air measurement to use for input to the CALMET model for 2007 and 2008 remain the same as previously. Choices of CALMET model settings had already been thoroughly examined when creating the 1999 model domain wind fields, so this was not a major factor in creating the wind fields for the grant study. **Appendix B** describes the process of validation of all assumptions and CALMET model settings which were used to create the final meteorological fields used in both the 1999 study and the current grant study.

Meteorological fields based on the 200 meter spacing were produced for modeling on the domain covering a 16 kilometer by 16 kilometer area centered over urban Burlington. The first fields produced were monthly files, starting in April 2007 for use in testing the modeling system prior to the collection of actual benzene ambient monitoring data which was not scheduled to begin until mid to late June 2007. The CALPUFF modeling system allows the establishment of three spatial domains in which input parameters or output parameters are specified by the correct coordinates. Meteorological fields need to cover the largest extent. Within the coverage of the meteorological fields, a "calculation domain" in which dispersion and calculation of ambient concentrations is done by the model needs to be specified. This region must encompass all of the emission sources desired to be included in the modeling. Finally, if a set of equally spaced receptors is to be used for displaying a spatial pattern of the concentration output from the model, this set of receptors, the "sampling grid" must be specified as a subset of the calculation domain. For the 2007 – 2008 modeling study a simpler sampling grid was decided on, because of the time involved in calculating results from thousands of road-link based "on-road" emission sources that were to be included in the modeling. Initially, only 13 discrete receptors were to be modeled, but after some validation of results from these had been seen, a set of 72 other discrete receptors established in 9 latitudinal rows and 8 longitudinal rows created a grid of receptors covering an 8 km x 9km sampling domain within the larger meteorological domain of 16km x 16km.

Figure 2 shows the area of Chittenden County covered by the **meteorological fields (GREEN)** prepared for 1999 which were used by CALPUFF to disperse and transport benzene emissions within the **calculation portion (BROWN)** of the final domain of approximately 16 km x 16 km which was utilized in this study.



Sources of Benzene Modeled & Creation of Hourly Emission Inventories for Modeling

Please see the 1999 Modeling report in Appendix A for discussion.

Modeling Results Compared to Measurements

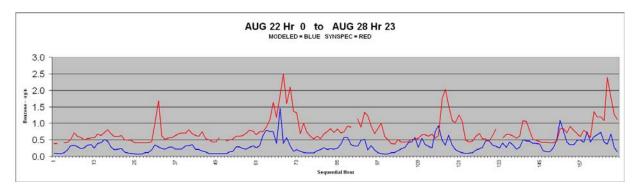
The procedure for evaluating model performance was to compare time series of hourly benzene predictions to benzene measurements (in $\mu g/m^3$) for the continuous monitoring location at the trailer located in downtown Burlington and to also compare the sets of benzene values obtained from both 3-liter 6-hr canister samples and 6-liter 24-hr canister samples to modeled averages for the same time periods at the various canister sampling locations. Thus measurement data was paired in space and time with model predictions. One of the primary goals of the modeling portion of the grant study was to be able to extend our understanding of ambient levels of benzene in the air that people living and working in Burlington are exposed to over time periods of months and years. The short-term (hourly and 24-hourly) exposure to benzene was not considered to be so important to replicate as the longer term average concentrations. We wanted to be able to estimate the spatial gradients of long-term average exposure to better quantify risks that benzene poses to people's health in Burlington, Vermont.

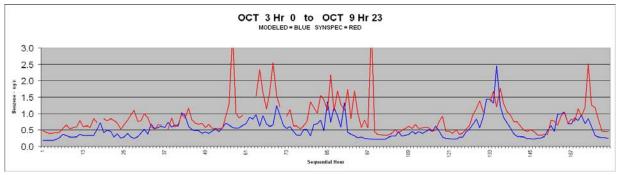
Time Series Plots

The semi-continuous hourly benzene measurements obtained with the SynSpec GC955 instrument at the trailer (8425 valid hourly values for benzene in $\mu g/m^3$ from June 20, 2007 through June29, 2008) were compared to modeled values for this location over the same time period. A background adjustment for transport of benzene into the domain was based on a smoothing into hourly estimates for the entire year developed from 24-hr average measurements from a TO-15 analyzed canister sample taken every 12th day at Underhill, Vermont, about 25 kms from Burlington in a very rural location.

Hourly time-series of the modeled vs the monitored benzene revealed important time periods when modeling was not performing well. In general, it was quite encouraging to see that the model was able to replicate the variability reasonably well. There clearly is a bias toward under-prediction on the longer term averages, and very short time period spikes were generally not matched by the modeling.

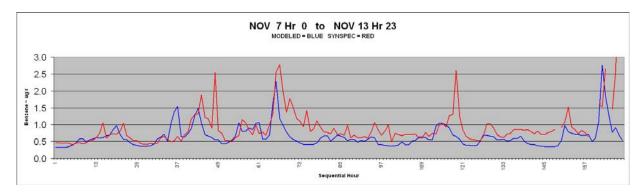
The figures below illustrate several examples of time periods during the model year showing some of these features. Each figure is a two week time period. The sequential day in the two-week period is on the X-axis. Modeled Hrly benzene in $\mu g/m^3$ is in BLUE, while SynSpec GC955 sampled Hrly benzene in $\mu g/m^3$ is in RED.

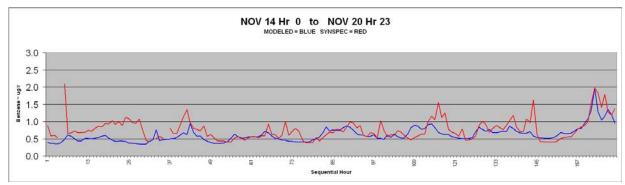


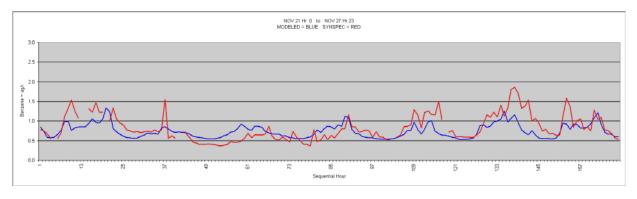


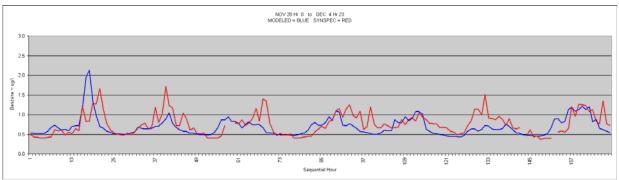
Comparisons of the patterns for particular short time periods, while taking into account wind speed and direction, and cross-checking video images of re-fueling activity for particular dates with gasoline service station emissions assumed by the monthly and daily

apportionment algorithm used to create model input estimates, caused us to conclude that our representation of gasoline station hourly emissions of benzene was probably not matching the variability actually occurring.

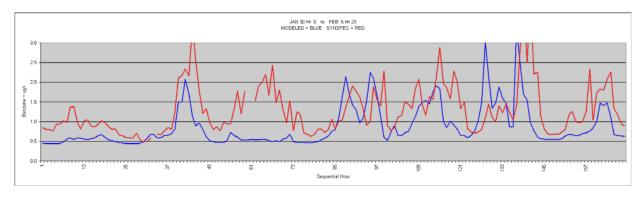


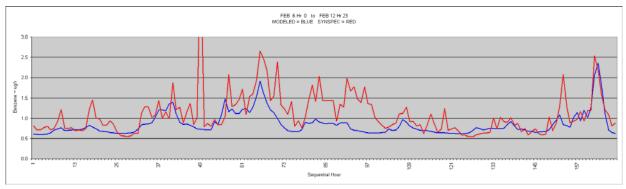


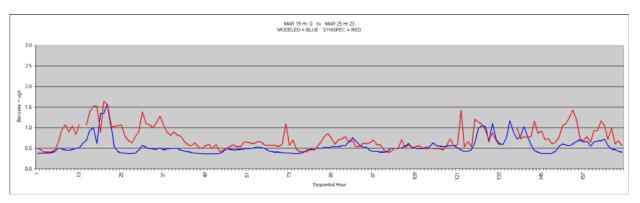




Although not all of these disparities in model prediction with actual measurement can be attributed to uncertainty in the gasoline marketing portion of the impacts, a number of these time periods can reasonably be concluded to have been due to this uncertainty, particularly when short-time period events of unusual nature, such as gasoline fuel deliveries, occur that cannot be predicted by the model.







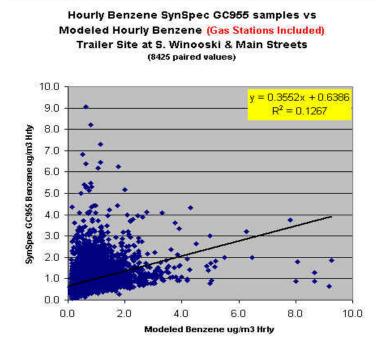
The overall <u>annual</u> emissions from gasoline stations probably can be estimated reasonably well, but creating the appropriate diurnal hourly and day-specific emissions based on refueling activity and other meteorological factors surely affecting evaporative emissions at the stations required more accurate temporal resolution of re-fueling activity than was possible with program resources. It had been believed that diurnal profiles could be developed from camera data such that more accurate hourly emissions estimates could be assigned to gasoline marketing sources. This proved to be too resource intensive to develop appropriately resolved emissions for the entire year period. Meteorological

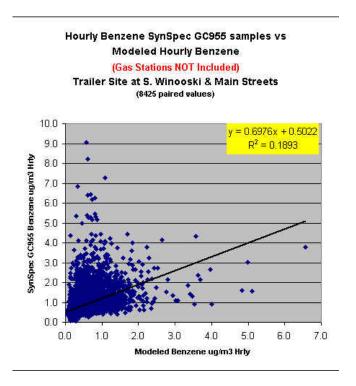
factors such as wind speed and temperature also play a role that has not been accounted for well enough in our gasoline marketing emissions inventory development.

Regression Plots

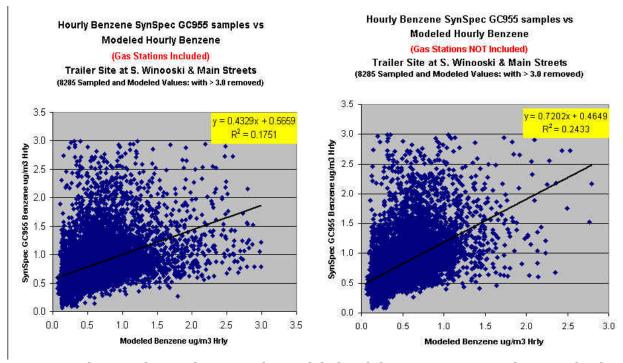
The hourly benzene sampled for the full year period from June 2007 to June 2008 and the concurrent modeling of hourly benzene impacts at the downtown Burlington trailer location were compared to create a set of four regressions of the modeled and monitored values paired in space and time. All 8425 hourly values for which both a valid modeled value and a valid SynSpec GC955 value could be obtained were regressed in the most inclusive case. Because time-series examination of this data-set described above caused us to feel less confidence (particularly for the temporal assumptions) in the modeled gasoline marketing emission impacts at this monitoring site, a 2nd version of the full data-set was created to allow us to compare whether better correlations between the modeled and monitored values were shown when gasoline marketing impacts were not included in the modeled impact. A subset of the full data-set was created by removing all hours having a greater than 3.0 µg/m³ for the hourly benzene concentration at the trailer location for either the model value or the SynSpec GC955 value. Removal of these "more extreme" hourly values reduced the overall N of the regressed data-set to 8285, i.e., this removal resulted in not including 140 hours of paired values. The removal of these particular hours implies of course, that we are not confident in the model's ability (as configured and run) to predict the highest hourly benzene concentration values that occur at this site.

The first two figures show the full set of data:





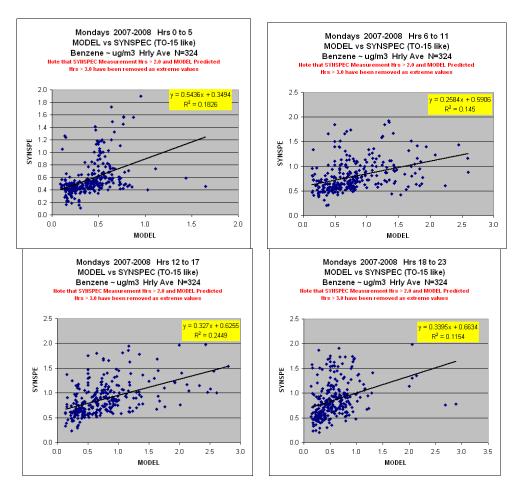
The next two figures show the regressions when the <u>highest modeled or measured hourly</u> <u>benzene values have been removed as extreme values</u>:



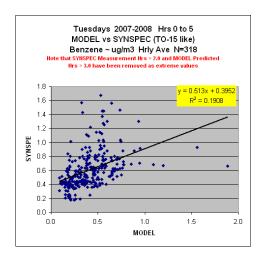
Examining the correlations between the modeled and the measurement values involved creating a very large number of subsets of the data from which only a selection are included here. In each case, a subset was created to explore whether characteristics inherent in the selection could reveal a possible way to improve the model (for example,

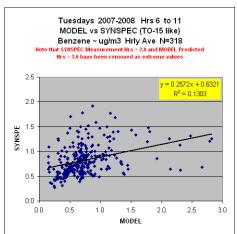
whether bias of the model was greater on some days of the week than others, whether certain wind directions showed the model performed better than others which in consideration of the directions of sources could offer a clue as to how to better refine emissions estimates or dispersion assumptions, whether particular wind speed regimes caused poorer model performance, etc.). Examples from the selection of different days of the week and different time periods during the day are shown below. Selection of the time periods during the diurnal cycle for which to create subsets corresponded to the four 6-hr sampling periods used in the intensive 3-Liter canister sampling program. Subsets of the periods from midnight to 6am, from 6am to noon, from noon to 6pm, and from 6pm to midnight were regressed.

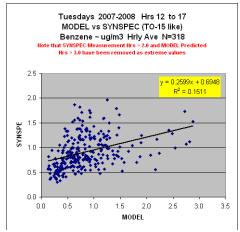
Regression Plots: Paired Values for Mondays during the June 2007 to June 2008 Year

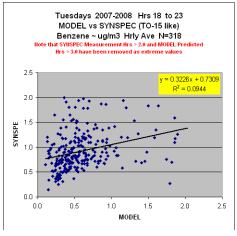


Regression Plots: Paired Values for Tuesdays during the June 2007 to June 2008 Year

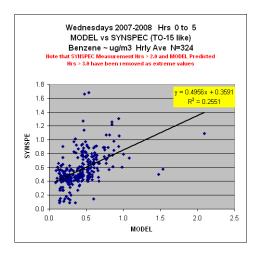


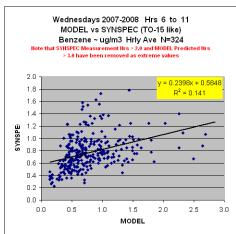


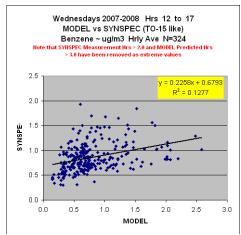


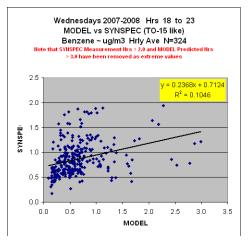


Regression Plots: Paired Values for Wednesdays during the June 2007 to June 2008 Year

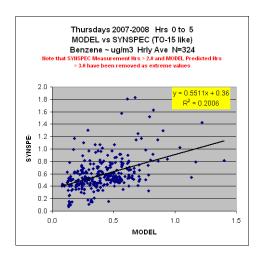


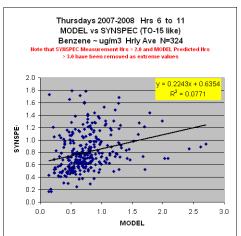


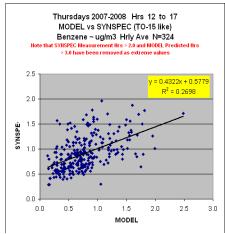


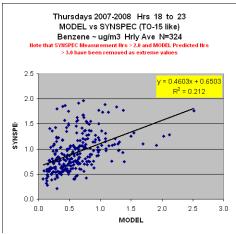


Regression Plots: Paired Values for Thursdays during the June 2007 to June 2008 Year

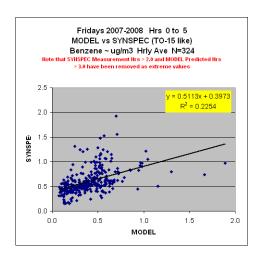


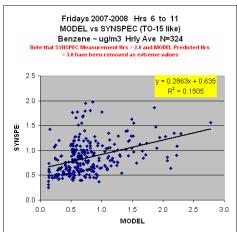


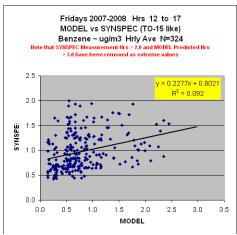


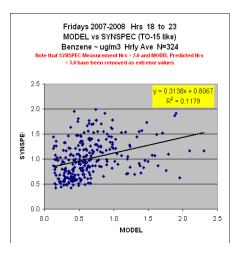


Regression Plots: Paired Values for Fridays during the June 2007 to June 2008 Year

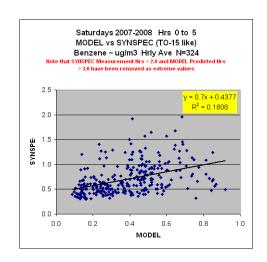


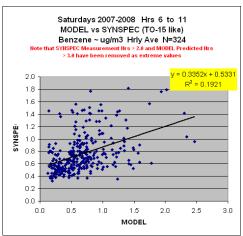


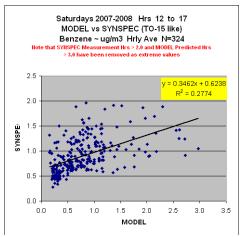


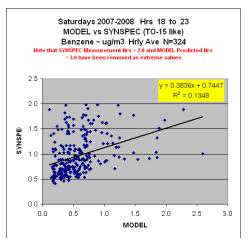


Regression Plots : Paired Values for Saturdays during the June 2007 to June 2008 Year

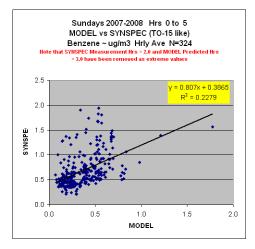


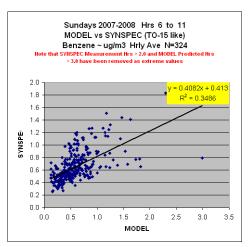


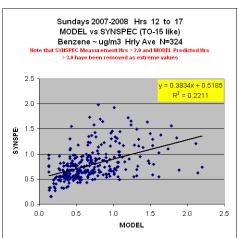


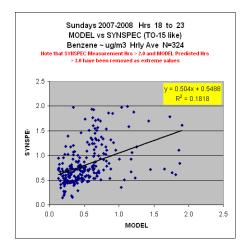


Regression Plots: Paired Values for Sundays during the June 2007 to June 2008 Year





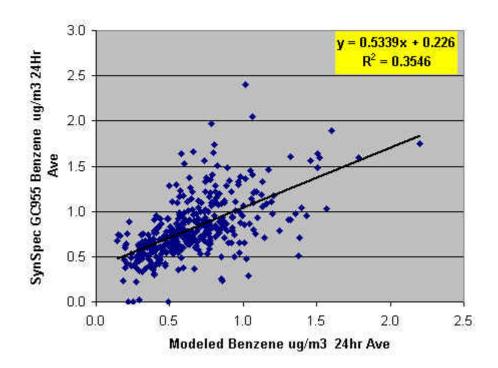




Comparing the various regressions for the different 6hr periods in the day and for different days of the week, it is not clear why the model seems to do better at certain times and on certain days of the week. Sundays appear to have the best overall full day performance. It has less traffic overall than other days of the week generally. The time period from Noon to 6 pm usually has better model performance than other time periods, except for Wednesdays and Fridays. Whether any of these relationships can be examined more closely to help improve the modeling approach remains to be determined. Time was not available to examine these relationships more closely.

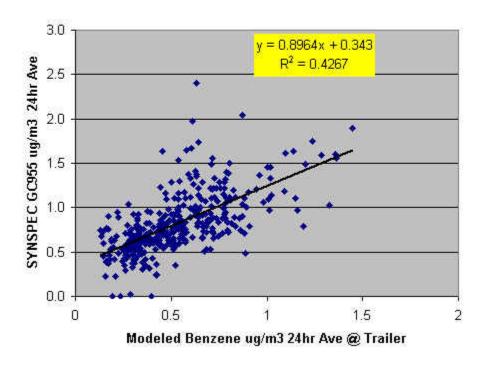
The hourly modeled impacts at the downtown trailer site were also averaged into 24hr averages for each of the days in the modeling period. The resulting regression between paired daily modeled impacts of benzene concentration at the trailer site and measurements at that site using the average 24hr SynSpec GC955 instrument (corrected to TO-15 like measurement from a relationship derived using co-located TO-15 canister data and the SynSpec GC955 instrument data) revealed a fairly good predictive ability of the model at the trailer site on a 24hr basis. The model tends to under-predict. We hypothesize that this under-prediction is partly a result of not including all of the local benzene source influences accurately (gasoline marketing as well as on-road emissions beyond the range of the modeling domain, but still relatively local to Chittenden County) and perhaps an underestimation of the regional transported component.

Modeled Daily 24hr Ave Benzene vs Measured SYNSPEC 24hr Ave Benzene June 20, 2007 to June 29, 2008 N=377



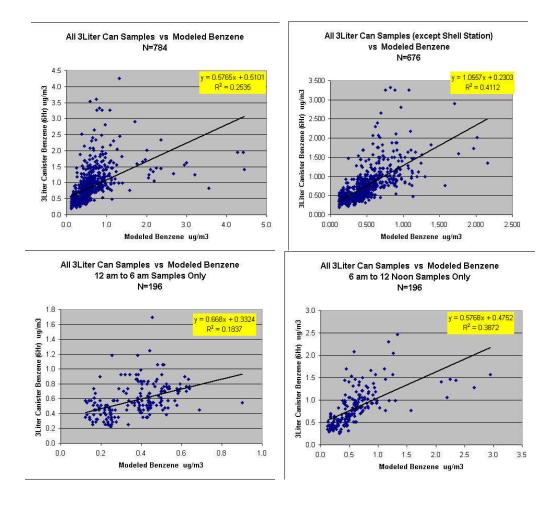
Modeled Daily 24hr Ave Benzene vs Measured SYNSPEC 24hr Ave Benzene June 20,2007 to June 29, 2008 (N=377)

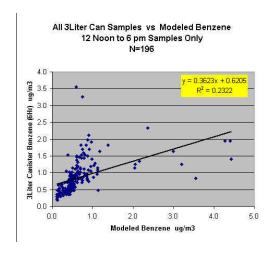
(Gas Station Impacts NOT included)

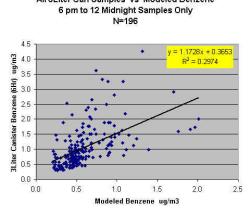


Results for 6 Hr Sampling Program: 3 Liter Canisters at 7 Sites for four week-long intensive sampling periods (seasonally)

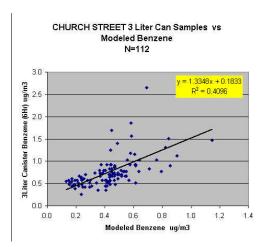
The grant sampling program using 3-Liter Canisters analyzed using TO-15 methods described in Part 2 produced a very good micro-scale data set for benzene concentrations in the downtown center of the Burlington urban area. The four weeks of intensive sampling was conducted with very little problems (but a lot of dedicated work by volunteer technicians). Out of a total of 28 six hour samples possible at each of 7 locations during each of the 4 sampling weeks (maximum possible valid samples = 784), only 1 sample was lost due to problems with switching out canisters at the beginnings of each six hour block of time during the week long periods. Regressions of the modeled 6hr average values expected at the 7 receptor locations during the same time periods when measurements were being taken compared to the integrated 6-hr canister benzene measurements are presented below.

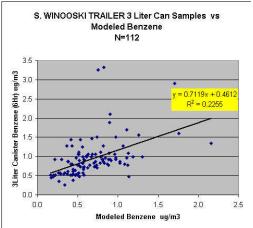


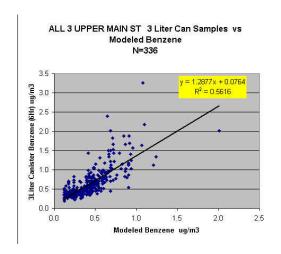


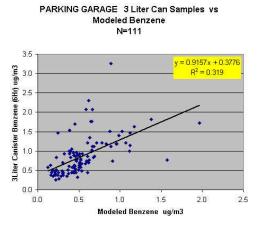


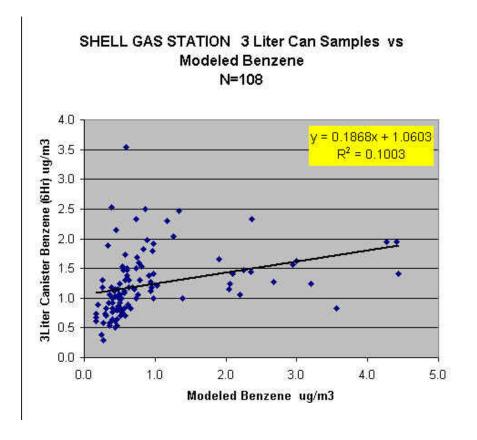
All 3Liter Can Samples vs Modeled Benzene





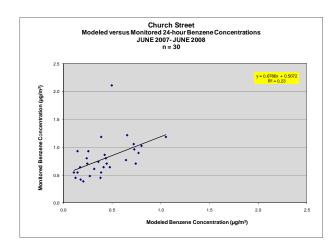


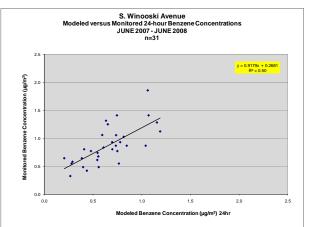


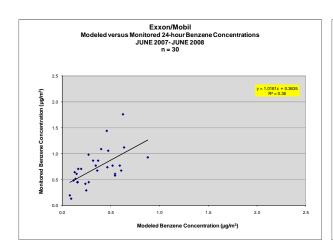


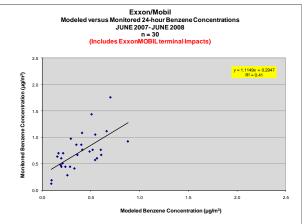
Results for 24 Hr Sampling Program: 6 Liter Canisters at 8 Sites every 12th day during the period from June 2007 thru June 2008

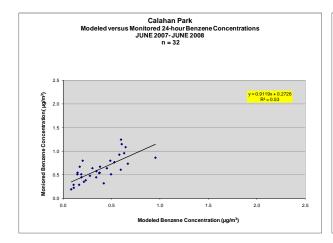
The grant sampling program using 6-Liter Canisters analyzed using T0-15 methods described in Part 2 produced a significant number of samples throughout the year at selected points in the domain. This data set for benzene concentrations was spatially extensive and covered portions of the domain being modeled that were somewhat different in character. The intent was to be able to validate model results at locations throughout the domain in addition to at the downtown trailer location for which an extensive long-term record of concentration data already exists. The every 12th day sampling produced roughly 30 24hr average samples spaced over the year at each of the 8 locations discussed in Part 2. Regressions of the modeled 24hr average values expected at the 8 receptor locations during the same time periods when samples were being collected compared to the integrated 24-hr canister benzene measurements are presented below.

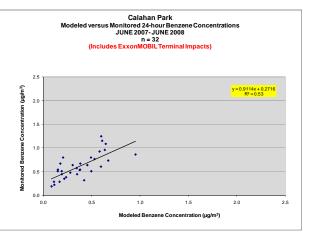


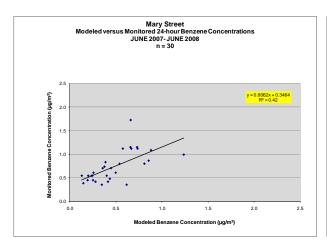


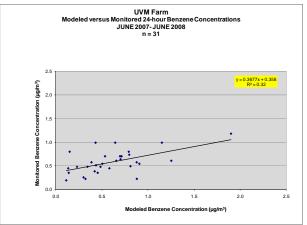


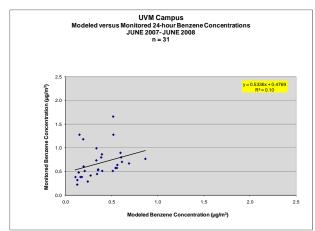


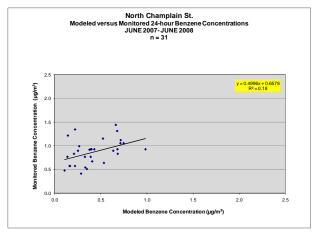


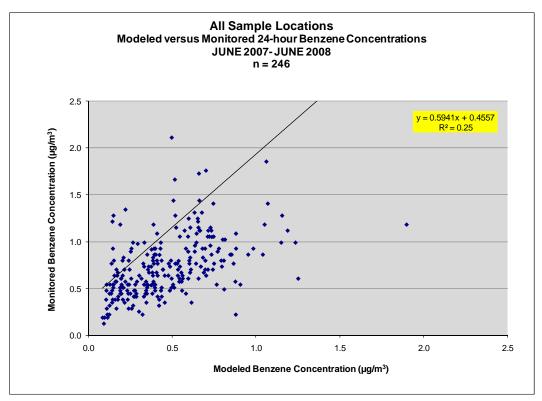












Spatial Results and Conclusions

Gridded Modeling For Estimation of Human Exposure

Background Discussion:

Health effects of benzene are likely related to long-term exposure (represented by an annual average concentration exposure for example) rather than short-term periods such as a 24-hour period or a month. This contaminant is identified as one which causes increased risk of cancer. The standard established in Vermont regulation is an annual standard set at $0.12~\mu g/m^3$. To determine whether a particular location has ambient benzene levels in excess of the standard, measurements are made as frequently as practicable over a long time period. Benzene is only one of a number of volatile organic compounds for which it is desirable to take measurements in the ambient air to determine compliance with hazardous air contaminant standards. Many of these volatile organic compounds (VOCs) can be measured using the same sampling and analytical methodology.

Measurement Method for Benzene:

The standard methodology used for determining ambient benzene concentrations (and other VOCs) involves the use of an automated canister sampler located inside the shelter at the monitoring site location. This method is very resource-intensive; therefore samples collected are limited to a regularly scheduled sample every 12 days throughout the year. Each calendar year a total of about 30 samples are collected and analyzed in this way. See Part 2 for details on all the ambient monitoring methods used for this study.

Estimation of Human Exposure from Ambient Measurements:

The "annual average" measured ambient benzene at the sampling location is determined as a simple average of the 30 or so samples. If this average is greater than $0.12~\mu g/m^3$ (the standard established in Vermont Air Pollution Control Regulations) then we believe that human exposure for someone living primarily at that location (or locations with similar ambient benzene levels) would be at more than one in a million risk of getting cancer from the benzene exposure alone.

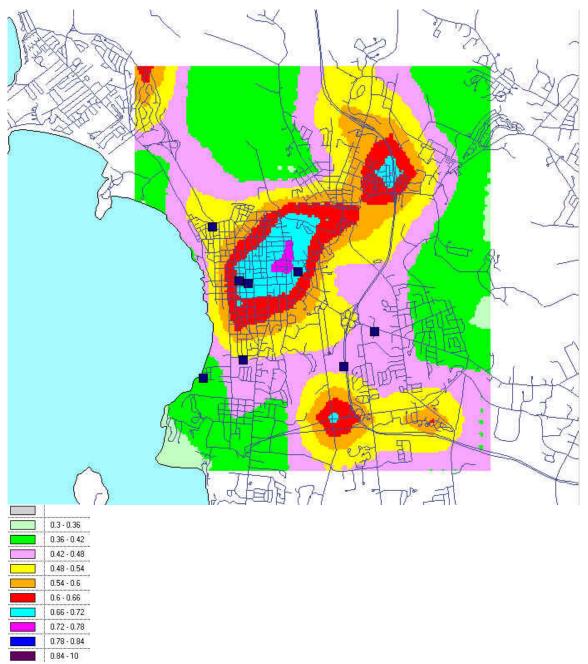
It is difficult and very costly to sample at many locations, especially when all sampling should be done during the same 24-hour time periods to get spatial patterns, even though this might only be done every 12 days. By using a model such as CALPUFF (set up to predict spatial and temporal ambient concentrations of a contaminant such as benzene) that has been evaluated and judged to perform well when its predictions are compared to measurement data at one or more locations, it is possible to extend the information we have about the concentration of benzene over a larger area than just the location of the actual measurements. This is the primary purpose of the current modeling study. The study gives more confidence in the abilities of the modeling approach to identify gradients

of benzene than we had before because unlike the 1999 study, under the grant enhanced monitoring for an entire annual time period and at several locations, it has been possible to identify the major weaknesses of the inventories (primarily the short-term diurnal emission rates) and to potentially improve on them.

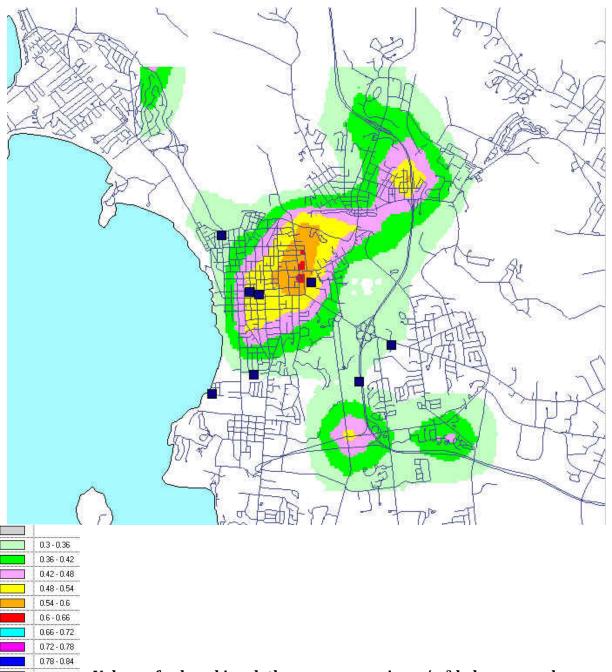
Maps which show patterns of monthly average benzene concentration in the modeling domain for all the months during the grant study are shown below. These are numbered from 18 to 34. Map 18 is the annual average benzene concentration gradients (equivalent to the Map 17 in the Executive Summary). Maps 19-22 show the seasonal average benzene concentration gradients, and Maps 23-34 show the monthly average benzene concentration gradients.

An average even from the full 12 months still only represents a partial exposure estimate for this area, since emissions patterns and meteorological patterns may change over years. Nevertheless, the patterns of estimated benzene exposure for people living within the Burlington area are better described by the modeled benzene concentrations depicted in these maps than what may have been known with as much confidence before. The modeled representation of benzene exposure in this area is not likely to change that much in its pattern over the coming years, but it is likely to continue to become less and less as benzene is removed from gasoline and more control is applied to emissions of benzene from the major sources identified through this study and the one completed in 1999. As a final comparison, map 35 shows both the 1999 modeling map for January and the January 2008 gradient map.

18. Annual Modeled Benzene $\sim \mu g/m^3$ for Jul 07 – Jun 08



19. Quarterly AVG Modeled Benzene ~ μg/m³ for Jul 07 - Sep 07

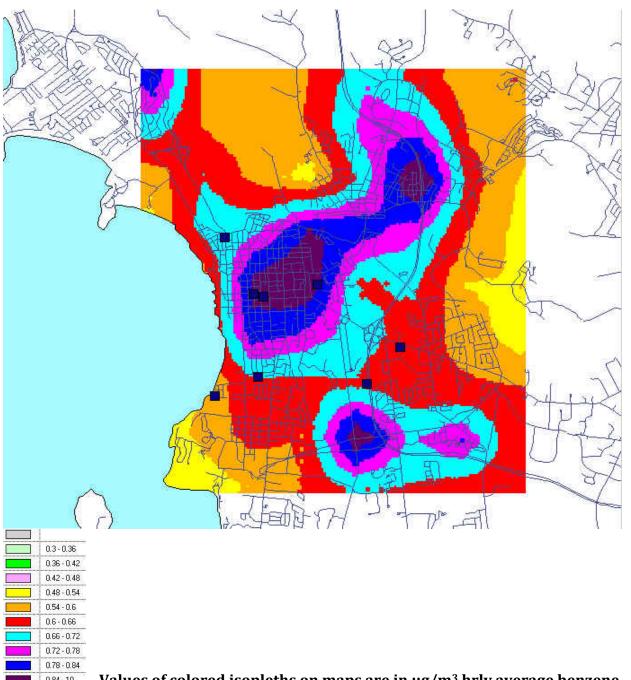


0.3 - 0.36 0.36 - 0.42 0.42 - 0.48 0.48 - 0.54 0.54 - 0.6 0.6 - 0.66 0.66 - 0.72 0.72 - 0.78 0.78 - 0.84 Values of colored isopleths on maps are in $\mu g/m^3$ hrly average benzene. 0.84 - 10

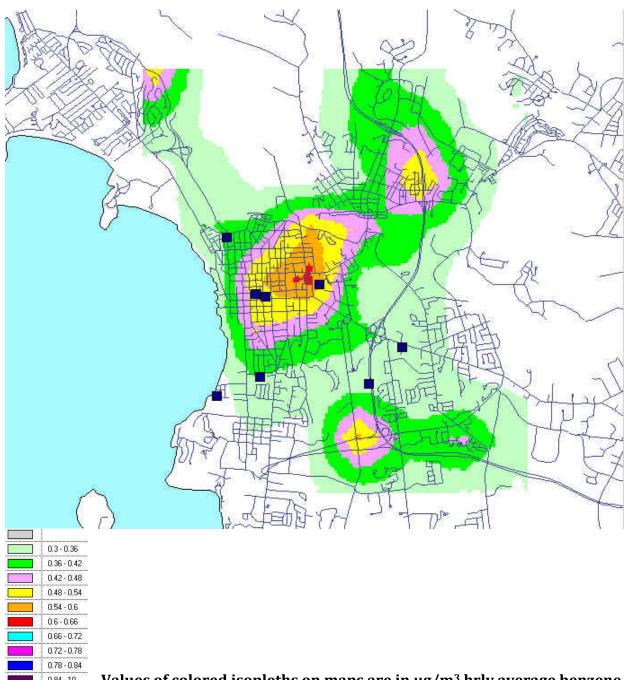
20. Quarterly AVG Modeled Benzene ~ μg/m³ for Oct 07 – Dec 07

The dark squares are the locations of the 6-Liter Canister Monitoring Sites.

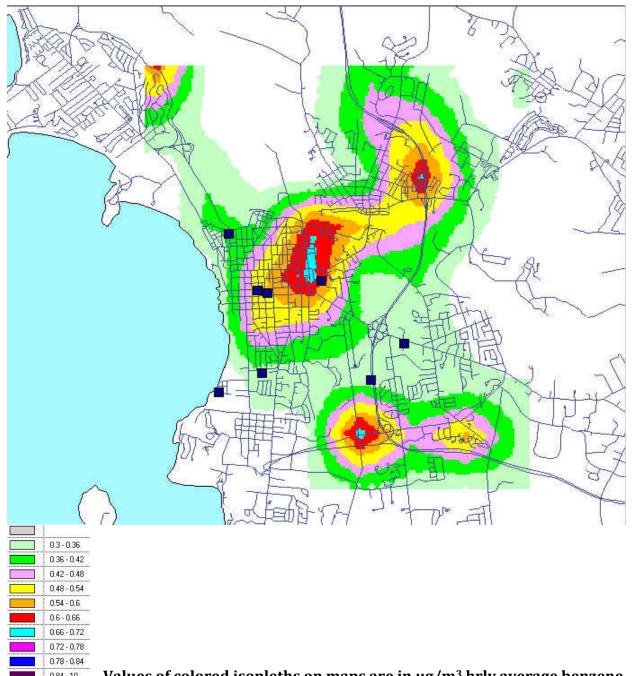
21. Quarterly AVG Modeled Benzene ~ μg/m³ for Jan 08 - Mar 08



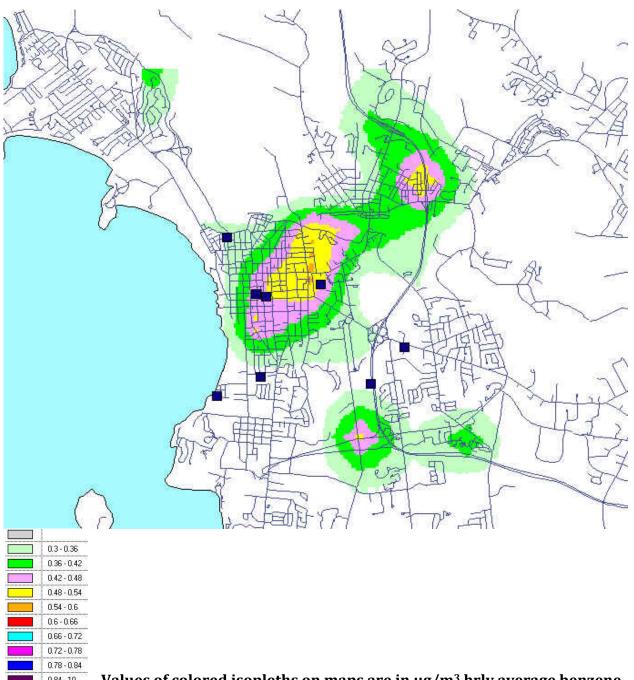
22. Quarterly AVG Modeled Benzene ~ μg/m³ for Apr 08 – Jun 08



23. Monthly AVG Modeled Benzene ~ μg/m³ for July 2007

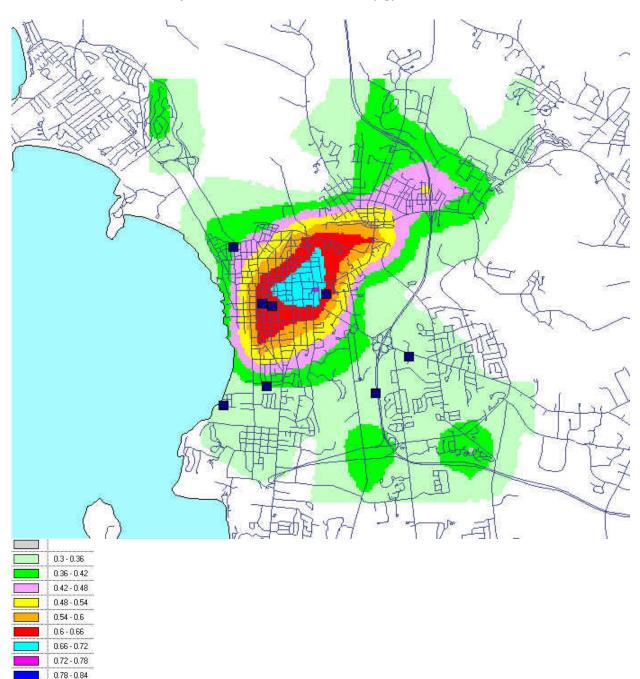


24. Monthly AVG Modeled Benzene ~ μg/m³ for August 2007



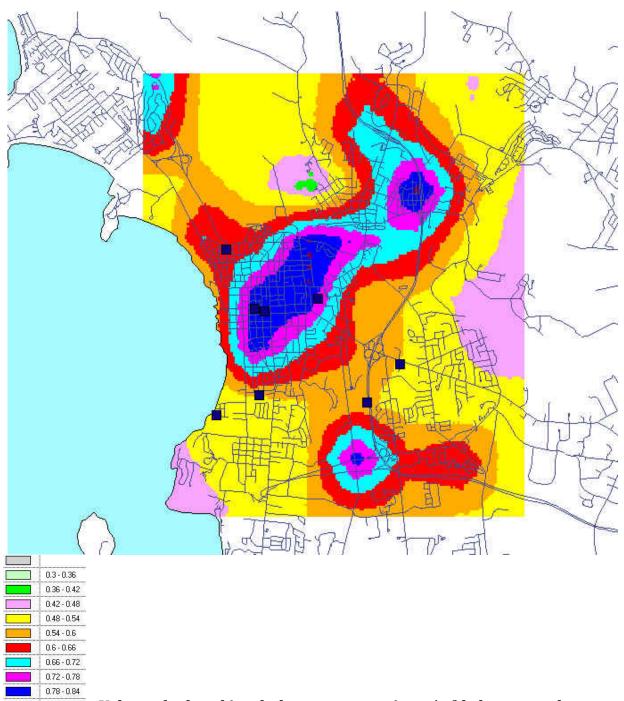
0.3 - 0.36 0.36 - 0.42 0.42 - 0.48 0.48 - 0.54 0.54 - 0.6 0.6 - 0.66 0.66 - 0.72 0.72 - 0.78 0.78 - 0.84

25. Monthly AVG Modeled Benzene ~ ug/m³ for September 2007

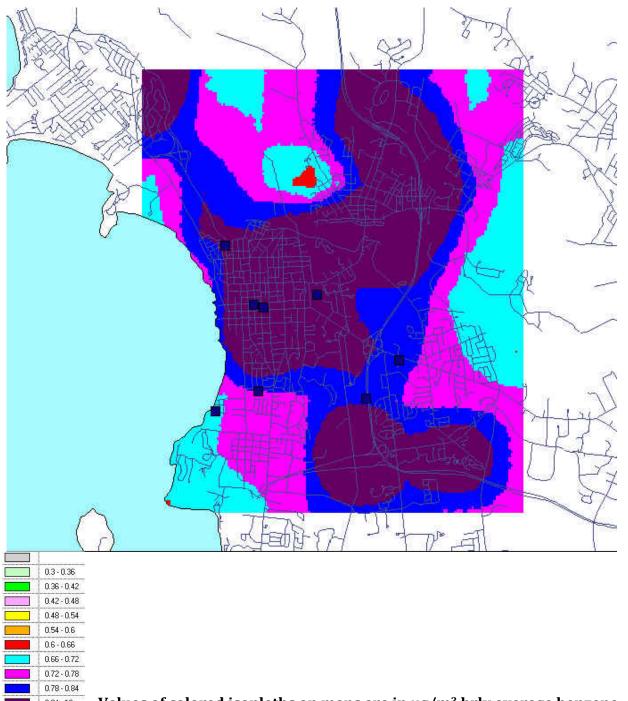


26. Monthly AVG Modeled Benzene ~ μg/m³ for October 2007

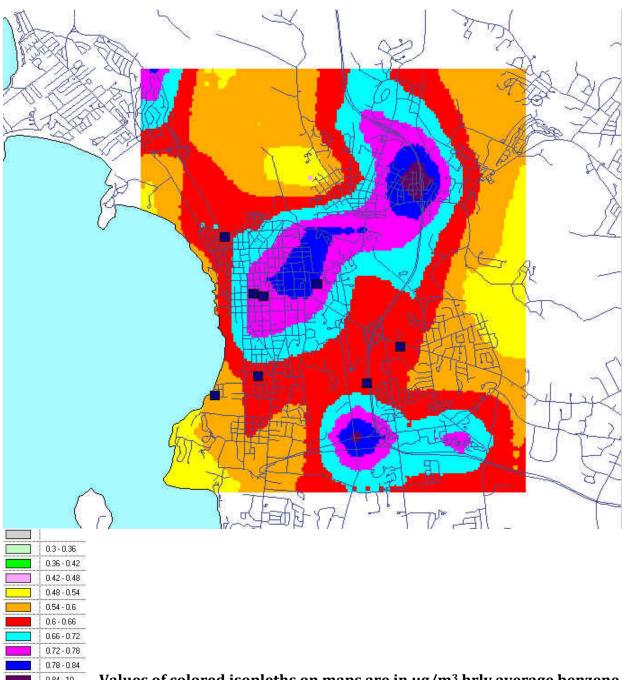
27. Monthly AVG Modeled Benzene ~ μg/m³ for November 2007



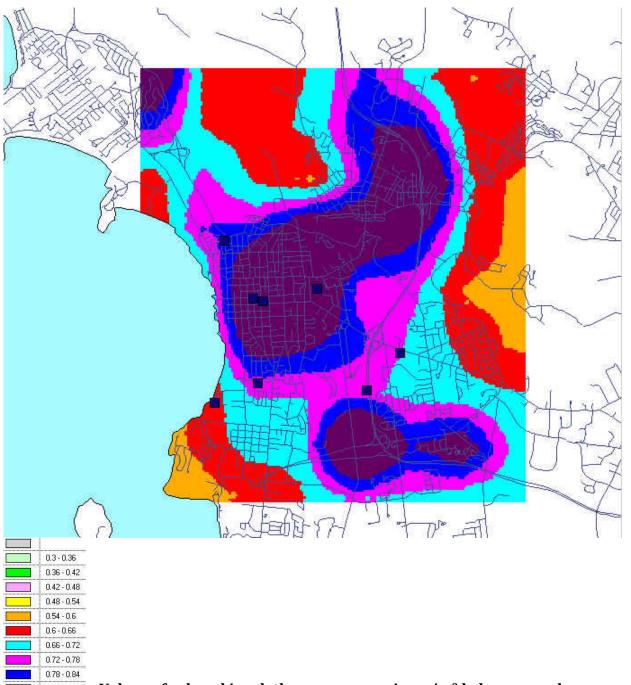
28. Monthly AVG Modeled Benzene ~ μg/m³ for December 2007



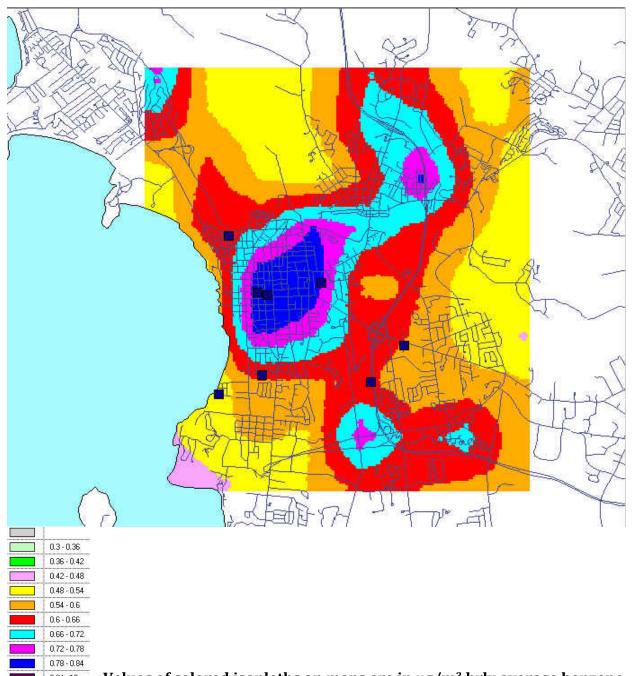
29. Monthly AVG Modeled Benzene ~ μg/m³ for January 2008



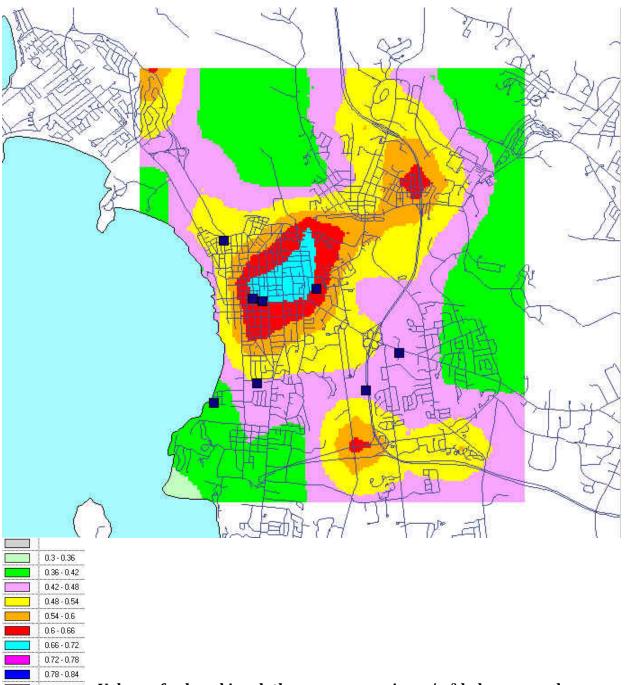
30. Monthly AVG Modeled Benzene ~ μg/m³ for February 2008



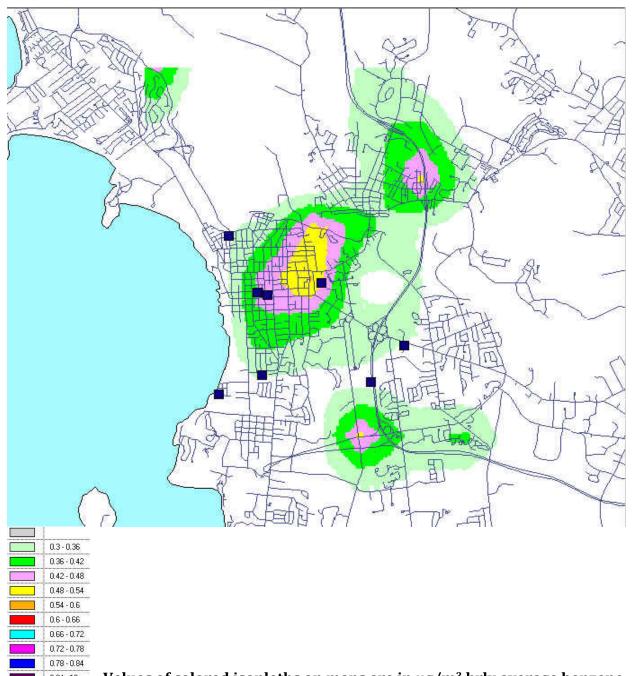
31. Monthly AVG Modeled Benzene ~ μg/m³ for March 2008



32. Monthly AVG Modeled Benzene ~ μg/m³ for April 2008

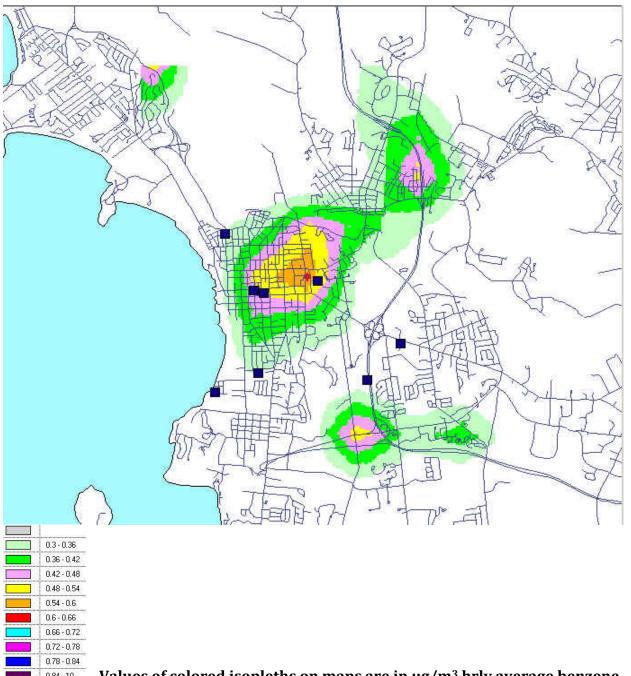


33. Monthly AVG Modeled Benzene ~ μg/m³ for May 2008



Values of colored isopleths on maps are in μg/m³ hrly average benzene. The dark squares are the locations of the 6-Liter Canister Monitoring Sites.

34. Monthly AVG Modeled Benzene ~ μg/m³ for June 2008



Values of colored isopleths on maps are in $\mu g/m^3$ hrly average benzene. The dark squares are the locations of the 6-Liter Canister Monitoring Sites.

Comparison of 1999 January Monthly Average Benzene (µg/m³) & 2008 January Monthly Average Benzene (µg/m³).

BOTH models were CALPUFF but the 1999 modeling used a much less precise depiction of on-road emission locations (many less sources to model so a more refined spatial grid of receptors could be used). They appear relatively consistent. There has been a slight overall drop in benzene concentrations in the Burlington Urban Core based on actual measurements taken in both years at similar locations.

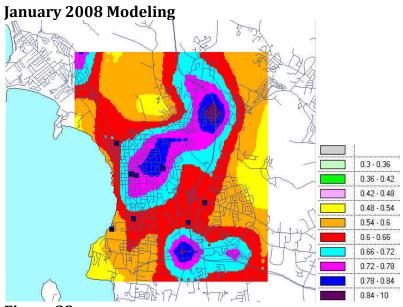


Figure 33.

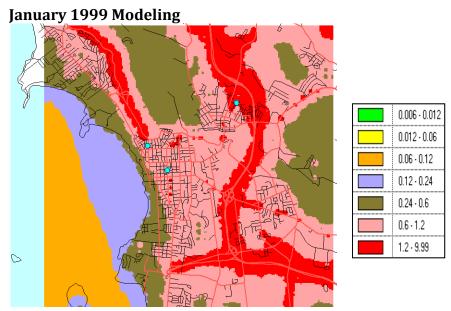


Figure 34.

Part 2 Monitoring Results Summary

Introduction

As discussed in Part 1 of this report a 3-component ambient monitoring network was operated in Burlington Vermont to determine average ambient benzene concentrations for various time intervals and locations to validate dispersion modeling results. All of the components of the ambient monitoring were performed following the *Quality Assurance Project Plan For the Vermont Local-Scale Air Toxics Ambient Monitoring Grant, May 29, 2007* which was approved by EPA-New England (Region 1) on June 28, 2007. Below is a summary of the monitoring methodology used to collect valid results for this study. For additional detailed information, please refer to the QAPP identified above. All required ambient air quality results collected during this study period has been submitted to the EPA's AQS. The Results section below includes a general summary of the benzene data collected from both canister and semi-continuous methods.

Methods

Network Design: Beginning in June, 2007, Vermont APCD collected 6-hour and 24-hour canister samples at 13 locations throughout greater Burlington, Vermont. At the permanent monitoring location on the corner of Main St. and S. Winooski Ave, a semicontinuous BTEX analyzer was operated to collect and analyze15-minute samples for benzene, toluene, ethylbenzene and xylenes concentrations which are used to generate 1-hour averages. The monitoring site locations are listed in Table 1. All of the sites are considered micro or neighborhood scale. With the exception of the permanent monitoring location, all sampling locations utilized existing utility or light poles or a portable tripod as necessary. With the exception of the Courthouse site, the weather proof shelter containing the canister, flow controller and timer (if applicable) is mounted to provide a sample inlet height of approximately 3.5 meters above ground level. The Courthouse site is located outdoors on the upper deck of a 1-story parking garage (2 levels of parking basement and outside on upper deck).

Table 1. Project VOC Monitoring Site Locations in Burlington

Sampling Location	Collection Method	Monitoring Objective	Representativeness	Sampling Frequency	Site Description
Monitoring Station; S. Winooski St.	3Lcanister* 6Lcanister* BTEX	Population	Neighborhood scale	6-hours** 1-in-12 day Continuous	Trailer located at the 150 S. Winooski Ave. in a commercial/residential downtown area.
Route 2 /Mary St.	6L canister	Population	Neighborhood scale	1-in-12 day	Mary St on Utility pole 54836. Sampler is mounted on pole.
UVM Farm/I-89	6L canister	Source impact (interstate)	Micro-scale	1-in-12 day	UVM Farm property next to I-89 between exits 13 and 14. Tripod Site
UVM campus	6L canister	Population	Neighborhood scale	1-in-12 day	Light pole in common area on campus between Cook Physical Sciences and Buckham Hall.
Church St.	3L canister 6L canister	Population	Neighborhood scale	6-hours** 1-in-12 day	Light pole on Church Street Marketplace in front of Firehouse

					Gallery
North Champlain St.	6L canister	Source impact (roadway)	Micro-scale	1-in-12 day	North Champlain Street next to Barnes School driveway on utility pole 2038
Calahan Park	6L canister	Population	Neighborhood scale	1-in-12 day	Calahan Park between RT 7 and Pine St., Located on utility pole 503 near Baseball field
Exxon/Mobil	6L canister	Source impact (fuel storage)	Micro-scale	1-in-12 day	Off Harrison Ave. Tripod Site
Upper Main Street (3 locations)	3L canister	Source impact (roadway)	Micro-scale	6-hours**	Off Main Street near Champlain College; 3 locations in a direct line with each other parallel with S. Willard St.; 1. light pole on main street, 2. Tripod located approximately 40 ft from Main St. between parking lot and Main St.3. light pole in parking lot.
Gas Station	3L canister	Source impact (gas station)	Micro-scale	6-hours**	Near the corner of S. Winooski and Main St. on light pole next to Main St. across the street from the permanent location.
Court House	3L canister	Population	Micro-scale	6-hours**	Light Pole on 1 st level of S. Winooski St. Parking Garage

^{*:} Collocated site for 24 hr and 6 hr canister samples **: Every 6-hours for 1-week each calendar quarter

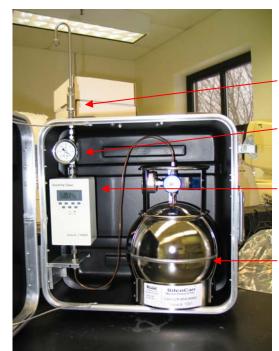
Sample Collection

VOC canister samples were collected following EPA Method TO-15 guidelines. Subatmospheric VOC samples at the permanent Burlington monitoring shelter were collected in pre-cleaned, certified 6-liter canisters using automated samplers as specified in applicable sections and the SOP found in the *Vermont QAPP for Air Toxics and NATTS*. See this document for details. Other VOC samples for this study were collected following the procedures summarized below and identified in the applicable SOPs in Appendix A of the *Quality Assurance Project Plan For the Vermont Local-Scale Air Toxics Ambient Monitoring Grant, May 29, 2007*. For all canister samples, cleaned, certified and evacuated canisters were picked up by the Environmental Technician at the DEC Laboratory, transported at room temperature to each site, and installed a prior to the scheduled sample date or period (6-hour samples).

For collection of sub-atmospheric 24-hour, 6-liter canister samples at all sites in Table 1 other than the permanent station location, a pre cleaned, certified $RESTEK\ Silco\ Can$ canister is attached to a $NUTECH\ 2700$ battery-powered timer/controller which is then attached to a $RESTEK\ Passive\ Air\ Sampling\ Kit$ flow controller, which has been calibrated to seasonal conditions. The NUTECH electronic timer is programmable and contains a solenoid/latching valve to control sample flow into canister. The RESTEK stainless steel passive flow controller uses an orifice and back pressure regulator to provide a constant nominal sample flow (3 and 5 ccpm for 24-hr and 6-hr samples, respectively) into the canister during the sample period. All the connections in this assembly are leak-checked during the sample setup procedure prior to sample collection. The assembly is housed inside a weather-tight enclosure and connected to an external $\frac{1}{4}$ " stainless steel sample inlet with a $Swagelok\ 2-\mu$ sintered stainless steel filter attached to the end of the inlet. The NUTECH timer is programmed to automatically begin and end sample collection at

midnight-midnight EST beginning on the proper date (based on the project sampling schedule). The sample collection information is recorded on the Field Datasheet for each canister sample. The assembly is hoisted to a bracket (on the respective utility or light pole) or tripod pole which is elevated to provide a sample height of approximately 3 meters, consistent with the manifold inlet at the permanent monitoring shelter. Figure 1 shows the sampler assembly used for 24-hour passive sample collection and Figure 2 shows this sampler and a smaller 3L version hoisted to a bracket at the Church St. site.

Figure 1. 6-liter Passive Canister Sampler



Swagelok 2-µ sintered stainless steel filter

RESTEK Passive Flow Controller

NUTECH 2700 Timer

RESTEK 6L SilcoCan

For sub-atmospheric 6-hour, 3-liter canister sampling, the above information applies with the exception of the *NUTECH* timer, which was not used and 3L *RESTEK* canisters which were *TO-Can* models rather than *SilcoCan*. Six-hour sample collection periods were scheduled for 1 week during each calendar quarter. Sampler assemblies for 3-liter canisters as described above will be deployed by the Environmental Technician for the initial collection period. Each 6-hour canister sample collection will be started and stopped manually by the Environmental Technician by opening and closing the canister valve and then documenting the time. Technician teams were required to recover and install canisters at multiple sites (within vicinity) for each sampling period throughout the intensive week. This led to an unavoidable minor difference in the exact start and stop time for each monitoring location. Nevertheless, the start and stop times for all 7, 6-hour canister sample locations were within 30 minutes of each other during all 4 intensive weeks. This relatively short time period relative to the 6 hour sample period is considered to not have created any particular relative bias in the samples collected at each site and thus they can be considered the same collection period and inter-compared. The sampler

assembly will remain at each location during the entire 1 week collection period. Additional 3-liter canisters will be transported to the applicable locations and quickly installed every 6 hours (after previous sample recovery) for consecutive sample collection during the entire designated intensive 1-week period.





As soon as possible after the sample collection period has ended, all sampling enclosures (and canisters for 6-hour samples) are recovered and returned to the DEC Lab. Canisters, flow controllers and timers are disassembled and each canister is logged into the DEC LIMS by the Environmental Technician and delivered to the designated area in the DEC organics lab. Samplers undergo battery re-charging, cleaning and certification in between sample collections.

Semi-continuous sample collection (and analysis) was performed using a *Syntech Spectras GC955 Series 600 BTEX* analyzer, manufactured in the Netherlands by *Synspec*. The analyzer is rack mounted inside the permanent Burlington monitoring station and was connected to the common glass manifold which meets *40 CFR Part 58* guidelines. The common manifold provides a large volume of excess ambient air from above the roof at sampling height of approximately 3 meters. The sample inlet line connecting the *Synspec BTEX* analyzer to the glass manifold is ¼" stainless steel (GC-grade) with a *Swagelok* 2-µ sintered stainless steel filter on the inlet. The BTEX analyzer has an internal calibrated piston/cylinder assembly which slowly draws an integrated air sample through the internal *Tenax* trap during each 15-minute sample period.

Method precision for VOC canister sampling for both 24-hr and 6-hr passive was assessed using collocated samplers at the permanent monitoring station on the corner of Main and S. Winooski Ave. Precision for the BTEX analyzer was assessed following EPA requirements for continuous ambient monitoring in 40 CFR Part 58 using a weekly input challenge of a mid-level BTEX calibration gas.

Analysis

Canister Analysis: Ambient concentrations of benzene and related VOCs in 6-hour and 24-hour canister samples were determined by the Vermont DEC Laboratory following TO-15 Guidelines and the EPA approved *Vermont QAPP for Air Toxics and NATTS* and their TO-15 SOP. The analytical equipment used for canister analysis at the DEC lab consists of an *ENTECH 7100* pre-concentrator, a *Hewlett-Packard 6890* gas chromatograph connected to a 5973 mass spectrometer (GC/MS) with a mass selective detector operated in the scan mode. The software used by the HP GC/MS is *HPCHEM Enviroquant*. The pre-concentrator has a 16-port auto-sampler, to which the canisters are connected. A sample volume of 500 ml is withdrawn from the canister and concentrated in the *ENTECH 7100* micro-scale purge and trap system. Water and $\rm CO_2$ are removed while the VOCs in the sample are concentrated on a series of two sequential focusing modules. The concentrated VOC compounds are then finally refocused on a third module at -160°C. The sample is then released by thermal desorption and carried into the GC column where the compounds are separated. The column terminates in a quadrapole mass spectrometer, which was used to identify and quantify the compounds in full scan mode.

The canister cleaning system used to prepare sample canisters for use and reuse after analysis consists of an *AADCO 737-series* pure air generator combined with an *ENTECH 3100A* canister cleaning system. The cleaning system includes a heated oven for canister vacuum/pressure baking cycles, a roughing pump for initial canister evacuation, and a molecular drag pump for final evacuation. Canisters are cleaned following the procedure identified in the Standard Operating Procedure (SOP) for *Determination of Volatile Organic Compounds in Ambient Air By GC/MS (TO-15)* in Appendix A of the EPA-approved *Vermont QAPP for Air Toxics and NATTS*. The system is computer controlled using *ENTECH* software.

Semi-continuous Analyzer: Ambient concentrations of benzene, toluene, ethylbenzene and xylenes for 15-minute samples were measured at the Burlington monitoring station using a *Syntech Spectras GC955 Series 600 BTEX* analyzer which is fully automated and computer controlled. This analyzer is specifically designed for this application and uses a pre-concentrator to trap ambient VOCs during each 15-minute sample period. Ambient air is drawn in from the common glass manifold by an internal bypass pump. A slip-stream flow is slowly drawn through the pre-concentrator by a calibrated piston/cylinder assembly at regular intervals over a 15-minute sample period. Benzene and other hydrocarbons in the ambient air are captured and concentrated on a *Tenax GR* trap. The concentrated VOCs are quickly thermally desorbed (180°C) into ultra-pure nitrogen carrier gas and transported to a series of 2 columns. At the proper retention time when the last of the target compounds have exited the first column and entered the second column (EPA624 equivalent), the first column is back flushed to provide optimal separation from

interfering VOCs. Sample run time is 15 minutes and the concentrations are determined using a photo ionization detector. The dual column design and PID ensures a high specific sensitivity to benzene and other aromatic hydrocarbons. The analyzer is considered to be "semi-continuous" in operating design as it collects and concentrates a new ambient air sample for the 15-minute period during which the "previous" 15-minute air sample is being analyzed through the column. The BTEX analyzer was calibrated, operated and maintained following the manufacturer's recommendations. Field activities included performance verification, calibration, precision and accuracy checks and data review and processing.

Analytical precision for the TO-15 method was assessed using replicate sample analysis. Analytical accuracy was assessed by analysis of performance evaluation audit samples prepared EPA Contracter for the NATTS PE program. Accuracy of the BTEX analyzer was assessed by introducing known audit input concentration (of BTEX compounds) at the calibration range midpoint from a certified cylinder independent from the primary calibration standard (Second source).

Quality Assurance and Quality Control

The sample collection and analysis for ambient monitoring results collected for this project was performed following the specifications in both the *Vermont QAPP for Air Toxics and NATTS* and **the** *Quality Assurance Project Plan For the Vermont Local-Scale Air Toxics Ambient Monitoring Grant, May 29, 2007.* Table 2 below summarizes the measurement quality objectives for the ambient monitoring results obtained for this study. Tables 3-6 summarize the precision, accuracy and completeness for the monitoring results of the various components of this study and indicate that all MQO criteria in Table 2 were met. Consequently, the valid benzene canister and analyzer results collected at all monitoring locations listed in Table 1 between July-2007 and June 2008 are of known and acceptable quality for use in the model validation portion of this study.

Table 2. Measurement Quality Objectives - VOC Canister Samples, BTEX Analyzer

Method	Reporting Units	Precision	Accuracy/ Bias	Representativeness	Comparability / Method Selection	Complete- ness	Benzene Minimum Detection Limits (ppbv)
VOC (3L and 6L canisters)	ppbv (analysis) μg/m³ (AQS)	Collocated samples; 30% RPD, 15% CV	± 30%	See Table 1.	GC/MS (TO-15)	> 75%	0.01
Synspec BTEX analyzer	ppbv (analysis) μg/m ³ (AQS)	Repeatability of Mid- range gas; ±15%Diff;	± 20%	See Table 1.	GC/PID	> 75%	0.07*

^{*:} Average of 4 MDLs during the study period. MDL is equivalent to the "y-intercept" of the non-linear calibration relationship

Table 3. Precision Assessments for All Benzene Monitoring Components for Study Period (RPD% and CV% for July-2007 through June-2008)

Component	Comparison	# of pairs	RPD %	CV % (equation from NATTS TAD)
24-hr 6L Collocated Canisters (Active Sampling at Burlington Station	Primary and duplicate collocated 6L canisters (Automated)	31	3.2	3.8
24-hr 6L Canister (Passive sampling on roof of Burlington Station	Passive 6L canister compared to Average of Automated Collocated 6L canisters	23	14.9	12.7
6-hr 3L Collocated Canisters (Passive sampling on roof of Burlington Station)	Primary and duplicate collocated 3L canisters (passive)	23	3.6	3.4
6-hr 3L Canister (Passive sampling on Burlington Station roof and Church St. sites (average of four, 6-hr samples vs 6L 24 hr sample	Average of four separate 6-hr canister compared to collocated 6 L canister	8	14.0	14.0
Synspec BTEX Analyzer (% difference of 2 ppb input)	Analyzer Response to 2 ppb input BTEX calibration gas	44	-6.5*	5.3

^{*: %} difference= [(known-response)/known] x 100

Table 4. Data Completeness Summary for Various Benzene Monitoring Components During Study Period (July-2007 through June-2008)

Monitoring Site	Sample Type	Data Completeness (%)
Monitoring Station; S. Winooski Ave.	6-L collocated (automated)	100
Monitoring Station; S. Winooski Ave.	3-L passive	100
Monitoring Station; S. Winooski Ave.	Synspec BTEX analyzer	93
Route 2 /Mary St.	6 L Canister passive	97
UVM Farm/I-89	6 L Canister passive	97
UVM campus	6 L Canister passive	97
Church St.	6 L Canister passive	97
Church St.	3 L Canister passive	100
N. Champlain St.	6 L Canister passive	97
Calahan Park	6 L Canister passive	100
Exxon/Mobil	6 L Canister passive	94
Upper Main St.	3 L Canister passive	100
(3 separate locations)		
Gas Station	3 L Canister passive	99
Court House	3 L Canister passive	99

Table 5. Performance Evaluation Audit Results (Accuracy) for Synspec BTEX Analyzer 2007-2008

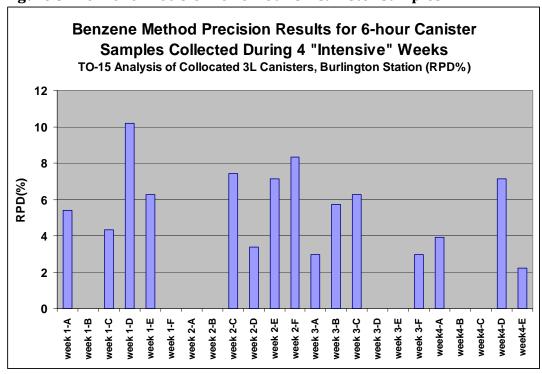
Audit Date	Input Concentration second source standard (ppbv)	Synspec Response (ppbv)	%Difference
5/7/07	1.4	1.1	-21
8/31/07	2.71	3.01	11.1
4/24/08	3.00	3.01	0.3
8/3/08	2.02	2.00	-1.0

Table 6. NATTS Performance Evaluation Audit Results (Accuracy) for Vermont DEC Laboratory TO-15 Analysis during 2007-2008

NATTS Audit Date	Known Concentration (ppbv)	TO-15 Response (ppbv)	%Difference
5/4/07	0.76	0.77	1.3
7/10/07	0.79	0.97	-18.6
10/1/07	0.71	0.80	-11.3
4/17/08	0.59	0.65	-9.2

Source: NATTS PE Audit Reports provided by Alion

Figure 3. Benzene Precision for 6-hour 3L Canister Samples



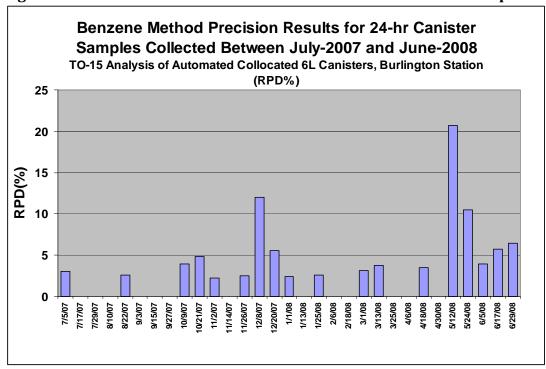
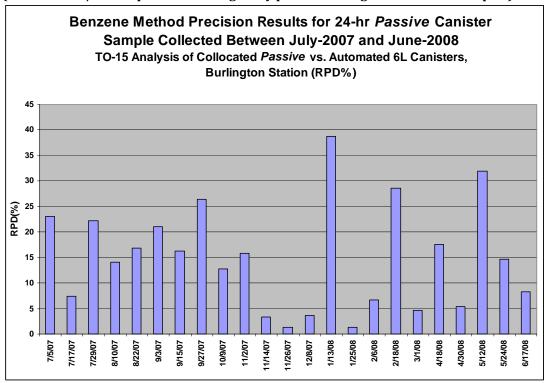


Figure 4 Benzene Precision for 24-hour 6L Automated Canister Samples

Figure 5 Benzene Precision for 24-hour 6L Passive Canister Samples (Note: some 1/12 sample dates during study period missing due to invalid samples)



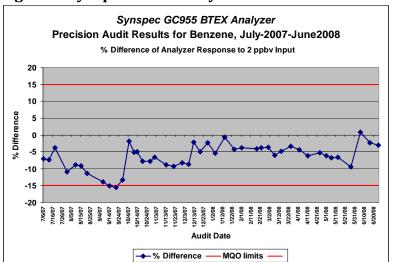


Figure 6. Synspec BTEX Analyzer Precision Results

Ambient Benzene Results

Intensive Weeks (6-hour samples)

Six hour VOC samples collected in 3L canisters during the intensive weeks were analyzed for benzene, ethylbenzene, toluene and xylenes. All 6-hr benzene average results from 3L canisters was reported to AQS and summarized below.

Table 6. Summary of 6-hr Average Benzene Concentrations (μ g/m³) at 7 Monitoring Locations Surrounding the Burlington Monitoring Station. (1 Week average of Passive 3L Canisters collected every 6 hours during 4 separate intensive sampling weeks)

Location (AQS site code)	Week 1 7/15/07- 7/21/07	Week 2 10/21/07- 10/27/07	Week 3 1/13/08- 1/19/08	Week 4 4/12/08- 4/18/08
		(Benzene	e μg/m³)	
Church St.				
(500070020)	0.38	0.71	0.86	0.86
Court House				
(500070019)	0.77	0.73	1.02	0.96
Gas Station				
(500070018)	1.44	1.09	1.24	1.37
S. Winooski				
(500070014)	0.9	0.83	0.95	1.07
Upper Main-Far				
(500070015)	0.44	0.49	0.74	0.59
Upper Main-				
Mid				
(500070017	0.46	0.53	0.79	0.63
Upper Main-				
Near				
(500070016)	0.66	0.67	1.03	0.87

Expanded monitoring (24-hour samples)

Samples collected as part of our expanded monitoring throughout Burlington were sampled for the TO-15 compounds. Summary benzene data is presented below.

Table 7. Summary of 24-hr Average Benzene Concentrations ($\mu g/m^3$) at 7 Expanded Monitoring Locations (12-month average of Passive 6L Canisters collected every 12th day between July-2007 thru June-2008)

Location			
(AQS Code)	(Benzene μg/m3)	n	st dev
Calahan Park			
(500070024)	0.63	34	0.27
Church St.			
(500070020)	0.82	33	0.34
Exxon/Mobil			
(500070025)	0.73	32	0.35
N. Champlain St.			
(500070023)	0.91	33	0.33
Mary St.			
(500070021)	0.74	33	0.32
S. Winooski Ave.*			
(500070014)	0.89	31	0.32
UVM Campus			
(500070022)	0.69	33	0.32
UVM Farm			
(500070026)	0.62	33	0.33

^{*} Results from automated 6L canister inside Burlington permanent monitoring station.

Semi-Continuous BTEX Analyzer (15-minute samples)

All valid 15-minute average benzene results from the Synspec BTEX analyzer used in this model validation study have been reported to EPA's Air Quality System Database (AQS). The applicable AQS codes for these results are as follows: Site code 500070014, Parameter code 45201, POC 5. Benzene 1-hour averages were calculated from any clock hour with at least 3 valid 15-minute averages. For reference, the estimated annual average for benzene using the 15-minute average Synspec BTEX results = 0.69 μ g/m³ (based on 8,178 valid hourly averages between July1-2007 and June 30-2008)

Figure 6 presents a time series graph of the 1-hour benzene average concentrations ($\mu g/m^3$) measured during the study period (July 2007 – June 2008) by the Synspec BTEX analyzer. The graph includes reference to two of many confirmed gasoline related emission events noted during the study period.

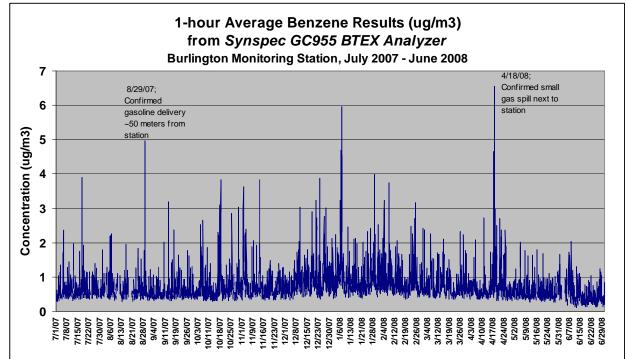


Figure 6. 1-hour Benzene Results (μg/m³) from Synspec GC955 BTEX Analyzer

GASOLINE

Gasoline activity data, and analysis were also conducted and results incorporated into the CALPUFF model.

Discussion & Conclusions

The CALPUFF model was able to reasonability predict ambient air concentrations throughout Burlington. The model performance was improved over longer time scales. Further, the CALPUFF model was not able to capture short-term peaks in benzene concentrations, due to unexpected activities. However, using the CALPUFF model over complex terrain to estimate benzene concentrations throughout an urban community may have great utility. This modeling platform may be transferred to NH, if the modeling expertise is available.

The results from our expanded monitoring network indicate that our existing monitoring location on S. Winooski Ave. has a higher annual average benzene concentration than other monitoring locations in Burlington. This monitoring location may exist at one of the higher exposure and risk areas in the city, as expected due to location. Therefore, the risk within and across Burlington due to benzene exposure may be less than previously indicated based on data solely from one monitoring location.

References

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- (3) "Mobil Oil Corporation Burlington, Vermont Gasoline Terminal Air Toxics Modeling Analysis Report", 12 April 1999, Radian International
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- (5) *"Urban Benzene and Population Exposure"*, <u>brief communication</u>, Cocheo, Sacco, et. al. <u>NATURE</u>, <u>Vol 404</u>, <u>March 9</u>, <u>2000</u>, <u>www.nature.com</u>, 2000 Macmillan Magazines Ltd.
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- (8) "Ambient Benzene Modeling Study, CHITTENDEN COUNTY, Final Report", Air Pollution Control Division (APCD), Department of Environmental Conservation, Vermont Agency of Natural Resources, July 2005.
- (9) "Quality Assurance Project Plan for Air Toxics Monitoring and National Air Toxics Trends Stations Network", Revision 2.3, Air Pollution Control Division (APCD), Department of Environmental Conservation, Vermont Agency of Natural Resources, April 2006.
- (10) "Quality Assurance Project Plan for the Vermont Local-Scale Air Toxics Ambient Monitoring Grant, Project Title: Spatial and Temporal Concentrations of Benzene in Two Northern New England Communities: A Modeling Validation Study", Air Pollution Control Division (APCD), Department of Environmental Conservation, Vermont Agency of Natural Resources, May 2007.

Appendix A

Ambient Benzene Modeling Study CHITTENDEN COUNTY

Final Report

Air Pollution Control Division (APCD)

Department of Environmental Conservation

Vermont Agency of Natural Resources

JULY 2005

Authors

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Purpose of this Report

This report was prepared as technical information to support the proposal of a Toxic Action Plan (TAP) for benzene to address measured levels of this hazardous air contaminant (HAC) for which monitoring data has shown ambient concentrations exceeding health-based standards existing in Vermont Air Pollution Control Regulations (Section 5-261 & Appendix C). The modeling study which is the subject of this report was initiated in early 2003 and designed to examine ambient concentration gradients for benzene in the most urbanized portion of the state, the City of Burlington. Benzene is one of the highest priority compounds for which a TAP is being developed. Act 92 of the 1993 Adjourned Legislative Session directed the Agency to, among other things, 1) establish a monitoring program to measure the presence of HACs in the ambient air, 2) identify sources of HACs, and 3) assess health and ecological risk to prioritize those HACs for which additional studies would be conducted. A program measuring hazardous air contaminants in Vermont's air has now operated for more than 10 years. This current study is intended to spatially and temporally extend the information obtained in the monitoring program and will be used to inform future decisions and policies (to be summarized in TAPs) regarding control and management of benzene (and other similarly emitted HACs) in the ambient air.

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Executive Summary

The purpose of this modeling study: To confirm sources of and to define spatial gradients and temporal differences of ambient benzene concentrations in Burlington, Vermont and its surrounding area during 1999. 1999 was the most recent full year of available benzene data.

Long-term air quality monitoring of ambient benzene has been conducted in the urban center of Burlington (S. Winooski & Bank Street intersection) from 1993 to 2000 and from 2003 to present (S. Winooski & Main Street). This monitoring is part of the State Air Pollution Control Division's hazardous air contaminant management program. The measurements obtained are specifically applicable to the monitor locations but are also representative of locations in the immediate vicinity of the monitors.

For 1999 the data indicates that the monitoring location 10 meters to the east of the S. Winooski & Bank Street intersection had ambient concentrations of benzene which exceeded the Vermont hazardous ambient air standard for benzene (0.12 ug/m3 on an annual average basis) by roughly a factor of 20.

Defining the extent of applicability of the measurement data requires either 1) sampling at many more surrounding locations or 2) use of a model to represent the behavior of benzene emitted into the air from all possible sources and to account for its dispersion and transport in the urban area. Because significant resources are required to operate many sampling stations, an urban-scale modeling study was initiated in 2003 to apply a state of the art air quality model (**CALPUFF**) to the Burlington urban area for a one-year time period (1999).

The study involved several steps:

- 1. Preparation of spatially detailed (200m horizontal resolution) hourly 3-dimensional meteorological wind fields for a large portion of Chittenden County.
- 2. Identification of all local sources of benzene emissions to the ambient air.

Five primary source groups were identified from the emission inventory work.

Group 1: on-road motor vehicles (urban-core)

Group 2: on-road motor vehicles (non urban-core)

Group 3: home-heating fuel burning

Group 4: gasoline service station activity

Group 5: large industrial sources (only 2 warranted inclusion)

These groupings allowed examination of each particular set of similar sources independent of the remaining sources.

3. Estimation of the mass of benzene emission each source contributed in each hour during 1999. Characteristics of how benzene emission occurred (such as whether this was best estimated as a concentrated point emission or as a relatively spread

- out emission from a particular area, and whether emission was close to the ground or from points elevated above the ground) were also determined.
- 4. After the relative emission potential from the various known source categories (as well as the largest industrial point sources) was evaluated for significance, the "emission inventory" was finalized and prepared as computer files which allowed its input to the CALPUFF dispersion and transport model. A level of 15 pounds per year benzene emission from any industrial point source was determined to be the cut-off for inclusion in the modeling. This level of emission was considered to be "insignificant" on the domain receptor scale compared to other source categories being modeled. In this context, insignificant implies that if incorporated as an individual point source it would likely not quantitatively change the model results at any domain-wide gridded (non source-oriented) receptors used for the modeled benzene emission sources. Source-oriented receptors were not utilized for all individual point sources of benzene on the domain in this study.
- 5. Several candidate benzene source **categories** were **not included** in the modeling study based on a reasonable understanding that their emission potential was either significantly less than the other sources included or uncertainty in how to locate where the emission would occur. Asphalt paving operations, airport operations, and off-road vehicles such as tractors, lawn-mowers, all-terrain vehicles etc. were not modeled for one or the other of these reasons.

In the case of one source category not included in the modeling study (<u>portable gasoline containers</u>), although total emissions annually are estimated to be comparable to home-heating fuel burning emissions of benzene from chimneys, the characteristic of emission (ground level & evaporative) is much different and likely to result in less domain-wide influence than fuel burning, but probably more concentrated short-term exposure to the individual utilizing the portable container.

Dispersion of air contaminants in the ambient air (what the CALPUFF model does):

The magnitude of the overall emission from a source type in the domain is not a good indicator of which source type actually causes the highest impact of ambient benzene measured at any location in the domain. The actual air quality at any location is a result of these emissions being dispersed and transported from their sources to the receptor (measurement location). Modeling the emission and the dispersion and transport of the benzene to all parts of the domain indicates that although emissions from motor vehicles traveling on roadways generally determine the overall benzene concentration patterns because the roadways are fairly uniformly distributed across the domain, hot-spots of even higher concentration on average will exist in close proximity to gasoline service stations and other point sources of benzene emission.

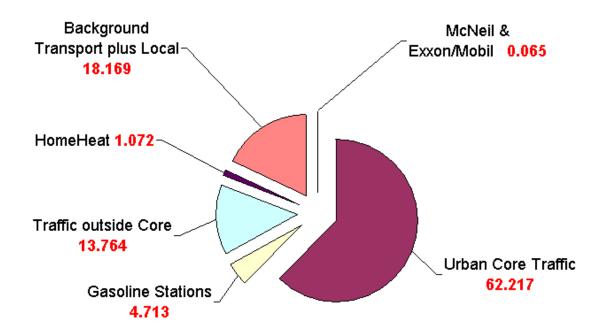
Results:

Summarizing what the modeling study has found:

On-Road vehicle traffic represents the most significant contributor to both short time period (24-hr average) and the monthly or annual average ambient benzene concentrations in the Burlington urban area. Annual ambient concentration impacts modeled in the Burlington domain from on-road vehicles over the whole domain were anywhere from 5 to 20 times the Vermont health standard (0.12 ug/m3) for benzene.

The monitored value for 1999 annual average ambient benzene at a typical location (**S. Winooski & Bank St. vicinity**) in the urban core was 2.44 ug/m3. When our estimate of average transported <u>non-local</u> benzene impacts (0.45 ug/m3 based on Underhill, Vt. data for 1999) is subtracted, the 1999 monitored impact due to local benzene sources at the S. Winooski monitoring location is estimated as 1.99 ug/m3 (17 times the standard). Modeled results including most local sources were predicted to be 2.03 ug/m3. <u>93% of this modeled local source annual impact is due to on-road vehicle traffic</u>. The chart below indicates the percent of total benzene measured at the S. Winooski/Bank Street monitoring location which was due to the various source categories. Note that 18.2 % of the annual impact is estimated from regional transported background and local sources not accounted for in the modeling.

PCT of Ambient Benzene Annual 1999 Impact Monitored 2.44 ug/m3 at the S. Winooski/Bank Monitoring Site Major Local Source Categories & Background & Local Srcs Not Modeled



Modeled Results Compared to Measurement Data:

Modeling for all months of the year was completed for 9 discrete receptor locations and the model results compared to actual measurements at one of those locations (S. Winooski & Bank Street monitoring site).

- The model predictions were shown to be well representing the temporal variation in measurements at the monitor, particularly over seasonal and annual time periods.
- Short-term predictions (24-hr averages) were somewhat less representative of the monitored values but still quite acceptable.

Thus the model has been validated as a useful tool for analysis of various changes in the emission source categories and will be used in evaluation of benzene emission control strategies to be developed for the benzene toxic action plan.

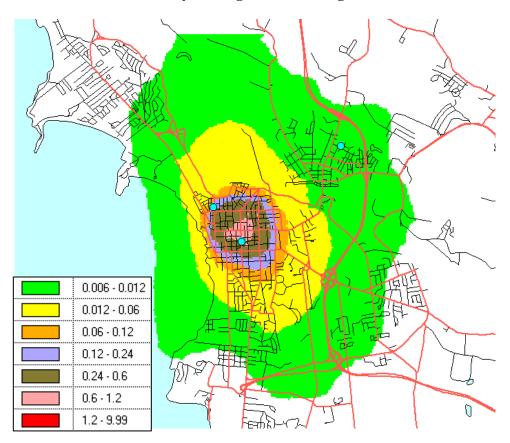
Modeled Results Used to Depict Spatial Concentration Gradients:

- Gridded modeling has only been completed fully for the month of January.
- Several grids of evenly spaced receptors covering the full domain or smaller portions
 of it have been used to evaluate the spatial gradients of ambient benzene which the
 model predicts should be experienced.

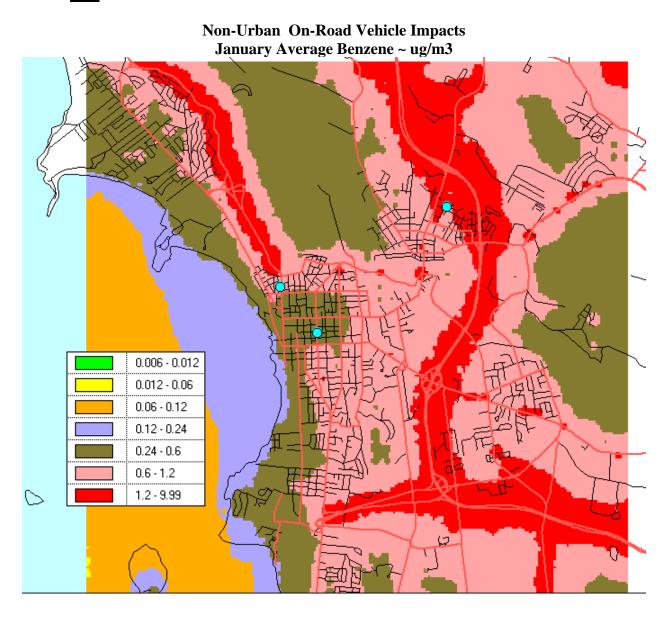
To summarize the gradients of benzene predicted by the model for the domain in modeling completed to date, a series of gridded model isopleth maps for the month of January 1999 are shown below.

1. January average benzene predicted by CALPUFF on the Burlington domain is shown for all **urban-core on-road vehicle emissions** of benzene.

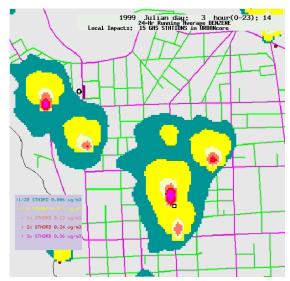
Urban – Core On-Road Vehicle Impacts January Average Benzene ~ ug/m3



2. January average benzene predicted by CALPUFF on the Burlington domain is shown for all emissions of benzene produced by <u>vehicles traveling on roads outside the urbancore</u>.



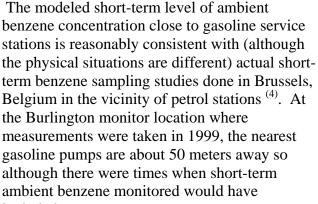
3. Gasoline service station activity creates smaller pockets of elevated ambient benzene concentration. Increases over the short time period (24-hr) and also the monthly or annual average base urban benzene concentrations in the immediate vicinity of the station gas pumps are seen (impact decreases significantly as distance increases beyond 50 meters). As expected, stations with Stage II vapor control systems showed significantly lower average and maximum impacts. Highest impacts from the stations for 24-hr time periods occur within 50 meters of the pumps and for uncontrolled stations typically represent an additional short-



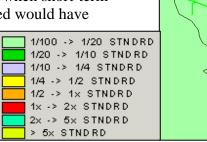
term concentration of 3 to 5 times the Vermont health standard (0.36 to 0.60 ug/m3) in the range of distances from 10m to 50m from the pumps. Within 10m of the pumps even higher concentration levels are predicted.

Since urban concentrations are already quite uniformly elevated by on-road vehicle traffic as indicated above, ambient benzene exposures from all sources at locations within a range of about 50 meters of gasoline service station pumps could be 3.0 ug/m3 or more on an annual average basis (25 times the Vermont standard).

Downtown Gasoline Station Impacts January Average Benzene ~ ug/m3



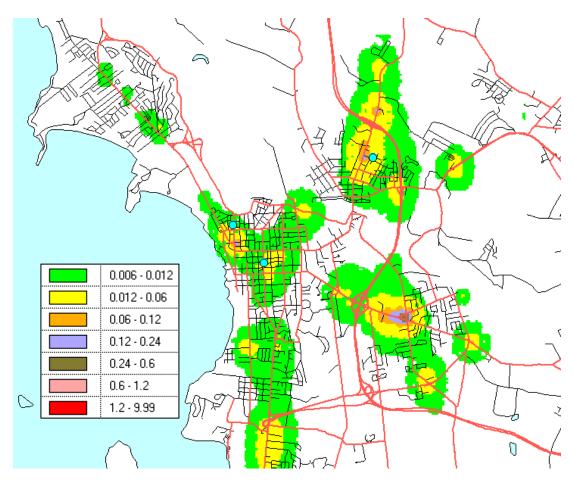
included more significant gasoline station source impacts than at other times, the modeling study indicates that the annual average





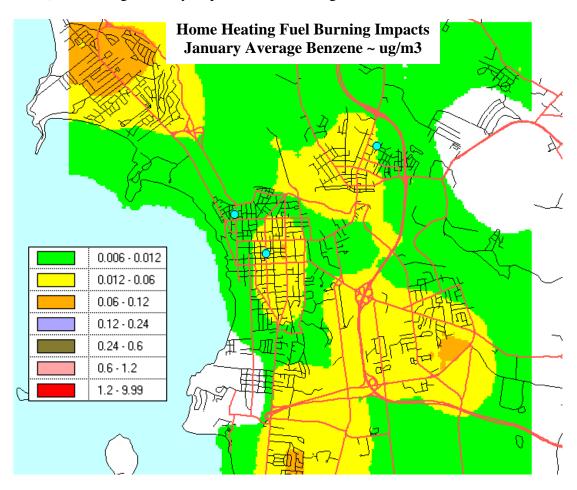
contribution to monitored benzene levels in the urban core from gasoline service station emissions represented 0.12 ug/m3 and although this is only 6% of the total local annual benzene impact in 1999 at the monitor, it is equivalent by itself to the Vermont health standard.

All 104 Domain-wide Gasoline Station Impacts January Average Benzene ~ ug/m3



4. Home heating fuel burning impact is much less than either on-road traffic or gasoline service stations. The impact it does have is predominantly caused by the wood-combustion fraction of home heating, and in the Burlington urban area the maximum contributions to ambient benzene concentrations from this source category are relatively confined to the neighborhoods where most wood-burning occurs. Impacts on the order of 1/10 to ½ the Vermont annual standard are typically experienced during the month of January for instance.

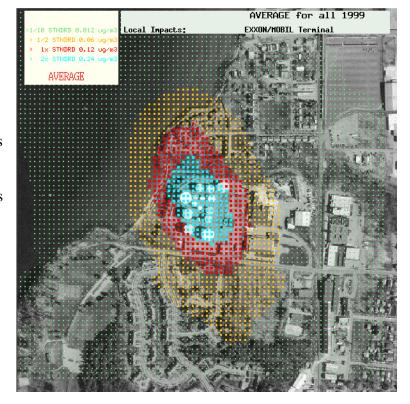
In neighborhoods for which estimated wood combustion was highest (NW portion of domain shown below), the average January impact could be as high as the standard.



5. Large industrial point sources of benzene are very few in the Burlington area. The two sources modeled in this study were of distinctly different character.

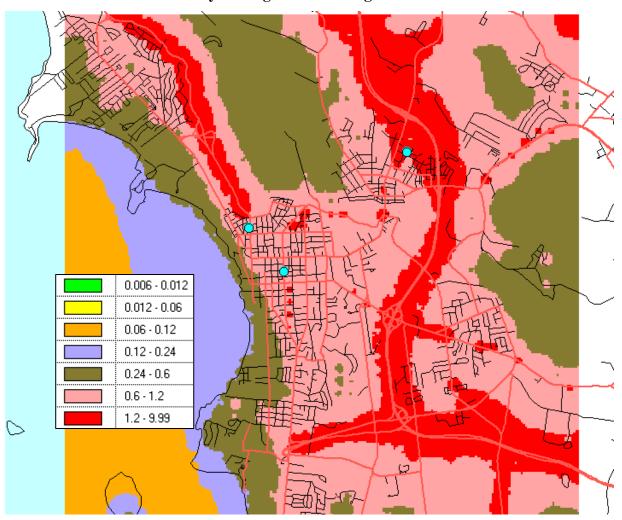
McNeil Generating Plant is a tall stack combustion emission source. The benzene emitted comes from the large quantities of wood combusted. Although the benzene emission estimated in 1999 from McNeil is of comparable magnitude to overall home heating emissions the predicted impact on the urban area is relatively small. This is because wood fuel use at McNeil was spread fairly evenly over the entire year rather than taking place only in the heating season, and because resulting benzene emissions were from a tall stack which allowed much more dispersion prior to impact at ground levels. The McNeil Plant is predicted to contribute much less than 1% of overall ambient annual benzene concentrations at the monitoring site and similarly low levels at all other locations in Burlington.

The Exxon/Mobil Bulk Gasoline Terminal contributes to Burlington ambient benzene concentrations at a magnitude somewhat comparable to gasoline service stations. Generally, the predicted CALPUFF impacts on ambient benzene are found to occur at levels above the Vermont standard at locations within the plant property boundaries (2x standard or more (BLUE). The model also shows impacts at above the level of the standard (RED) in some relatively small areas surrounding the plant.



In this final summary display, January average benzene predicted by CALPUFF on the Burlington domain is shown for <u>all local sources of benzene</u>. Interstate Highway route 89 is predicted to be the road corridor associated with the highest levels of long-term benzene concentrations in the ambient air, and the pattern of influence from roads with high traffic volumes is easily seen in the predicted average monthly concentration.

All Local Source Category Impacts January Average Benzene ~ ug/m3



Exposure To Benzene Not Limited to Ambient (outdoor) Air Breathed

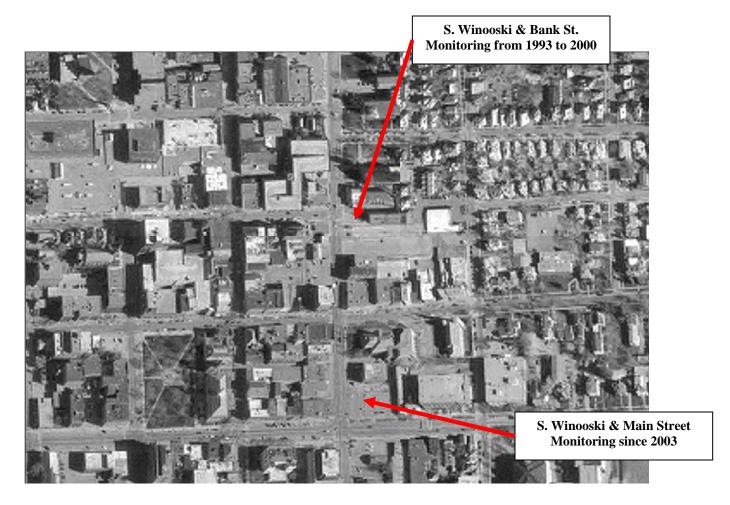
Exposure of an individual to benzene through the air is not solely determined by the ambient concentration levels in urban settings. Most people, especially those living and working in urban centers spend the majority of their lives in an indoor environment. Studies ^{(5),(6)}, done mainly in Europe, have shown that indoor levels of benzene actually tend to be higher than levels measured in the ambient air of the urban centers where homes and businesses are located. For the towns in Europe studied using personal exposure samplers carried by volunteers, it was found that indoor benzene concentration levels were on average 1.51 times the ambient outdoor benzene levels, and the studies also found that people spent 59.1% of the time at home ⁽⁵⁾. With respect to both the indoor and the outdoor air concentrations, these studies also indicate that meteorological hourly variation and/or differences in meteorological conditions over longer time frames "strongly affects the benzene concentrations" ⁽⁶⁾ measured at any monitoring site. Although Burlington, Vermont's situation may differ somewhat from that in European cities, these basic findings are likely to be generally true for urban Burlington.

24-hour average impacts predicted by the CALPUFF model should not be directly compared to the Vermont health-based standard because that standard was established based on long-term exposure to average ambient concentrations for time periods of more than a year. The 24-hour modeled impacts shown in this report are presented to show the variation in impacts that occur over short time periods from the several source categories independently and also when all are combined. Short-term (24-hr) exposure to levels of benzene in the ambient air which are greater than the Vermont standard is not currently believed to cause the same health effects as exposure for long time periods to the same or lower ambient levels of ambient benzene.

Specific life-style habits such as smoking also influence the amount of benzene a person is exposed to over the long-term. Smoking tobacco is one of the most direct ways that long-term benzene exposure is increased, particularly for the individual smoking but also for those in the same indoor environments as smokers. A study on motor vehicle emission related exposure of humans to benzene ⁽⁷⁾ published by the U.S. Environmental Protection Agency in 1993 indicates that "active smoking of tobacco" accounts for "roughly half of total population exposure to benzene, which is over and above that from motor vehicles. Outdoor concentrations of benzene, due mainly to motor vehicles, account for roughly one-quarter of the total".

Introduction:

Benzene monitoring has been conducted in downtown Burlington routinely since mid-1993. The site at which the sampling was done from 1993 thru 1999 on a regular "every 12th-day" schedule was located in a parking area next to the police station opposite the intersection of Bank Street with S. Winooski Avenue (see figure below). Since mid-2000 there was a period of about three years during which benzene monitoring was suspended while a new site was established several hundred meters away in a parking area on the corner of S. Winooski Avenue and Main Streets. Monitoring for benzene on the same schedule as previously was resumed in January 2003 at the new location and has continued since that time.



In addition to these urban area monitoring sites in Burlington, benzene has also been monitored for varying coincident time periods in several other urban centers (Brattleboro, Winooski, and Rutland) as well as in Waterbury and also at the Proctor Maple Research Center in Underhill, Vermont. The Underhill site serves as a rural background type of site which is useful for evaluating relative local and regional-scale source influences, particularly with respect to the Burlington downtown sites. A report of the State Toxicological Advisory Committee dated

February 1998 ⁽¹⁾ describes in detail the data collected from the entire hazardous air contaminant monitoring program conducted in Vermont through that time.

Figure 1 shows the historical trend of monitored benzene in downtown Burlington at the S. Winooski Avenue & Bank Street intersection for the time period between mid-1993 and 1999.

Figure 1

Burlington VT BENZENE Air Quality Every 12th day sampling 1993-1999 Red Line is 5 Period Moving Average

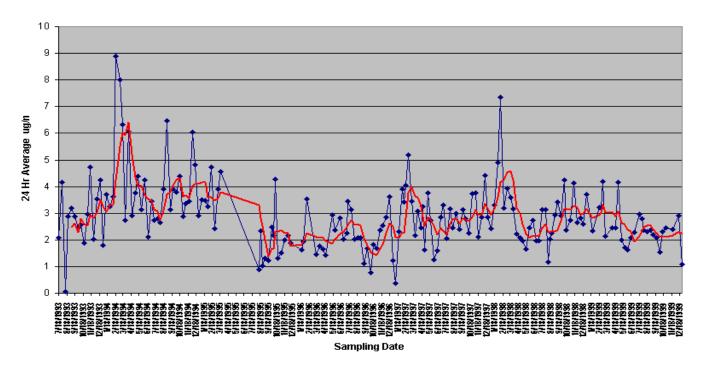


Figure 1 does <u>not</u> show any discernable strong trend in 24-hour sampled benzene values monitored in downtown Burlington from 1993 to 1999. At the beginning of the period the monitor was recording average levels just above 2 ug/m3 and at the end of the period levels appear to have been very similar, although there is a lot of variability in the individual measurements throughout the entire period. For a variety of reasons, including the availability of important meteorological databases necessary for creating wind fields required by the air quality model chosen for the modeling study, the Division selected the year 1999 as the time period for which the study would be conducted.

Table 1 S. Winooski & Bank Street Monitored 24-Hr Benzene (1999)

site	sample date	ug/m3	compound name
burlington	01/24/99	2.33	BENZENE
burlington	02/17/99	3.23	BENZENE
burlington	02/23/99	3.20	BENZENE
burlington	03/01/99	4.19	BENZENE
burlington	03/13/99	2.14	BENZENE
burlington	04/06/99	2.45	BENZENE
burlington	04/18/99	2.45	BENZENE
burlington	04/30/99	4.15	BENZENE
burlington	05/12/99	2.00	BENZENE
burlington	05/24/99	1.70	BENZENE
burlington	06/05/99	1.63	BENZENE
burlington	06/17/99	2.08	BENZENE
burlington	06/29/99	2.27	BENZENE
burlington	07/17/99	2.97	BENZENE
burlington	07/29/99	2.78	BENZENE
burlington	08/04/99	2.36	BENZENE
burlington	08/16/99	2.30	BENZENE
burlington	08/28/99	2.36	BENZENE
burlington	09/09/99	2.20	BENZENE
burlington	09/21/99	2.08	BENZENE
burlington	10/03/99	1.53	BENZENE
burlington	10/15/99	2.30	BENZENE
burlington	10/27/99	2.46	BENZENE
burlington	11/20/99	2.40	BENZENE
burlington	12/14/99	2.91	BENZENE
burlington	12/26/99	1.09	BENZENE

Table 1 shows the available benzene monitoring data for 1999 which was ultimately used to evaluate model results and confirm that the model was representing ambient concentration at this location in urban Burlington with acceptable accuracy. The applicable ambient air quality standard for benzene established by the State of Vermont and most recently amended in January 1993 is set at 0.12 ug/m3. This standard, called the Hazardous Ambient Air Standard (HAAS) ⁽²⁾, is a value reflecting an annual average exposure at that concentration. It represents an annual average exposure that below which would imply a less than 1 in 1 million risk of developing cancer from the benzene exposure. Taking the average of the 26 daily values monitored during 1999 (2.44 ug/m3) as representative of an actual annual exposure at the monitoring site, it is clear that the levels of benzene in the ambient air at the downtown Burlington monitoring site exceeded the HAAS by more than an order of magnitude in 1999.

Choice of Model and Domain:

During April 2003, staff of the Air Division Planning Section began examining the appropriateness of several models for use in the benzene modeling study. It was quickly determined that EPA's Guideline on Air Quality Models did not preclude the use of a regional scale puff dispersion model called CALPUFF for the study. Although the recommended use of CALPUFF in complex terrain situations at that time was on a case-by-case basis, the fact that model evaluation against actual monitored data was included as one aspect of the study implied that the use of CALPUFF for the study would certainly be appropriate. Also the location of Burlington, which was to be the primary focus of the modeling, is in the relatively smooth Champlain Valley making considerations due to complex terrain less important.

Several specific reasons made the choice of CALPUFF very appropriate as well as advantageous. For one thing, the other complex terrain models available at that time would not have been able to accommodate as many sources and would not have been able to account for innumerable smaller terrain features embedded in a domain of the size of Chittenden County. The CALPUFF model system is able to account for such features using a spatially and temporally varying wind-field created with a model system component called CALMET. CALPUFF is also capable of handling shoreline fumigation situations that might develop near Lake Champlain as well as capable of handling air stagnation situations that might occur.

With respect to the domain of the modeling exercise, our <u>initial</u> desire was to model as much of Chittenden County as possible and to incorporate the remote "background" site at Underhill as a point in the domain to allow better evaluation (and calibration if necessary) of the modeling setup.

Meteorology:

Initially therefore, CALMET was used to create meteorological fields which were based on a resolution of 40km so that wind-fields for each hour of 1999 could be produced covering almost the entire extent of Chittenden County, including the Underhill monitoring site on the slopes of Mt. Mansfield. Some initial work with preliminary versions of the emission inventory was carried out in 2003 to better assess the resource requirements for modeling such a large domain. It soon became apparent that emission inventories needed for such a large domain would necessarily have to be very coarse to comply with other limits of the computer model such as number of individual sources that could reasonably be run at one time.

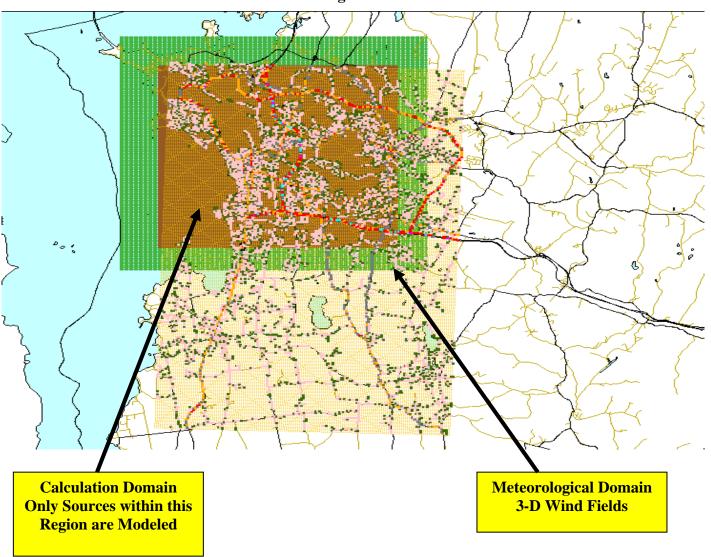
Therefore as work progressed on development of detailed benzene emission inventories for input into CALPUFF, it also soon became apparent that we would need to reduce the extent of the domain to avoid getting into very severe problems related to run-time of the computer model code and storage and management of the emission inventories. It would have been possible to minimize these problems on the larger domain but that would have meant using a much coarser spatial representation of all the inputs and the meteorology, which would have defeated the primary objective of getting highly resolved spatial concentration gradients in the Burlington urban-core.

In mid-2003, a meteorological field resolution at 200 meter grid spacing covering a square of 16 kilometers was determined to be the maximum domain size for which computer resources would be able to produce results in reasonable time frames. Aside from computer resource issues involved in the decision about domain size, it was also necessary to insure that our choices of meteorological field grid size and the quality of input data needed were consistent and appropriate. There were several possible approaches to creating hourly meteorology for the entire year of 1999. These involved decisions concerning the actual measurement data at the earth's surface that would be used and which representation of the upper air should be incorporated into the CALMET model runs. The quality of the actual measured meteorological parameters used as input had a big influence on how representative of the real situation the meteorological fields generated by CALMET would be. Choices of CALMET model settings were also critically important. During the latter half of 2003 these issues were thoroughly examined. **Appendix B** describes the process of validation of all assumptions and CALMET model settings which were used to create the final meteorological fields used in this study.

As a result of all the preliminary work, in December 2003 final meteorological fields based on a 200 meter spacing were produced for modeling on a domain covering a 16 kilometer by 16 kilometer area centered over urban Burlington. This scale of resolution of wind fields was determined to be the most detailed that could be produced given the computer resource constraints. The CALPUFF modeling system allows the establishment of three spatial domains in which input parameters or output parameters are specified by the correct coordinates. Meteorological fields need to cover the largest extent. Within the coverage of the meteorological fields, a "calculation domain" in which dispersion and calculation of ambient concentrations is done by the model needs to be specified. This region must encompass all of the emission sources desired to be included in the modeling. Finally, if a set of equally spaced receptors is to be used for displaying a spatial pattern of the concentration output from the model, this set of receptors, the "sampling grid" must be specified as a subset of the calculation domain. For this study a number of different sampling grids were eventually used.

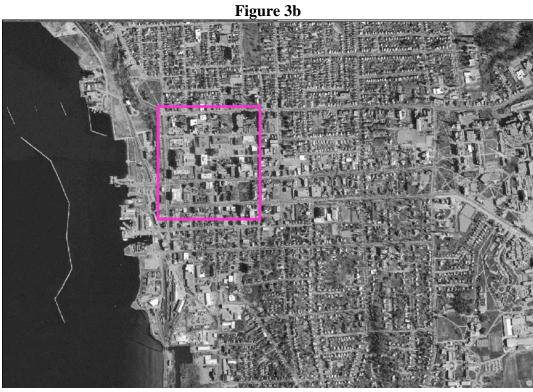
Figure 2 shows the area of Chittenden County covered by the **meteorological fields** (**GREEN**) prepared for 1999 which were used by CALPUFF to disperse and transport benzene emissions within the **calculation portion** (**BROWN**) of the final domain of approximately 16 km x 16 km which was utilized in this study.

Figure 2



Figures 3a & 3b illustrate the location of the urban-core portion of the 16 km square domain. Figure 3a covers roughly the overall calculation domain while Figure 3b identifies the subportion of that domain for which more detailed emission patterns were determined.





Emission Inventories:

One of the major initial steps in setting up the modeling project involved collecting available information about local emission sources of benzene in Chittenden County during the year 1999. Most of the work on this portion of the project was carried out during May and June of 2003. Inventories developed at that time were used for preliminary modeling to determine model runtimes and scale of modeling source inputs that could be handled by the computer systems available to the Division. These earliest inventories were later refined during 2004 as input files were being finalized for the actual modeling runs for each month of 1999. A great deal of time was spent in creating hourly emission estimates from all the primary benzene emitting sources that would reasonably represent the pattern of significant emissions actually occurring over the entire Burlington domain. A summary of source categories is shown in Table 2.

Table 2

Categories of Benzene Emitting Sources Burlington Modeling Domain

Annual Estimated Emissions to Determine Significance of Category

Source Category	1999 Annual Benzene	Modeled
On-Road Mobile Sources ($1.2 \times 1.3 \text{ km}$ Urban Core around Mo	nitor) 3,405 lbs	Υ
On-Road Mobile Sources (outside Core within 16x16 km domai	n) 177,174 lbs	Υ
Gasoline Service Stations (104 within domain)		
25 Stations with STAGE II Vapor Control (31,270,596	Gals) 603 lbs	Υ
79 Stations without STAGE II Vapor Control (19,737,402	Gals) 1642 lbs	Υ
Pt Sources (2 Large Industrial Facilities with > 100 lbs Benzene)	
BED McNeil Wood-Fired Electric Generating Unit	1,048 lbs	Υ
Exxon/Mobil Bulk Gasoline Storage Terminal	351 lbs	Υ
Residential Home Heating	2,155 lbs	Υ
Filling & Utilization of Portable Gasoline Containers	2,200 lbs	N
Outboard Engines in Domain portion of Lake Champlain	~ 1,000 lbs	N
8 Diesel Generators & 15 other point sources	51 lbs	N
Lawn & Garden & Snowmobiles	not estimated	Ν
Airport Operations	not estimated	N

On-Road Mobile Sources:

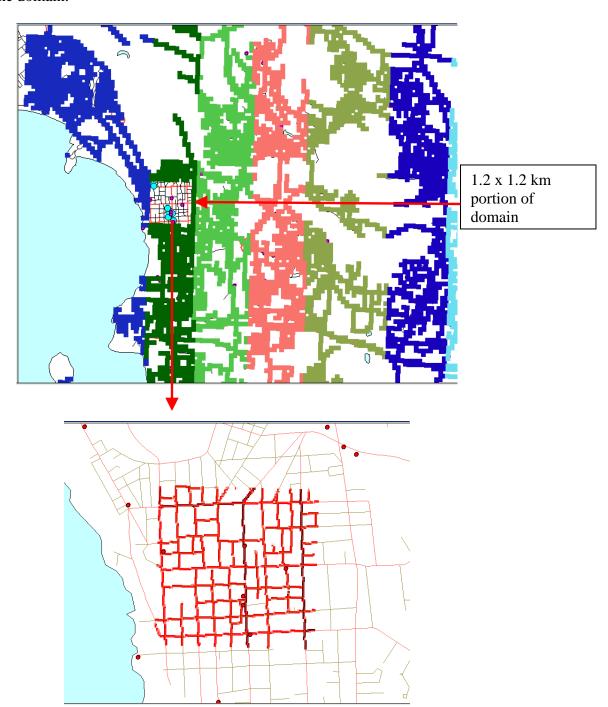
The development of benzene emission estimates from vehicles traveling on roads in Chittenden County involved applying a process that had been used previously by the Air Pollution Control Division for reporting emission estimates from on-road vehicles to federal EPA as part of National Emissions Inventory submittals required under the federal Clean Air Act. This process had not previously been used to estimate Hazardous Air Contaminant emissions from this source category but it was easy to extend it to the air contaminant benzene because the newest version of the on-road emission model (MOBILE6) available in 2003 allowed quantification of the benzene portion of volatile organic compound emissions calculated by the emission model.

The MOBILE6 emission model requires scenario-specific input information in order to make estimates of tailpipe and evaporative emissions from operating on-road vehicles. Each individual vehicle type (light-duty passenger vehicle, heavy-duty diesel truck, or motorcycle for example) emits differently than other vehicle types. The same vehicle type will emit differently in colder months than in warmer ones, at higher speed than at lower speed, and as it gets older. Average vehicle mix on roads of various types needs to be estimated. Because of temperature differences, the populations of vehicles operating on the various roads need to be estimated for at least each of 12 monthly periods in order to accumulate overall annual totals of emissions. Better yet would be actual measurement counts of vehicles and speeds on actual roadways for every day of the year. The available measurement data is only from representative types of roadways and the vehicle mix must usually be estimated from either statewide registration data or other estimation techniques. It might be possible to model a short section of roadway for a specific short time period during which traffic counts and speeds were measured, but in order to estimate an annual time period ambient air impact from on-road vehicle tailpipe benzene emissions across the entire domain being modeled, many assumptions must be made and only average types of conditions can be incorporated into a series of monthly time periods to approximate the annual model runs.

Since the CALPUFF model does not accept line sources (sources which emit along a linear path such as a roadway) in the way that some road-link specific air quality models do, it was necessary to accumulate the emissions from vehicles traveling along all the roads within each gridded section of the domain and treat the emission from each grid as a so-called "area source". The CALPUFF model takes such area sources and disperses the average emission from the entire area covered by the source. This has the effect of spreading emissions out (in a way, diluting them) prior to releasing them as a puff which is then dispersed and transported around the domain by the wind fields. It is therefore important not to specify any receptor locations very close to such area sources otherwise the true maximum effects may be under-estimated from these area sources. For this reason, it was determined that small area sources on the order of the actual road widths themselves would need to be utilized in the urban-core areas of the domain in which specific receptors would need to be evaluated. Representing the on-road vehicle emissions as area sources arrayed as a series of 10-meter squares linked together following the roadways is a reasonable way to represent exhaust emissions from moving traffic that creates relatively well mixed source concentrations over the surface of the roadways. Because the use of

10-meter squares as area sources creates a very large number of sources to model, this approach could only be taken in the urban-core portion of the domain. The urban-core encompasses roughly a 1.2 kilometer by 1.2 kilometer portion of the domain.

Outside the urban-core, on-road emissions were accumulated in 100-meter sized squares to limit the total number of area sources that would be necessary to insure inclusion of all the on-road sources in the domain.



Whereas each area source grid in the urban-core was comprised of only one type of road classification, many on-road area sources outside the urban-core could contain emissions from more than one road classification and several road-links intersecting at different angles etc.

Figure 4

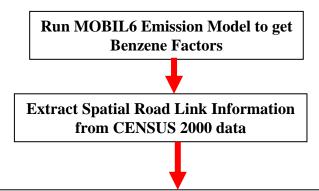


Estimation of on-road vehicle tailpipe emissions for a particular location must incorporate all the variables that affect what the emission factor of benzene would be from eight general types of vehicles traveling on an average section of each of several road types in each "area source" for each hour during the year. Information from the Agency of Transportation (AOT) such as vehicle count data at numerous locations, information related to road types such as average speed of vehicles on these roads and the location of these road types spatially, estimates of total vehicle miles traveled on each of these road types during 1999 broken out by county, counts of vehicles on representative road types during an average 24-hour diurnal period, Department of Motor Vehicle (DMV) estimates of the vehicle age distribution for the year 1999, etc. Other environmental information such as the average temperature in Chittenden County during each month of the year 1999 has also been obtained from National Weather Service archives and other sources.

10 m x 10m

The APCD has developed a set of computer programs which, when run sequentially, will create on-road vehicle benzene emission input files specific to each of the 12 calendar months. These

input files are directly readable by CALPUFF. Diurnal variation associated with each month is built into the hourly emission estimates. The flow chart shown below summarizes the steps involved in running this sequence of computer programs.



Match Agency of Transportation VMT data by Road Type (Speed&Volume), Vehicle Type (LDGV:HDGV:HDDV etc), Month (Temperature)

To Spatial Road Link Information and appropriate MOBILE6 Benzene Emission Factors

Run Code to Allocate Road Link Lengths to a set of 100m x 100m Grid Squares
And also to a set of
10m x 10m Grid Squares for the Urban Core Road Links

THEN Compute Base Annual Average Emission of Benzene in each Grid

Due to all Vehicle Types

Run Code which Creates Specific Grid Square Benzene Mass Emission (Gram/Sec) Rate Applicable to each Month of 1999 based on Monthly Traffic Volumes

Using AOT Traffic Count Data from eight to ten counting stations in Chittenden County Create the Diurnal Pattern of Emissions Applicable to each Month For each Grid Square and Retain the 24 hour Pattern for use in CALPUFF Input

Output these rates and diurnal patterns as 100m (or 10m) "Area Sources" in CALPUFF Input format

Gasoline Service Station Emissions:

Information about the benzene emission potential from operation of gasoline service stations was collected during the fall of 2003. An inventory of all the gasoline service station tanks registered in the Department of Environmental Conservation TANKS Database for 1999 identified 141 facilities in Chittenden County. Of these, 123 gasoline service stations had reported gasoline transfer throughput for the year 1999. There was no throughput data available for 18 of the facilities. These were examined for significance at a later stage in the development of this portion of the inventory through direct phone inquiries. All of the assumed throughput data obtained from the TANKS Database for 1999 and from the direct phone inquiries is documented in an EXCEL spreadsheet retained with other technical inventory development software at the APCD offices in Waterbury, Vermont. Of the facilities listed in the TANKS database, only 18 of them had specific GIS coordinate locations. For modeling the emissions from the gasoline service station sector of the benzene inventory it was necessary to obtain accurate spatial locations for all of the facilities modeled.

During a two-day period in October 2003, personnel from the APCD Planning Section surveyed all of the identified facilities in the TANKS database list within the anticipated extent of the domain centered on Burlington's Urban-core. Initially the list included 122 facilities, but later this number was reduced to 104 because the locations of some of the facilities fell outside of the eventual final source domain used for modeling. The survey included driving to each facility and positioning the vehicle near to the center of the retail service pumps and obtaining a GPS position using overhead satellite readings. These 104 gasoline service stations included 24 stations with Stage II vapor control (control of the retail distribution of gasoline into individual on-road vehicles through gas pumps) in place for calendar year 1999. The remaining 80 stations did not have Stage II vapor control installed and operating during 1999. Stage I control to minimize emissions of volatile compounds (including benzene) from tanker-truck transfer of gasoline product to the underground storage tanks at the stations is associated with the delivery tanker trucks themselves and was assumed to be in place and effective for all 104 gasoline stations included as sources of benzene emissions for the modeled domain.

The throughput data reported to the TANKS database allowed monthly variation in throughput to be incorporated in the development of station specific monthly benzene emission factors. Documented emission factors for each of several potential emission generating activities at each gasoline station were used to generate estimates for each individual station. The categories of activity for which emission factors are available includes: 1) balanced submerged filling operations (these are what is controlled by Stage I), 2) tank breathing losses, 3) vehicle refueling displacement losses, 4) and vehicle refueling spillage losses. These four components were summed to produce a single benzene emission rate in grams/sec applicable to each facility based on monthly gasoline throughput data in the TANKS database.

At the time of generation of this inventory in late 2003 the APCD was aware of two sources of emission factors that had been made available for generalized emission inventory work. EPA had published a set of benzene emission factors in a document entitled "Locating and Estimating Air Emissions from Sources of Benzene, March 1988" at Table 32 on page 150. The California Air Resources Board (CARB) publishes TOG (Total Organic Gasses) emission factors from

gasoline dispensing facilities in its emission inventory procedures document (Section 4.10 Table 1 page 4.10-5, March 1992). TOG emission may be adjusted by the ratio of benzene to TOG used in EPA's 1988 factor document. First test runs of the gasoline service station portion of the inventory done in early 2004 used the 1988 EPA factors. It was the APCD's intent to evaluate whether use of 1992 (or more recent) CARB factors might be appropriate. Prior to producing final CALPUFF input files for runs of the gasoline service station portion of the modeling for Chittenden County benzene, a third set of benzene factors from gasoline dispensing facilities was identified. These factors were found in a 1998 EPA publication "Locating and Estimating Air Emissions from Sources of Benzene, June 1998", EPA_454/R-98-011.

A decision was made in mid-2004 to utilize the original input files developed from 1988 EPA factors that had been used in earlier test runs. This was based on recognition that the ratio between sets of factors could be applied after-the-fact to this category and adjustment to impacts made if necessary as well as the recognition that it would require some significant further delays in the start of modeling to create new input files. The June 1998 EPA factors all indicate greater emissions of benzene per thousand gallons of gasoline throughput, therefore **the modeling results indicated for gasoline service stations in this report may be under-estimated by a constant factor because they were produced using the older EPA emission factors**.

Comparison between the two sets of EPA factors for benzene is indicated in this table below.

Dispensing Facility Activity	lbs/1000 gallons gasoline EPA 1988 Document	lbs/1000 gallons gasoline EPA 1998 Document
Balanced Submerged Fill	0.002	0.003
Underground Tank Breathing	Loss 0.006	0.009
Refueling (NO Stage II)	0.070	0.099
Refueling (Stage II Operating	0.007	0.0099
Spillage	0.004	0.0063

The constant factor that could be applied to "scale" the currently modeled impact predictions is simply the ratio of the total of the four component rates for each set, which turns out to be 1.43 for uncontrolled gas station emissions and 1.48 for controlled gas station emissions. Whatever set of gasoline service station emission factors is used, the uncertainty of the methods available to supply specific variable monthly, daily, and hourly gasoline service station benzene emission grams/sec rates as CALPUFF input probably is as significant for ambient concentration impact prediction as the differences between factor sets.

Table 3 lists the locations of gasoline service stations included in the modeling study and the 1999 average monthly throughput of gasoline for each of them. Stations with Stage II controls are also identified. It will be noted that for three of the facilities, 1999 throughput of gasoline was undetermined and emissions are set at zero.

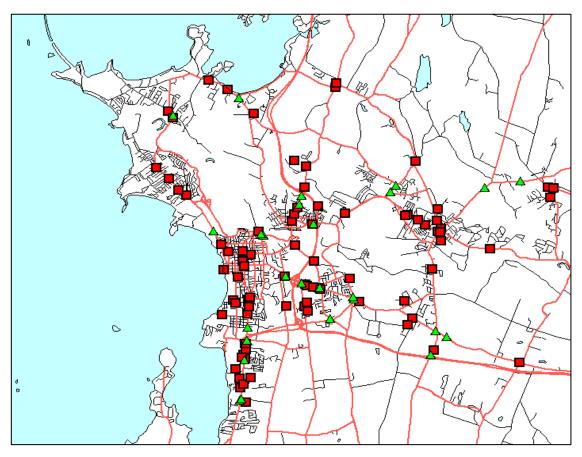
Table 3

		Gasoli	ne Dier	nensina	Facilitie	es Modeled
						asoline throughput)
Model #	Field ID					m) 1999 MonthlyAVE (gallons)
1	809	Olago II		-73.24465	75	22464
2	812			-73.21120	61	3554
3	815			-73.21061	66	24051
4	818			-73.20857	66	30561
5	827			-73.20352	70	200
6	822		44.46191	-73.21606	45	8412
7	823		44.46104	-73.21498	59	59002
8	826	Υ	44.48819	-73.20069	75	87185
9	814		44.47788	-73.21126	68	27000
10	816		44.47130	-73.21364	52	5000
11	813		44.47850	-73.21127	68	20000
12	863		44.47427	-73.22121	37	7260
13	810		44.51101	-73.24977	86	10307
14	811		44.51537	-73.25643	67	27841
15	804		44.48044	-73.20733	92	38000
16	821		44.46317	-73.20750	76	4606
17	819		44.45945	-73.20792	62	9182
18	825	Y	44.48868	-73.20185	79	118537
19	807	Υ	44.48991	-73.22647	84	76449
20	820		44.46293	-73.20759	73	6828
21	817		44.46240	-73.20821	76	22582
22	805		44.48152	-73.21887	81	30000
23	808		44.50423	-73.24086	80	20250
24	806			-73.22230	82	33000
25	791			-73.17262	109	2125
26	752			-73.21428	67	0
27	749.1			-73.24791	58	47157
28	755		44.55021	-73.16382	80	32845
29	754			-73.16454	60	32049
30	780			-73.15877	98	46028
31	749.2			-73.24791	58	25000
32	792			-73.18506	103	1963
33	788	Υ		-73.18144	111	77654
34	750	, ,		-73.23003	65	38247
35	747	Y		-73.24806	54	86327
36	748			-73.25055	54	10632
37	751			-73.22008	44	5000
38	789			-73.17979	114	40000
39	790			-73.17910	103	34000
40	753			-73.20630	70	3400
41	770		44.49/19	-73.12647	109	19135

42	758		44.51873	-73.12284	128	54250	
43	776		44.49477	-73.11151	123	13200	
44	772	Υ	44.50890	-73.13264	109	53765	
45	768		44.49300	-73.11737	120	25221	
46	777		44.49942	-73.11119	114	1000	
47	769		44.49515	-73.12120	114	33119	
48	771	Υ	44.50601	-73.13571	110	260000	
49	759	Υ		-73.08708	158	150000	
50	766			-73.11080	125	55000	
51	765			-73.10930	120	15350	
52	767			-73.10955	116	35850	
53	773			-73.12779	112	1500	
54	775			-73.10917	112	1000	
55	828			-73.18962	111	40234	
56	838			-73.15104	102	2000	
57	859	Υ		-73.20903	71	95000	
58	840	'		-73.17944	107	857	
59	872			-73.17443	97	4958	
60	858			-73.20933	68	30650	
61	832			-73.17499	103	29819	
62	846			-73.21428	54	4250	
63	856			-73.21420	65	1800	
64	847			-73.21130	52	1956	
65	833			-73.21233	103	25000	
66	871			-73.17100	116	8000	
67	830	Y		-73.13001	108	115289	
68	849	Y		-73.10092	64	67223	
69	855			-73.21242	67	0	
70	860	Y		-73.20860	76	69322	
71	839	Y		-73.20000	109	191422	
71	861	ı ı		-73.1039 <i>1</i> -73.20923	75	6159	
73	799	Y		-73.20923	111	100754	
		Y					
74	829			-73.18929	110	121136	
75 76	851 834	Y		-73.21152	57 109	91483 1546	
				-73.12604			
77	841			-73.17771 -73.18425	107	2350 0	
78	873				66		
79	848			-73.21203	51	3745	
80	843		44.44451		76	40000	
81	857		44.44227		72	55000	
82	845		44.44022		85	40416	
83	854	Y	44.43772		65	80964	
84	800	Y	44.46353		119	62712	
85	803		44.46878		104	29243	
86	802		44.46736		108	46468	
87	853		44.43072		83	145.8	
88	842		44.46125	-73.17818	109	750	

89	852		44.42808	-73.21018	54	1500	
90	801	Υ	44.46725	-73.17166	115	58448	
91	831		44.46817	-73.17826	101	19000	
92	796	Υ	44.44037	-73.11400	149	108525	
93	794		44.45525	-73.12357	121	19121	
94	798		44.46240	-73.12768	106	2450	
95	795	Υ	44.44767	-73.10592	145	53500	
96	793	Υ	44.45023	-73.11160	141	108444	
97	774		44.47532	-73.11353	118	68000	
98	797		44.44238	-73.11261	143	5200	
99	781	Υ	44.49299	-73.17533	95	171744	
100	785		44.49718	-73.18505	83	60000	
101	782		44.49300	-73.17561	92	43368	
102	787	Y	44.50098	-73.18277	115	200000	
103	784		44.49399	-73.18641	81	17343	
104	786		44.49955	-73.18349	115	50284	

Figure 5
Locations of Gasoline Service Stations in the Domain Modeled



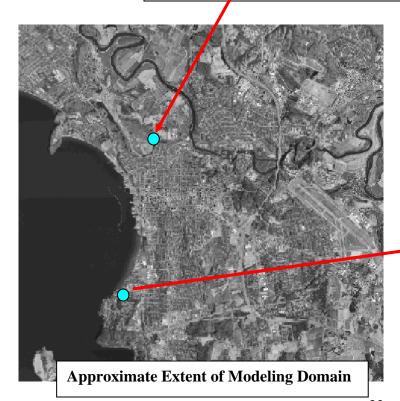
Green Triangles = Stations with STAGE II

Red Squares = Stations Uncontrolled 1999

Two Largest Individual Point Sources of Benzene:

Air pollutant emissions from industrial activity have been reported and entered into databases maintained by the APCD through an annual registration program for many years. Applicability requirements (including fees based on quantity of emission) for such reporting is specified in regulations adopted in April 1988. Fees (and consequently also the quantification of individual hazardous air contaminant emissions) were later expanded under authority obtained from the State Legislature in 1993 to include emissions of hazardous air contaminants, including benzene. The databases maintained by the APCD identified only two point-sources of benzene in the domain to be modeled which were significant enough to warrant their being included in the modeling as separate point sources. These two facilities are the Burlington Electric Department's McNeil Generating Plant and the Exxon/Mobil Bulk Fuel Terminal. The McNeil Plant burns very large quantities of wood-fuel and based on emission factors from EPA's AP-42 emission factor document the calculated emissions of benzene from the burning of wood in this type of facility was estimated to be 1048 pounds in 1999. For the Exxon/Mobil facility, several large storage tanks for gasoline fuel and the operations involved in transferring this gasoline from or to delivery rail cars and/or tank trucks are the primary sources of benzene emission to the ambient air. Some of these operations are controlled with pollution control devices. Using standard techniques for quantification of the emissions of benzene from bulk terminals applied to fuel storage and transfer data reported by the facility and also data used by consultants for the facility who had previously performed modeling used for permitting the facility in 1998, the APCD determined that 1999 emissions of benzene from the various operations at the facility in 1999 amounted to approximately 351 pounds.

Burlington Electric McNeil Plant



Exxon/Mobil Bulk Terminal Plant



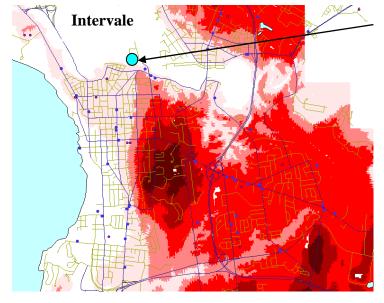
32a

The largest other potential industrial or commercial point sources of benzene known within the modeling domain all emitted less than 15 lbs of benzene during 1999. This level of emission was determined to be insignificant on the domain receptor scale compared to other source categories being modeled. In this context, insignificant implies that if incorporated as an individual point source it would likely not quantitatively change the model results at any gridded (non source-oriented) receptors used for the modeled domain-wide benzene emission sources. Therefore the only two individual industrial-scale facilities modeled in the domain were the McNeil Wood-Fired Electric Generating Plant and the Exxon/Mobil Bulk Gasoline Storage Terminal.

The McNeil Generating Plant – Individual Source # 1:

For the McNeil Plant, wood-fuel burned during the year 1999 was assumed to have been burned in quantities allocated to hours that the plant operated based on the heat input rate reported by the plant to the EPA as part of requirements under the federal Clean Air Act's emission reporting requirement pertaining to sources of Acid-Rain precursors. The hourly pattern of heat input when wood-fuel was combusted serves as a reasonable way to allocate the mass of wood burned throughout the year into estimated hourly quantities. The McNeil Plant was modeled as a stack emission from a single point source using CALPUFF. The hourly emission rate of benzene from wood combustion at the McNeil Plant during each hour of the year 1999 was input to the CALPUFF model through a single file structured to be read by the model directly.

Benzene produced by the combustion of wood fuel at McNeil was emitted into the atmosphere from the top of a relatively tall stack, 78.6 meters above its base level. Topographic data utilized in creating the wind-fields used by the CALPUFF model to transport and disperse the emission took account of the relative terrain heights surrounding the stack itself.



Because the McNeil Plant is located in the Intervale region of Burlington, the effective height of emission above ground located to the south of the Plant was 40 to 50 meters rather than the full stack height of 78.6 meters.

Terrain Height Above Sea Level: Meters AS	L
---	---

58.11 - 75.71
75.71 - 89.74
89.74 - 104.74
104.74 - 119.37
119.37 - 133.61

Note that the Intervale ground level is about 35 meters ASL

Even with this local topographic situation, modeled results for benzene impacts due to wood combustion emissions at the McNeil Plant were not seen to be significant anywhere in the domain modeled compared to modeled results for the non-point source categories. The relative impacts from these categories of sources is discussed at a later point in this report.

The Exxon/Mobil Bulk Gasoline Storage Terminal – Individual Source # 2:

Whereas the McNeil Plant could be modeled accurately using a single stack for the emission point, the activity and operations which produce benzene emissions at the Exxon/Mobil Bulk Terminal were better represented by a number of separate emission sources with different characteristics with respect to how the emission occurred. The approach used to model this facility was similar to the approach used by consultants in 1999 relative to the way the sources were configured and input to the model. Radian International ⁽³⁾ had modeled the facility for ambient impacts for a number of air toxic compounds (HACs) at the request of the VT Department of Environmental Conservation. This request had come after an investigation of the potential ambient air concentrations of these compounds had been conducted by the Federal Agency for Toxic Substances and Disease Registry (ATSDR) at this site.

Differences between the current modeling study and the Radian International modeling performed in 1999 include 1) the use of more spatially refined meteorological data (200m gridded wind fields) for a single year of 1999 rather than using 5-year wind speed and direction frequency distributions (1992-1996) derived from a single surface meteorological site at Burlington, Vermont and upper-air wind speed and direction from Albany, New York, 2) the use of actual 1999 annual throughput information reported to the APCD from which emission estimates were made consistent with the year of modeling (1999), and 3) the use of a puff dispersion model (CALPUFF) with spatial and time varying wind fields implicit in the meteorological data compared to the consultant's use of a straight line dispersion model (ISCST3). Both methods are appropriate because they were applied with different objectives in mind. The consultant modeling referenced was done focusing only on the Exxon/Mobil Bulk Terminal. The current study incorporates the modeled impacts for benzene from the Bulk Terminal as part of combined results for all local significant sources of benzene. Both studies included receptors as far as 5 or more kilometers from the facility.

The following describes how the current study characterized the emissions of benzene for input to the CALPUFF model. There is a vapor combustion unit (VCU) utilized to control captured volatile organic compound emissions occurring during operation of the facility loading rack. This VCU was modeled as a point source with the characteristics of a hot plume emitted from an elevated stack. The structures comprising the facility are located in such a way that it was determined necessary to include the potential for downwash of stack emissions due to the creation of turbulence around surrounding structures. Downwash flags and input information were activated in the model settings to model enhanced downwash impact potential for this one emission point. The loading rack itself was modeled for fugitive emissions (those not captured) as an area source. Representative diurnal patterns were applied to adjust the annual average emission rates to more appropriate rates specified in grams/sec units for each hour of the year. The diurnal pattern was selected to reflect fuel transfer and loading operations confined to the normal working hours in a workday, i.e., from 8 am to 5 pm.

Eight bulk fuel storage tanks were modeled as separate area sources of varying size. Four of these tanks store distillate fuel and four of them store gasoline. Each tank's emission rate of benzene was determined using factors applied to the annual throughput of fuel stored in each tank specific to 1999 registration data reported by the facility to the APCD. Because there was no readily available information as to how much fuel was in any tank at any specific time, it was not possible to allocate evaporative emissions from the tanks to specific months. The only adjustment to evaporative emissions from the storage tanks was to weight the emissions so they occurred primarily during daylight hours.

Residential Home Heating:

It was suspected that benzene emissions from wood combustion for home heating could amount to a sizable fraction of the overall non-road related benzene emissions for any locality burning a lot of wood in residential wood-stoves or fireplaces. A significant effort was made therefore to reasonably quantify the home heating source category for the modeling domain in Chittenden County. This quantification and development of benzene emissions from residential home heating (oil burning also contributes a small amount of benzene) had to rely on a number of surrogate datasets for spatially locating what was statistically believed to be a realistic distribution of the various wood and fuel oil burning homes in the domain.

The approach taken was to allocate total wood and oil use for home heating in census blocks within the domain by assigning an average county-wide oil or wood use to the percentage of homes which the census data identified as using that type of fuel. The census data does not allow for easy location of the individual homes, so distribution of the homes within the census block had to be in a somewhat subjective way. Homes generally are located within 100 meters of roadways however, so the location of home heating emissions is roughly coincident with the location of on-road vehicle emissions.

There are methods that might produce more exact spatial emission patterns of home heating emissions, but these would certainly require much more comprehensive survey information and a very large commitment of resources. Having a good idea of the mass of benzene emissions within the domain due to home heating as a proportion of the total benzene emissions estimated, the APCD believes that methodologies for spatially allocating home heating emissions need only be approximate for the primary goal of this modeling study.

Figure 6, 7, and 8 summarize steps in creating the assumed distribution of wood-burning in census blocks. This distribution was then used for developing benzene emissions estimates from residential home heating (both wood-burning emissions and oil-burning emissions) in the domain.

Figure 6

Chittenden County & Environs: Distribution of Wood-Burning in Homes 2000 Census Data Percent of State-wide Residential Wood Burning occurring in homes within & surrounding Chittenden County Red Squares are Census Blocks (sized based on total housing within block) Yellow Portion of map is the Burlington Urban Area modeling domain used for Air Toxics Evaluation 0% - 0.1% 0 - 0.001 0.001 - 0.002 0.1% - 0.2% Scale at right shows % of state total residential 0.002 - 0.003 0.2% - 0.3% wood burned in that

census block.

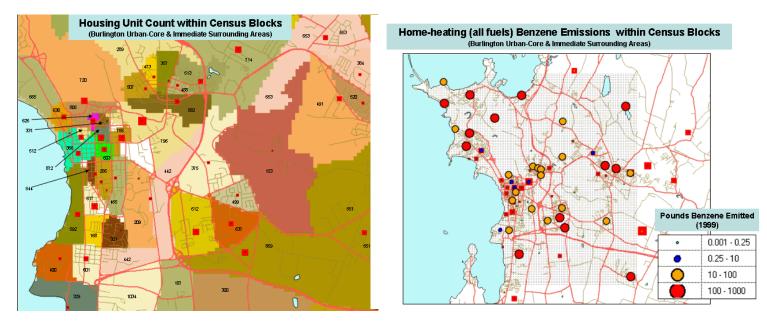
0.003 - 0.005

0.005 - 0.011

0.3% - 0.5%

0.5% - 1.1%

Figure 7 Figure 8

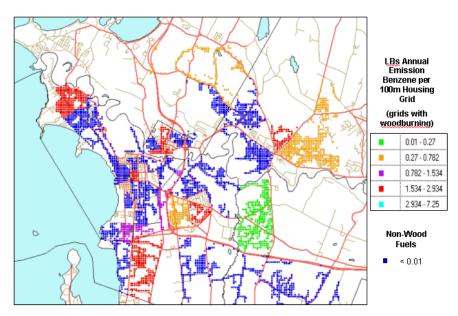


Home-heating emissions of benzene were accumulated in 100 meter grids to be used as area source inputs to the CALPUFF model. These 100 meter grids were positioned along the roads within each census block and all home-heating benzene emissions estimated for a census block were evenly distributed along the roads (except for interstate portions) in that block. Figure 9. shows the pattern that emerges when these assumptions are used.

Figure 9

Distribution of Home-heating Benzene Emissions

(Housing Pattern: placed along low-speed roads & constant AVE for Census Block)



Other Sources of Benzene Emissions:

There are several other potentially significant sources of benzene emissions within the modeling domain which have not been specifically modeled. In particular, a variety of off-road mobile vehicles and/or portable gasoline powered tools and equipment used by home-owners were considered as source categories for modeling when initially developing the source inventory for the domain. However, a decision was made in mid-2004 to concentrate on the largest overall source categories for which reasonably accurate emission estimates had already been made for volatile organic compounds of which benzene is a component. This decision was made partially because of resource constraints but also because it was recognized that establishment of a modeling approach which included the largest emission categories likely to impact the urbancore would serve to create a validated modeling tool that could later be improved through the addition of more (but probably smaller total annual emission) benzene source categories.

Table 2 identifies two likely source categories of benzene for which benzene emission estimates were <u>not quantified adequately</u> within the domain.

1. Lawn & Garden & Snowmobiles:

2. Airport Operations:

Both of these categories involve baseline data and inventory approaches which have not been used previously by the APCD for such sources in Vermont. The potential effort needed to adequately estimate benzene emissions from these categories was considered too excessive for the probable impact expected in the urban-core portion of the domain for this modeling study. A very rough estimate of annual benzene emissions for lawn-mowing was attempted but only served to convince us that this category was not critical to the modeling. In the one case (lawn & garden & snowmobiles) the dispersed nature of the activity and in the other case (airport operations) the relatively low level of activity caused us to postpone modeling of these source categories for this study. This decision does not preclude the later development of benzene emission input files including these source categories to amend the results of the modeling study obtained so far, should this be deemed important for development of toxic action plans.

Similarly, Table 2 identifies three other source categories of benzene for which emissions were quantified on an annual basis, but which were not included in the modeling to date.

3. Outboard Engines in Lake Champlain

A very rough estimate of benzene emissions from outboard engine operation in the portion of Lake Champlain included in the modeling domain was made. Benzene from this category in the small portion of the lake included was estimated at 1000 pounds during a typical year. Confidence in this estimate is low however and difficulty in spatially and temporally allocating these emissions known to be widely dispersed over a large area led the APCD to not include this emission category in the current modeling.

4. 8 Diesel Generators and 15 Small Point Sources:

An estimate of the benzene emission potential from a set of smaller point sources including eight diesel generators and fifteen other small sources which all together totaled only 51 pounds during 1999 led to a decision not to model these sources.

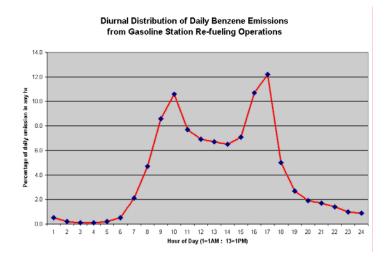
5. Portable Gasoline Container Usage:

Benzene emissions from the spillage and evaporation of gasoline associated with the filling and utilization of portable gasoline containers was also estimated for 1999. This amounts to approximately 2200 pounds of benzene, an amount that is both comparable in magnitude to the emissions from home heating and likely to be spatially emitted in a pattern similar to home heating emissions. The characteristic height of emission from portable gasoline containers is much different than from home-heating however. Benzene emitted as a combustion product from chimneys would occur 10 meters or more above the ground and would be part of a combustion gas stream at a temperature more than 100 degrees Fahrenheit above the ambient temperature with significant additional plume rise prior to dispersion in the ambient air. Benzene evaporating from spills and during transfer from portable fuel containers occurs at ambient temperature and very close to the ground. Temporally, it is believed that most of the portable gasoline container benzene emissions would occur during the warmer months, as opposed to the likely temporal pattern of the winter-time home heating emissions.

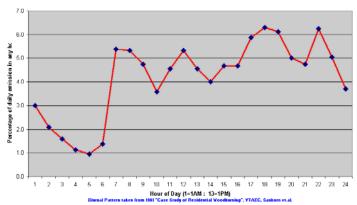
Winter-time home-heating ambient air benzene impacts in the urban-core portion of the domain constituted a relatively small part of the overall ambient benzene modeled. If the characteristics of emission were similar, the modeling of a comparable quantity of benzene emissions during warmer months would likely result in ambient air impacts from portable gasoline container filling and spillage of roughly similar magnitude. However, because portable gasoline container emissions occur so close to the ground, we believe the dispersion pattern would be much less extensive and that impacts from such sources in the urban-core portion of the domain would be less than those modeled for home heating benzene emissions. Due to time constraints toward the end of this modeling project, portable gasoline container emissions were not modeled specifically. However this is one of the source categories of benzene emissions which does have a relatively cost-effective and implementable control strategy associated with it (restricting the type of portable gasoline containers sold in Vermont to those which limit spillage and evaporation). For this reason, the modeling platform used for this current study may be used to quantify the air quality benefits of such a regulatory approach for portable gasoline containers when the toxic action plan for benzene is completed in the future.

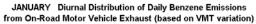
Diurnal Patterns of Emissions:

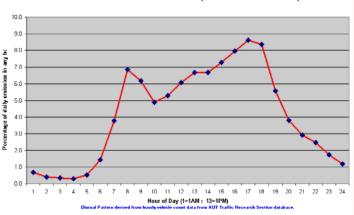
Diurnal patterns of emissions from each of the various sources of benzene are important when modeling the impacts on the ambient air quality. The following figures illustrate patterns used:



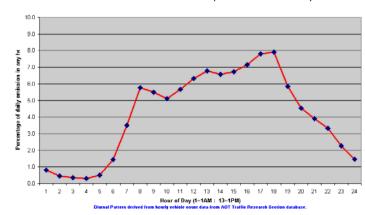








JULY Diurnal Distribution of Daily Benzene Emissions from On-Road Motor Vehicle Exhaust (based on VMT variation)



Modeled Benzene Emissions Summarized for 1999 by Month:

Table 4 shows the relative quantities of benzene emitted during each month of 1999 as estimated and input into the CALPUFF model runs. This table shows that over the entire 16 km by 16 km domain modeled, by far the largest contribution of benzene to the ambient air locally is the onroad mobile source contribution. This is the exhaust (and evaporative from hot engine) emission of benzene from motor vehicles traveling on all the various roadways in the domain. The urbancore portion (defined for this study for convenience as the 1.2 km x 1.2 km section of the domain centered on the downtown including the APCD benzene monitoring site) is broken out separately from the non-urban remainder which is all the remaining roads outside the defined core in a square domain of roughly 16 km size.

Table 4

Benzene Emitted from Source Groups in Domain Modeled

~ Lbs of Benzene by month in 1999

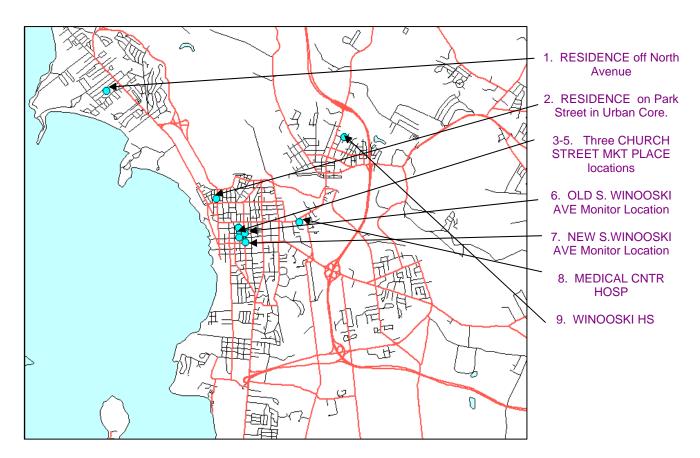
Month	Gasoline Stations	Urban Rds 1.2 km	NonUrban Rds 16 km	Residential Heat	2 Point Sources McNeil & Exxon/Mobil
Jan	168.3	339.9	17848.6	421.2	116.7
Feb	145.4	308.1	16146.9	341.7	116.7
Mar	174.4	318.4	16645.0	315.9	116.7
Apr	165.7	280.5	14589.2	195.6	116.7
May	191.1	256.4	13265.7	79.3	116.7
Jun	188.5	248.4	12835.7	8.6	116.7
Jul	220.8	245.7	12692.0	2.1	116.7
Aug	213.9	249.0	12863.7	19.3	116.7
Sep	191.4	237.8	12288.9	36.5	116.7
Oct	203.2	293.4	15251.8	184.8	116.7
Nov	178.9	277.9	14467.8	208.5	116.7
Dec	202.9	349.5	18279.8	341.7	116.7
1999	2244.5	3405.0	177175.1	2155.2	~ 1400.0

Receptors used for interpreting CALPUFF Model Results:

Modeling results discussed in detail below will illustrate that the magnitude of the overall emission from a source type in the domain is not always a good indicator of what source type actually causes the highest impact of ambient benzene measured at any location in the domain. Actual air quality at any location is a result of these emissions being dispersed and transported from their sources to the receptor (measurement location). Modeling the emission and the dispersion and transport of the benzene to all parts of the domain indicates that although emissions from motor vehicles traveling on roadways generally determine the overall benzene concentration patterns because the roadways are fairly uniformly distributed across the domain,

hot-spots of even higher concentration on average will exist in close proximity to gasoline service stations and other point sources of benzene emission.

Figure 10
9 discrete receptor locations were used for annual runs to determine the spatial influence of all benzene sources modeled in the domain.



Relative fraction of overall local source impact varies at each receptor:

At the 9 locations selected for assessment during the evaluation phase of the modeling, the PERCENT of ambient ANNUAL AVERAGE benzene impact due to each of the source groups identified above was seen to be quite different. The differences reflect the spatial location of the receptor with respect to the main sources and perhaps some slight differences in micrometeorology seen at that location. Sites very near to heavily traveled roadways are seen to be more affected by those roadway emissions than other sites further from the roadways might be. Typical results for two of the source groups are summarized here.

- Urban-Core On-Road traffic related benzene emission impacts ranged from <u>0.39% at Receptor 1</u> to <u>76.04% at Receptor 6</u>.
- Gasoline Station re-fueling related benzene emission impacts ranged from <u>0.30% at</u> Receptor 1 to 15.28% at Receptor 7.

Details of source category impacts for most of the 9 discrete receptor locations modeled for the year 1999 are discussed in the next section of this report.

Modeled Ambient Concentrations of Benzene:

Two modes of running the CALPUFF model were used to generate ambient benzene concentration impacts from the sources modeled. In the initial "evaluation" phase of modeling (during the last half of 2004 and the first few months of 2005), the objective was to predict the ambient benzene concentration at a relatively few specific receptor locations (see Figure 10), and in particular, the South Winooski & Bank Street monitoring location at which benzene monitoring was conducted for the period from 1993 to 2000. Since we were modeling specific 1999 meteorology and using our best estimates of 1999 local benzene emissions, the 26 dates on which 24-hour average benzene values were monitored at the South Winooski & Bank Street location in 1999 (see Table 1) served as the target dates we wanted to try to re-produce with modeled results. This mode of running the model, with relatively few receptors, does not allow much spatial detail to be predicted but because only a few locations need to be predicted the model runs quite fast compared to running it in a mode with many receptors. The objective was to be able to run the model for the full year of 1999 and to take the average 24-hour values predicted at the South Winooski & Bank Street monitoring location on the 26 dates monitoring had been conducted to compare these predictions to the 24-hour concentration values for benzene obtained from the monitored air samples. This procedure serves as an "evaluation" of how well the model is working.

As will be described in the section titled "Evaluation Phase Modeling Results" below, this comparison of predicted concentration to monitored concentration at the monitoring site produced very good results. The model appears to have incorporated all of the most important benzene sources that affected the monitoring site during 1999, predicting average benzene impacts during the four seasons very close to what was monitored on average for those seasons. The model also followed the individual 24-hour monitored benzene variation through the course of the year time period quite well.

Because the model's performance was judged to be very good in predicting benzene concentrations at the one location where monitoring had been conducted, a second phase of modeling began in early 2005 which set the model up to run in a slightly different mode. This mode included the use of dense grids of receptors instead of only a few locations specified individually. Several receptor grids were tried and the time required to run the model for all twelve months of 1999 was tested to determine whether useable results could be generated in reasonable run-times. As it turned out, the number of sources contained in the input files to represent the many road links throughout the domain as either 10m "area sources" in the urbancore (2160 different sources) or 100m "area sources" in places external to this core area (7038 sources) led to very long run-times to produce modeled results when these dense receptor grids were also incorporated into the modeling.

Consequently, there remains significant additional modeling time needed to fully complete the entire year of 1999 as a spatially detailed result showing gradients of benzene concentration over the entire domain. Results showing benzene concentration gradients for a single month (January) are currently available for the entire domain and for several smaller portions of the domain in varying degrees of detail. These January 1999 results are discussed in the section of the report titled "Gridded Receptor Modeling Results".

Evaluation Phase Modeling Results:

The graphs below show results of running CALPUFF for the entire year of 1999 meteorology with predictions at the nine discrete receptor locations identified in Figure 10. For clarification, the three Church Street Market Place locations were the intersection of Cherry and Church Street, the intersection of College and Church Street, and the NW corner of the Bank Street Parking Garage nearest to Church Street. The predictions at these locations were further enhanced by assuming three different heights of each receptor at the nine locations. Predictions were calculated by the model at 1 meter height, 5 meters height, and 10 meters height. Therefore 27 predicted results were obtained for ambient benzene for each hour (8751 hours) during 1999. Meteorology for 9 hours at the end of the year was not available. These 1-hour predictions were later accumulated into running 24-hour average impact predictions so that during the 24-hour periods during 1999 when the benzene monitor was sampling the air next at the S. Winooski Avenue & Bank Street location, a predicted 24-hour average value could be obtained for direct comparison to the sampled benzene concentration. The sampling inlet was located at approximately 3 meters above the ground. Modeling results obtained for the 1 meter height and the 5 meter height were averaged to produce a value of predicted ambient benzene for comparison to the sampled values.

Figure 11 shows how closely the individual 26 dates of predicted benzene concentration match the sampled values from the monitoring site at S. Winooski Avenue. There appears to be somewhat more under-prediction of the actual sampled value toward the end of the year 1999. For this comparison, the directly modeled value represents all the local sources of benzene modeled (which are probably slightly under-estimated since a few source categories were not included due to being relatively small and/or very dispersed) and a "non-local background" component. The "non-local component" represents benzene that may have been transported into the area of the modeling domain from anywhere else outside the domain. The monitoring site at Underhill, Vermont is a very rural site with few close local sources of benzene that have been identified. It is general practice in modeling studies such as this to select a remote background site to represent the component of concentration that might have been transported into the region. After some analysis of the meteorological wind fields on the dates of sampling (which were the same for Underhill as for the S. Winooski Avenue site) we concluded that the measured value at Underhill on each date of sampling would be a reasonable surrogate for regional background benzene for Burlington on that date. Table 5 summarizes the specific dates used in performance evaluation of the model at the S. Winooski Avenue & Bank Street monitor.

Table 5

SITE	SAMPLE DATE	ug/m3 MONITORED @ 3 meters ht	ug/m3 MODELED + BKGRD(Underhill) Ave of 1m & 5m modeled
S. Winooski Ave & Bank St	01/24/99	2.33	2.04
S. Winooski Ave & Bank St	02/17/99	3.23	1.25
S. Winooski Ave & Bank St	02/23/99	3.20	4.28
S. Winooski Ave & Bank St	03/01/99	4.19	2.83
S. Winooski Ave & Bank St	03/13/99	2.14	2.23
S. Winooski Ave & Bank St	04/06/99	2.45	1.90
S. Winooski Ave & Bank St	04/18/99	2.45	1.48
S. Winooski Ave & Bank St	04/30/99	4.15	4.44
S. Winooski Ave & Bank St	05/12/99	2.00	1.62
S. Winooski Ave & Bank St	05/24/99	1.70	0.64
S. Winooski Ave & Bank St	06/05/99	1.63	2.01
S. Winooski Ave & Bank St	06/17/99	2.08	2.20
S. Winooski Ave & Bank St	06/29/99	2.27	1.35
S. Winooski Ave & Bank St	07/17/99	2.97	3.36
S. Winooski Ave & Bank St	07/29/99	2.78	1.79
S. Winooski Ave & Bank St	08/04/99	2.36	1.32
S. Winooski Ave & Bank St	08/16/99	2.30	2.20
S. Winooski Ave & Bank St	08/28/99	2.36	1.51
S. Winooski Ave & Bank St	09/09/99	2.20	1.73
S. Winooski Ave & Bank St	09/21/99	2.08	1.16
S. Winooski Ave & Bank St	10/03/99	1.53	1.34
S. Winooski Ave & Bank St	10/15/99	2.30	1.00
S. Winooski Ave & Bank St	10/27/99	2.46	1.84
S. Winooski Ave & Bank St	11/20/99	2.40	1.48
S. Winooski Ave & Bank St	12/14/99	2.91	1.70
S. Winooski Ave & Bank St	12/26/99	1.09	1.73

Short-Term (24-Hr) Concentration Predictions:

The comparisons shown in Figures 11 and 12 have accounted for the regional non-local background by adding the concentration measured at Underhill to the predicted benzene concentration modeled prior to comparison to the measured benzene at the S. Winooski monitor.

Figure 11

Comparison between Modeled & Monitored Benzene at S. Winooski Avenue 24-Hour Averages

NOTE: 3m impacts were estimated by averaging 1m & 5m model impact predictions.

The Monitoring inlet was at slightly below 3 meters.

Monitored Burlington 24-Hr Ave Benzene vs 3m Modeled 24-Hr Ave Benzene
Background assumed to be 100% of Underhill Monitored 24-Hr Value on same date
(On-Road, Residential Heating, Gas Stations, 2 PT Srcs)

RED Series = Modeled BLUE Series = Monitored

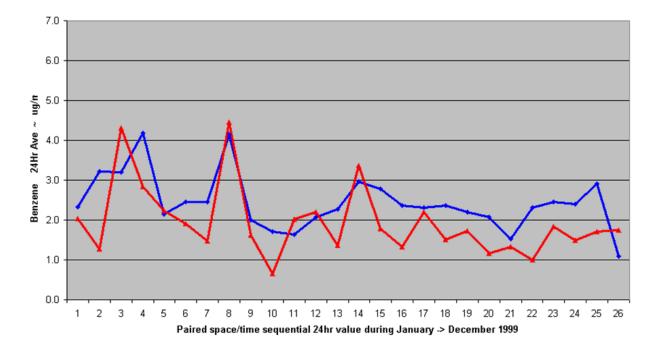


Figure 12

MODELED vs MONITORED Benzene 24Hr Average Impacts
26 Dates during 1999 Monitored at "old" S. Winooski Ave Site
Source Categories Modeled: On-Road, Gas Stations, Residential Heating, McNeil Generating
Plant & Exxon/Mobil Terminal

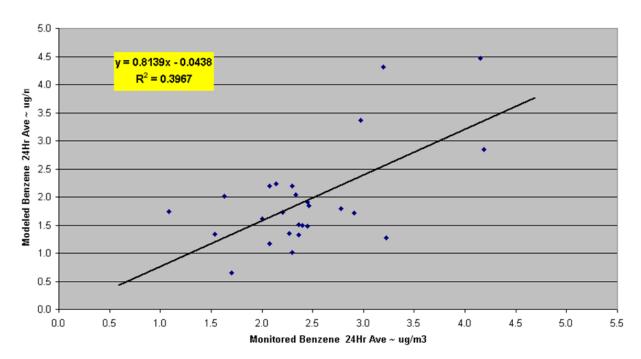


Figure 12 shows a linear regression of the modeled vs. the monitored 24-hour benzene concentration values. The model has performed reasonably well in matching the monitor values with the linear relationship passing through the graph origin at 0:0 as it should if most of the significant sources affecting the monitored value have been accounted for in the model. The slope of 0.8 is close enough to 1.0 for us to be encouraged that results are not overly biased at the higher predicted values. The R-squared value of 0.3967 is not as good as one would hope for, and it implies that the variability of over-prediction and under-prediction of short-term 24-hour benzene levels, though balancing out through the year, does not give us great confidence in any single predicted value. This is to be expected for such a complex set of sources with a great many assumptions having gone into setting the hourly emissions for each of them.

Long-Term (Quarterly 3-month Average) Concentration Predictions:

Longer term averages smooth out the variability of the shorter time periods so it is expected that the model predictions averaged over longer time periods should better match the actual monitored levels.

Figures 13 through 16 show the quarterly pattern of predicted 24-Hour ambient benzene concentrations at five of the discrete receptors used in the evaluation phase of the modeling. The 24-Hour values presented in these figures are "7-day running averages". This averaging allows us to examine the longer period trends of the model prediction throughout each quarter of the year. In all of these figures, the South Winooski Monitoring Site is identified as one of the receptors plotted and it is shown in the color black. Note that of the five chosen receptors shown, the S. Winooski monitoring site is always the highest predicted value from the model. This is only fortuitous, but it also indicates that the criteria used to site the monitor back in 1993 was well informed about the potential for measurement of highest impacts in the urban area. Generally, of the five receptors shown here, for which complete annual hourly modeled results were obtained, the Park Street residential location is seen to be the location with the next highest ambient benzene levels predicted, followed in order by the Medical Center Hospital location, the North Avenue residential location, and the Winooski High School location. These are simply five pre-selected locations used to illustrate the differences in the predicted annual benzene levels within the modeled domain. No special significance should be attached to these sites except that they were selected as representative of different types of localities in the domain to allow the APCD to draw generalized conclusions about the nature of the various source category impacts throughout the domain.

One characteristic of the patterns seen in these figures is that the 7-day average trend at each of the five locations appears to be correlated well with the others. When a period of predicted high concentration of benzene is indicated for one site it is also predicted for the other four sites as well. This probably is indicative of the ubiquitous nature of the most influential benzene source category, on-road motor vehicle traffic exhaust, as well as the fact that **much of the variation from day to day within the domain depends on meteorological factors**. Periods with higher wind speeds and therefore more ventilation of air into and out of the domain at faster rates would tend to produce less build up locally of the locally emitted benzene, or vice-versa.

Figure 13

1st Quarter MODELED 7-day Running Averages for 5 Locations

The 7-day averages shown plotted do not include any assumed non-local background



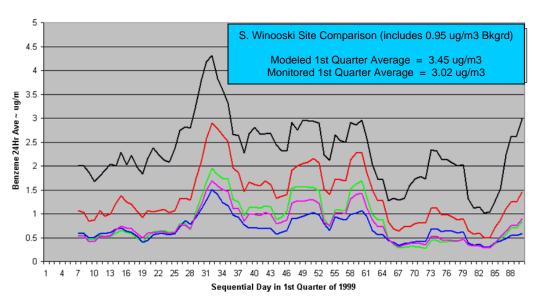


Figure 14

2nd Quarter MODELED 7-day Running Averages for 5 Locations

The 7-day averages shown plotted do not include any assumed non-local background



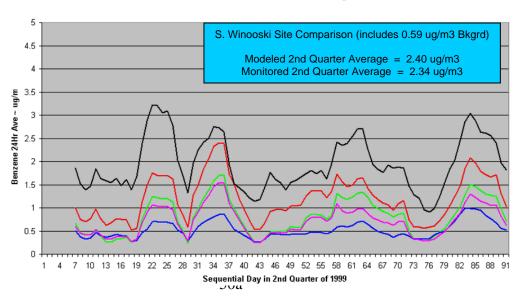


Figure 15

7-day Running Averages for 5 Locations 3rd Quarter MODELED

The 7-day averages shown plotted do not include any assumed non-local background

July-August-September Modeled Benzene 7-Day Running Averages ----- S.Winooski Monitor ----- Park Street Residential - Medical Center ---- North Avenue Residential ----- Winooski High School

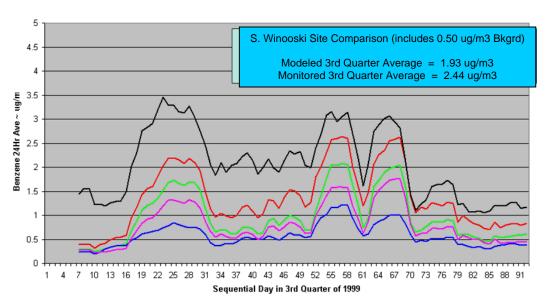
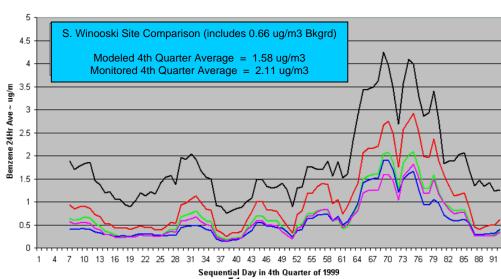


Figure 16

4th Quarter MODELED 7-day Running Averages for 5 Locations

The 7-day averages shown plotted do not include any assumed non-local background

October-November-December Modeled Benzene 7-Day Running Averages ----- S.Winooski Monitor ----- Park Street Residential - Medical Center --- North Avenue Residential ----- Winooski High School



Another meteorological parameter important in determining the ambient concentration levels of air contaminants at the earth's surface is the **effective "mixing height"** of the atmosphere during any given hour. The "mixing height" is the depth of the atmosphere above the ground surface in which the air is rapidly mixed vertically. Pollutants emitted into this mixed layer are dispersed and mixed vertically up to the mixing height but do not mix into those portions of the atmosphere above it. The top of the mixed layer is located physically as the height at which thermal buoyancy is not strong enough to allow the rising air parcels to move higher. This vertical level is sometime referred to as the location of an "inversion" due to the fact that the temperature of the atmosphere above the inversion layer is greater than the temperature of the atmosphere below it, whereas within the mixed layer the temperatures aloft are lower than those below. The lower the mixing height, the higher will be the likelihood of ambient air pollutant concentrations increasing at ground level. For the Burlington modeling domain, the incidence of Lake Champlain significantly affects calculation of mixing heights because of differences in surface heating, and indirectly influences the atmospheric wind field. Figure 17 below is a depiction of the diurnal variation in mixing height computed by CALMET for the downtown Burlington monitor location, and for an arbitrary point in the domain over the Lake.

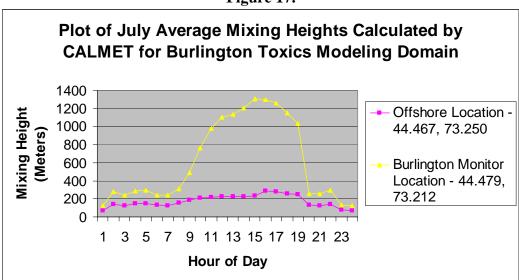


Figure 17.

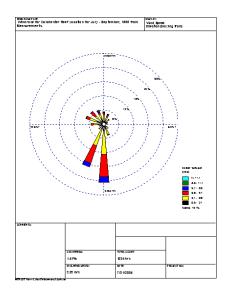
Note that model calculated mixing heights are much lower over the water in the daytime. When winds hold a trajectory from over the Lake to Burlington, the CALPUFF model will 'transport' the lower mixed height from over water to overland locations. However, the effect on overall modeled concentration predictions of the lower mixing height values is offset because of the obvious lack of emission sources when the wind is from the over lake directional sectors.

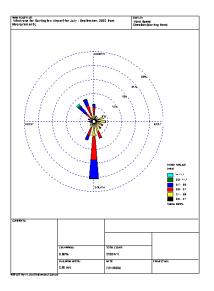
Therefore no consistent relation between mixing height values and modeled benzene concentrations exists. Further, it appears likely that no significant offshore lake breeze exists in Burlington.

<u>Figure 18,below, contains windroses of the measured surface winds for 1999 that were used to produce the gridded surface wind fields in CALMET.</u>

<u>Figure 18. July – September Windroses</u> (Colchester Reef (1999 data))

(Burlington Airport (2002 data)





The data constituting these plots was also utilized by CALMET to generate an interpolated domain wind field which also accounts for terrain effects. To examine the incidence of any 'lake breeze', Measured windfields were also plotted for day versus night time for the summer at the Colchester Reef measurement site and it was noted that there is no significant incidence of 'onshore' and 'offshore' winds for this location, where onshore winds would be from the easterly sector during the nighttime, and offshore winds from the west in the daytime.

To further examine the significance of any 'lake breeze' on benzene concentrations in Burlington, an examination of the variation of hourly CO concentrations by wind direction was performed, where it can be assumed the CO is a surrogate for benzene from the primary emissions category, mobile sources.

Hourly CO concns for 1999 were 'binned' and averaged by wind direction for the Colchester Reef site, to ascertain possible pollutant concentration relationships to wind direction because of source locations, and differences in mixing height and other meteorology for over-lake versus over-land areas. Hourly Wind Direction values were defined as offshore, onshore, Northerly, and South through Southeasterly to exclude directional sectors not definitively on or off shore, and to separately examine CO concentrations for the S thru SSE wind directions that are often so prevalent).

<u>The average CO concentrations calculated for these categories were rather uniform across Wind Direction:</u>

average CO for onshore wd eq = 0.45 average CO for offshore wd eq = 0.48 average CO for SSE wd eq = 0.45 average CO for N wd eq = 0.50 Therefore, as discussed above, it is difficult to draw any conclusions regarding likely correlation of benzene concentrations to the meteorological measures of wind direction and mixing height, especially because of the proximity of Lake Champlain to Burlington.

For wind speed, however, a correlation **does** exist in both modeled and measured wind speed vs. benzene plots. In the figure 19 (below)., the 24 hourly average benzene is plotted against measured wind speed.

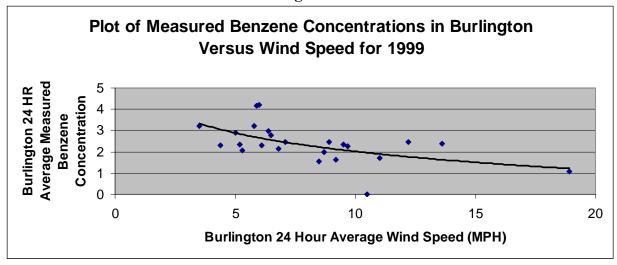


Figure 19.

<u>Similarly, figure 20</u> . is a plot of modeled benzene concentrations for December 12 and 13, when maximum benzene concentrations were predicted by CALPUFF.

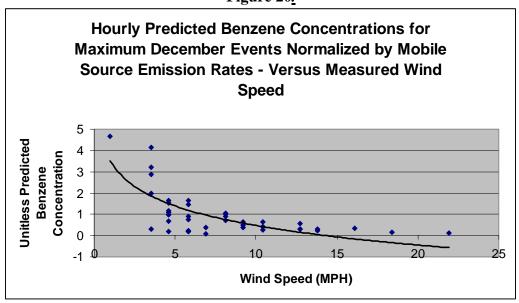


Figure 20.

In Figure 13 it can be seen that for all the discrete receptor sites tracked on the time-series, the time period ending around January 30 (the 30th day of the 1st quarter) is a time period when 7-day average ambient benzene concentrations were predicted to be highest for that quarter. Unfortunately there is no specific benzene measurement for the time period from January 24 to February 17. However, examination of the actual meteorology on January 30 identifies it as a date when wind-speeds in the domain were unusually low. Because there is apparent consistency between the expected model result for very low wind speeds and the low wind speeds seen from actual meteorological measurements on that date, the level of confidence about how the model is performing is enhanced. Two similar events are predicted by the model for the time period between December 9 and December 18 (between the 70th and 79th days of the 4th quarter).

Figures 13 through Figure 16 also show the quarterly average value predicted by the CALPUFF model compared to the quarterly average monitored value at the South Winooski & Bank Street monitoring site. This comparison appears in the blue box on each running average plot. The model has performed very well in capturing the quarterly average monitored, especially for each of the first two quarters.

(Please note that the 7-day average plots shown in these figures are purely the running averages of the model prediction <u>without</u> any non-local background added in. To represent a total benzene for comparison to monitored data, the quarterly average value comparison in the blue box on each figure was created using a quarterly regional background additive value derived from Underhill, Vermont measurements.)

The actual values monitored at Underhill, Vermont on the same Burlington sampling dates have quarterly average benzene values as follows:

Underhill background		_	_	_	_
benzene	Annual	Quarter 1	Quarter 2	Quarter 3	Quarter 4
Annual & Quarterly					
Averages	0.667 ug/m3	0.948 ug/m3	0.586 ug/m3	0.502 ug/m3	0.656 ug/m3

Table 6 summarizes the quarterly average modeled value comparison to measurements at the S. Winooski & Bank Street monitoring location for 1999.

Table 6
South Winooski & Bank Street Monitoring Site
Model vs Monitor Comparison

Quarter during 1999	Monitored Benzene	Modeled Benzene
	Quarter Average ug/m3	Quarter Average ug/m3
1 st	3.02	3.45
$2^{\rm nd}$	2.34	2.40
$3^{\rm rd}$	2.44	1.93
4th	2.11	1.58

Comparative Modeled Impact from Each LOCAL Source Category:

The culpability for benzene impact at the selected discrete receptors during 1999 was determined by comparing the individual model runs conducted using each of the categories of sources separately. Although more than 15 or 20 separate groupings of sources were actually modeled in distinct runs, it is most useful to look at five groupings of these distinct runs that essentially separate each of the types of sources as follows:

Group 1: All Urban Traffic emissions within the 1.2 x 1.2 km central urban core. Group 2: All Other Traffic emissions in domain outside this central urban core.

Group 3: Home-heating emissions.

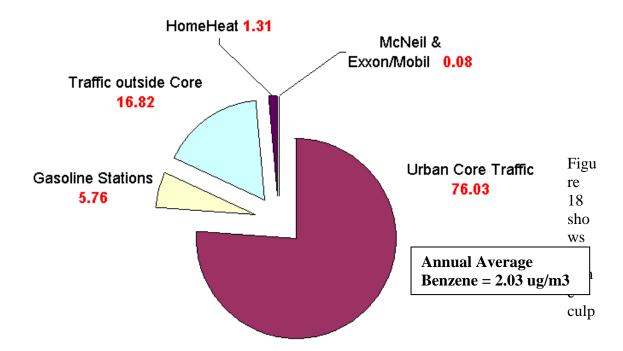
Group 4: Gasoline Service Station emissions.

Group 5: Significant point sources (McNeil Plant & Exxon/Mobil Terminal).

Figure 21 shows the culpability for the ambient annual benzene modeled at the South Winooski & Bank St. monitoring site during 1999. The **percentages** contributed by each of the five source groups **represent only the portion of the measured benzene which is contributed by local sources and do not include any contribution from non-local sources (regional background influences).** The local portion of the annual average benzene modeled amounts to an annual average of 2.03 ug/m3 predicted at 1 meter height during 1999 at the monitor site.

Percentage of Ambient Benzene Impact due to Source Category
S. Winooski Monitoring Site

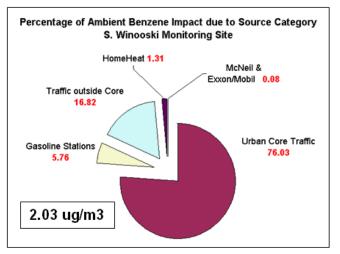
Figure 21

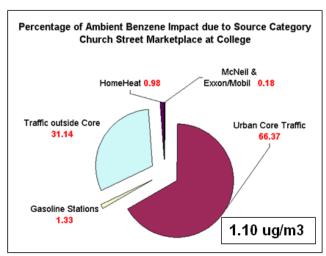


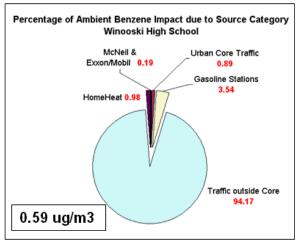
ability breakout for three other of the discrete receptor locations chosen for examination by the model in the evaluation phase of modeling. These locations include the Church Street & College Street intersection, Winooski High School, and Medical Center Hospital. The benzene annual averages indicated in **Figures 22 to 25** are predicted values for 1 meter heights at these locations and **do not include any added non-local background value**, the value shown being only that modeled for the five source groups identified.

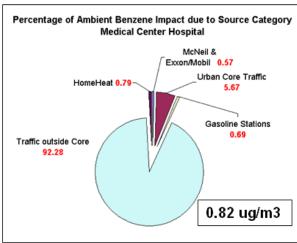
Annual Average Modeled Impacts at 4 Locations in Domain

Figures 22-25









Figures 26 and 27 show the culpability breakout for the two "residential" type neighborhoods identified as discrete receptor locations. These are distinguished from each other by the nature of traffic and land use in their vicinity. The **North Avenue residential location (Fig. 26)** is quite suburban in character and not much influenced by the urban core traffic. The **Park Street residential location (Fig. 27)** is on the edge of the densely populated urban-center on a one-way

street that has the particular characteristic of feeding quite heavy traffic flows southward into the city from points to the north-west, including traffic from Route 127 through the Intervale.

Figure 26
Percentage of Ambient Benzene Impact due to Source Category
North Avenue Residential

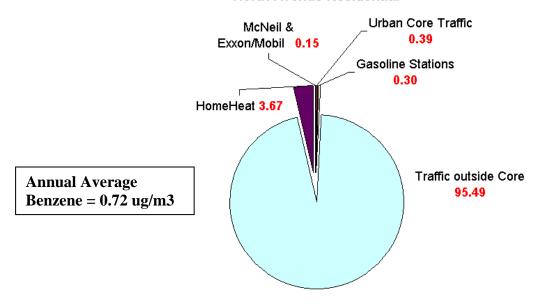
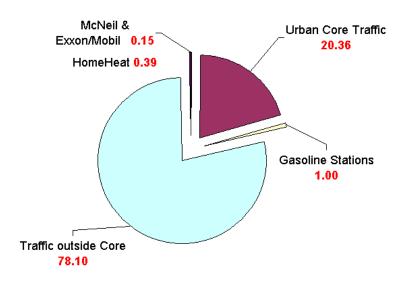


Figure 27

Percentage of Ambient Benzene Impact due to Source Category

Park Street Residential



Finally, the last figure in this set of results, Figure 28, shows the breakout of influence at the location of the new monitoring site which began collecting ambient benzene data during 2003. Figure 21 displays model results for this discrete receptor which represent the pattern of what would likely have been contributed to a monitor at this location from local sources of benzene in 1999. These modeled results may be useful for interpreting the new benzene data-set that is being accumulated by the monitor now operating there.

Figure 28

Percentage of Ambient Benzene Impact due to Source Category

New Monitoring Site S.Winooski & Main St.

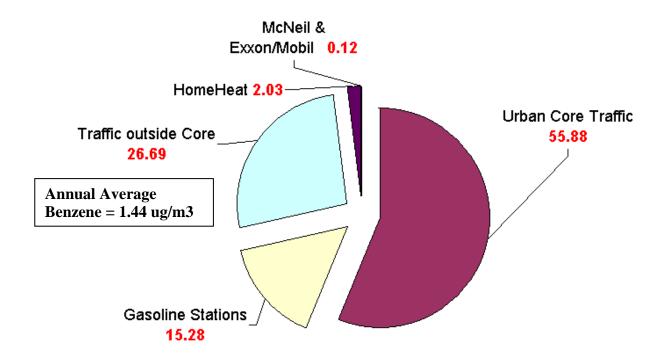


Figure 28 indicates one possible consequence of moving the monitoring location south on South Winooski Street from the Bank Street intersection to the Main Street parking lot; there is a higher % influence of gasoline service station emissions predicted at the new site than the old.

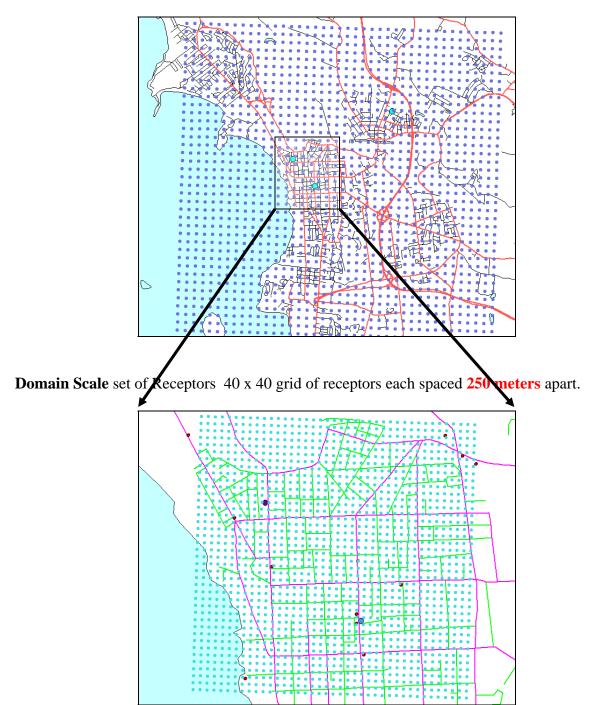
Gridded Receptor Modeling Results:

After completing evaluation of the CALPUFF modeling system at the nine discrete receptors discussed in the previous section, the modeling study began a 2nd phase of assessment in which instead of only a few discrete selected locations being used as receptors, grids of evenly spaced receptors were placed in the model system. Model performance can only be judged if actual measurements are available to evaluate the predictions. This was the case for the evaluation phase modeling at the single discrete receptor located at the monitor site. For gridded receptors,

none is at a location where monitored data exists, but based on the evaluation phase carried out, we have confidence that the model is working quite well and that the gradients of concentration defined by the gridded sets of receptors represents realistic patterns defining the differences in ambient benzene concentration likely to be experienced across the domain.

A cautionary remark with respect to gridded results: Gridded receptors are generated at equal intervals in a matrix from east to west and north to south. Where any particular receptor falls in the matrix has not been selected based on actual topography, land-use, or source distribution. If a particular receptor happened to be positioned very close to the location identified for a gasoline service station for example, it is likely that the model would predict much higher ambient concentrations at that receptor than other receptors surrounding it. The purpose of the model code is to disperse highly concentrated pollutant emissions from a source or multiple sources to emulate the effects of the real atmosphere on the concentration as the pollutant is carried on winds to other parts of the domain. The intent of the gridded receptor matrix is to be able to construct isopleths of constant ambient benzene concentration so that relative exposure to benzene might be roughly depicted over the entire domain. An individual receptor un-intentionally located right on top of an emission source should not be given equal consideration to all others in creating the overall domain-wide relative exposure pattern. The isopleths of constant concentration depicted in the figures associated with gridded receptor results in this study have been smoothed through typical averaging techniques to better depict the relative nature of concentration patterns rather than to identify the highest predicted impact locations.

Two Standard Sets of Gridded Receptors Used in this Study 1600 receptors at Domain Scale & also at Urban Scale



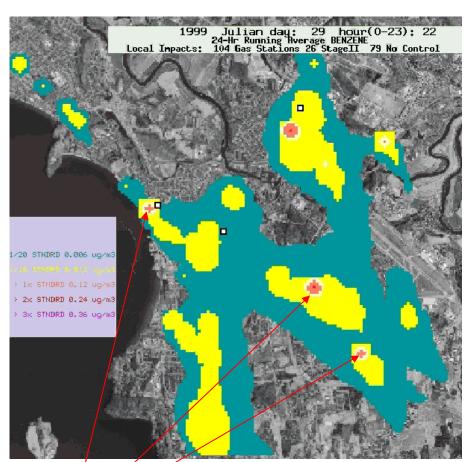
Urban Scale set of Receptors 40 x 40 grid of receptors each spaced 50 meters apart.

Besides the two standard sets of gridded receptors, a number of other specialized receptor sets were used in this phase of the study. Each set of receptors reflects the scale of detail which was desired for a particular reason. Receptor grids covering the entire domain modeled must be spaced further apart if model run-times are to be kept within reasonable limits. Sensitivity testing of various gridded receptor sets led us to conclude that the maximum number of receptors would have to be limited to 1600. Even with this limitation, running CALPUFF with the full set of benzene sources required time periods too long to be able to complete runs for the entire year using gridded receptor output. Detail within very small portions of the domain around specific subsets of sources could be produced for an entire year using a maximum of 400 receptors in a grid. The following examples show the standard receptor grids established for this phase of the modeling study.

APPROX. FULL DOMAIN SCALE GRIDDED RECEPTOR OUTPUT EXAMPLE

For <u>receptor grid modeling on</u> the scale of the entire domain we used a matrix of 40 x 40 (1600 total receptors) spaced <u>250</u> meters apart to cover a 10km x 10km portion of the domain focused on urban Burlington in general. This left the edges of the full domain without receptors, primarily those edges to the south and east.

1600 gridded receptors was the practical limit for reasonable model run-times.



Isopleths defined by color patterns showing areas of impact from Gasoline Service Stations in the domain.

For a more **detailed look at the down-town urban center** of Burlington a more densely spaced gridded set of receptors was used for that portion of the domain including the urban core roads.

URBAN-CORE SCALE GRIDDED RECEPTOR OUTPUT EXAMPLE

A matrix of 40 x 40 (1600) total receptors) spaced **50** meters apart to cover a 2km x 2km portion of the domain was used. This receptor grid was centered roughly on the monitor location and Church Street receptors.

The colored patterns of isopleths show the extent of areas of concentration greater than various levels of ambient benzene compared to the Vermont Hazardous Ambient Air Standard. In this example, the benzene impact from 15 gasoline stations is shown.



South Winooski & Bank Street Monitor

50m spaced 400 RECEPTOR **GRIDDED OUTPUT EXAMPLES**

Several smaller 400 receptor grids covering 1km x 1km portions of the domain were also useful for examination of particular groups of individual sources for time periods longer than one month. These receptor sets helped us identify the spatial influence of certain types of activity, a single section of road carrying traffic for example, or the two most significant point sources of benzene in the domain. Three examples of applications run on selected sources are shown below.

Example 1: Exxon/Mobil Bulk Gasoline Terminal

In the first case, the combination of point and area sources associated with the Exxon/Mobil Bulk Gasoline Terminal was run for the entire year of 1999. The example output shown represents the 24-hour average benzene concentration field surrounding the plant for the time period ending at 1 am on January 2, 1999.

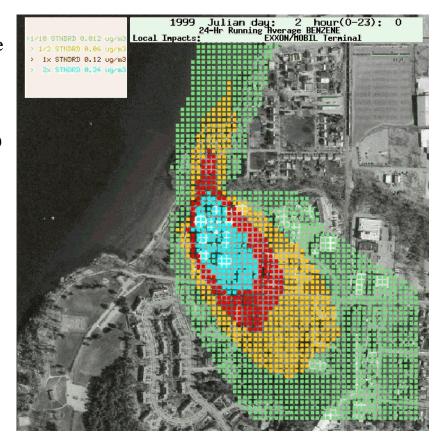
[note that Exxon/Mobil emissions modeled were not based on gasoline stored or unloaded specific to that date, but only representative of the average daily situation in January derived using annual gasoline and fuel oil throughput at the facility allocated to months and also using assumptions about diurnal cycles of activity: meteorology was representative of the specific date but again was derived from a small amount of actual surface measurement data and windfields derived from that measurement data and other physical parameters]

This example serves to illustrate the approximate spatial extent of the short-term (24-hour average) impact on ambient benzene by this single industrial facility.

Exxon/Mobil Bulk Gasoline Terminal

24-hour average benzene concentration field

For these situations, a matrix of 20 x 20 (400 total receptors) spaced **50 meters apart** to cover a 1km x 1km portion of the domain was used.



Example 2: Two Gasoline Service Stations (without STAGE II Control)

In this second case, average monthly throughput at two of the gasoline service stations which had not been required to apply Stage II vapor controls on their gas pumps by 1999 was modeled. These two gasoline stations were located in the northwest portion of the urban-core. The output shown represents the 24-hour average benzene concentration field surrounding these two gasoline stations for the time period ending at 7 pm on January 2, 1999.

[In the case of these two gasoline service stations, the average emission rates per hour were derived from specific data on January 1999 throughput at these stations. Assumed diurnal patterns of activity at the station were based on traffic counts on urban roads]



Example 3: Small Section of Urban Road (Vehicle Exhaust)

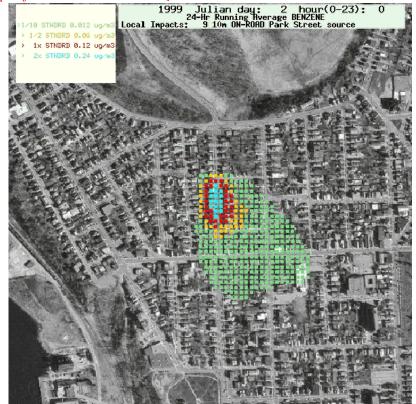
In order to determine the extent of <u>on-road motor vehicle exhaust benzene impacts in the vicinity of a specific roadway</u>, a subset of the 10 meter area sources representing a 90 meter section of road in the urban core portion of the domain along Park Street was created and modeled with a gridded set of receptors. Nine of the 10m x 10m "area sources" described in Figure 4 were chosen from the portion of Park Street running past the discrete receptor location previously selected for inclusion in the evaluation of the model. Thus a 90 meter portion of Park Street, with its estimated traffic flow based on Agency of Transportation Traffic Research

Section data applied to the location and type of road, was modeled for the entire year of 1999. The output shown represents the 24-hour average benzene concentration field surrounding this section of Park Street for the time period ending at 1 am on January 2, 1999.

[The average emission rates from vehicles traveling on Park Street were derived from average annual vehicle miles traveled (VMT) data that is adjusted to monthly values in Chittenden County based on Park Street's road classification. Assumed diurnal patterns of activity on Park Street were based on traffic counts on representative urban roads. The allocation is part of a VTAPCD procedure for creating state-wide on-road inventories. This method is necessary to create on-road inventories covering large parts of the state because the task would be prohibitive from a resource perspective if more detailed road-specific vehicle count data were available everywhere, which it is not. It may be possible to obtain day-specific traffic data for certain roads and time periods and to utilize day-specific data in creating the emission input "area sources" for small portions of roads. Park Street does have some actual hourly traffic count data for short time periods during 1995, 1996, and 1997, but using this data would not produce verifiable results for the main purpose of this study because there is no monitoring data available at this location for the same time periods. The CALPUFF platform is now available for further examination of road related air pollution should future specific studies be warranted]

24-hour average benzene concentration field

The receptor grid was comprised of a matrix of 20 x 20 (400 total receptors) spaced **50 meters apart** and covering a 1km x 1km portion of the domain centered on the Park Street residential site of the discrete receptor used in phase I evaluation modeling.



Gridded Modeling For Estimation of Human Exposure

Background Discussion:

Health effects of benzene are likely related to long-term exposure (represented by an annual average concentration exposure for example) rather than short-term periods such as a 24-hour period or a month. This contaminant is identified as one which causes increased risk of cancer. The standard established in Vermont regulation is an annual standard set at 0.12 ug/m3. To determine whether a particular location has ambient benzene levels in excess of the standard, measurements are made as frequently as practicable over a long time period. Benzene is only one of a number of volatile organic compounds for which it is desirable to take measurements in the ambient air to determine compliance with hazardous air contaminant standards. Many of these volatile organic compounds (VOCs) can be measured using the same sampling and analytical methodology.

Measurement Method for Benzene:

The methodology used for determining ambient benzene concentrations (and other VOCs) involves the use of an automated canister sampler located inside the shelter at the monitoring site location. Ambient air is drawn into the shelter through a common manifold where a portion is withdrawn at a known and constant flow rate by the canister sampler and diverted into a cleaned and evacuated specially-prepared 6-liter stainless steel canister. The sampler automatically begins and ends sample collection over a 24-hour period from midnight to midnight. The sample contents are identified and quantified in a laboratory using a gas chromatography/mass spectrometry (GC/MS). This method is very resource-intensive; therefore samples collected are limited to a regularly scheduled sample every 12 days throughout the year. Each calendar year a total of about 30 samples are collected and analyzed in this way.

Estimation of Human Exposure from Ambient Measurements:

The "annual average" measured ambient benzene at the sampling location is determined as a simple average of the 30 or so samples. If this average is greater than 0.12 ug/m3 (the standard established in Vermont Air Pollution Control Regulations) then we believe that human exposure for someone living primarily at that location (or locations with similar ambient benzene levels) would be at more than one in a million risk of getting cancer from the benzene exposure alone.

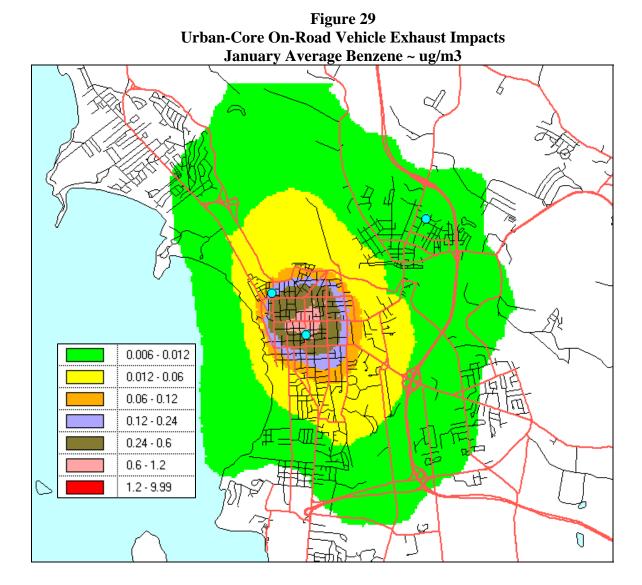
It is difficult and very costly to sample at many locations, especially when all sampling should be done during the same 24-hour time periods to get spatial patterns, even though this might only be done every 12 days. By using a model such as CALPUFF (set up to predict spatial and temporal ambient concentrations of a contaminant such as benzene) that has been evaluated and judged to perform well when its predictions are compared to measurement data at one or more locations, it is possible to extend the information we have about the concentration of benzene over a larger area than just the location of the actual measurements. This is the primary purpose of the current modeling study.

Maps which show patterns of monthly average benzene concentration in the modeling domain for the month of January 1999 follow. These maps represent only the first month of a set of 12 monthly patterns that will eventually be produced for the Burlington modeling domain. The January maps still cannot completely describe the locations across the Burlington area in which human risk from ambient benzene exposure alone would be relatively defined. An average even from the full 12 months of 1999 would still only represent a partial exposure estimate for this area, since emissions patterns and meteorological patterns may change over years. Nevertheless, the patterns of estimated benzene exposure for people living within the Burlington area are better described by the modeled benzene concentrations for the single year of 1999 (and to a lesser extent, the patterns for the single month of January 1999) than they could have been otherwise using only a single monitoring site with approximately 30 samples annually as reference.

Spatial Influence of Each of the Five Source Groups on Monthly Average Ambient Benzene Concentration: 250 Meter Spacing of Gridded Receptors

Modeling has not yet been completed on a gridded basis for the full 12 months that the model is now capable of examining. Spatially gridded results for a 10 km x 10 km portion of the domain representative of the month of January 1999 are presented below.

In Figures 29 through 34, the color scale representing ug/m3 is the same for each figure.



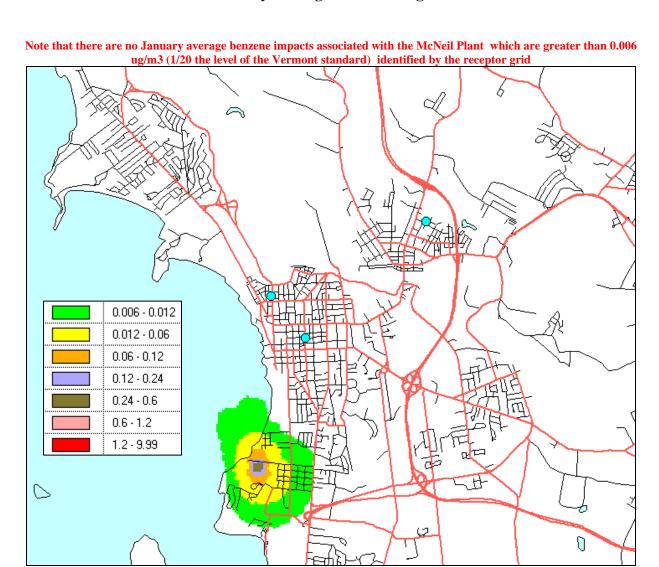
Gasoline Service Station Impacts

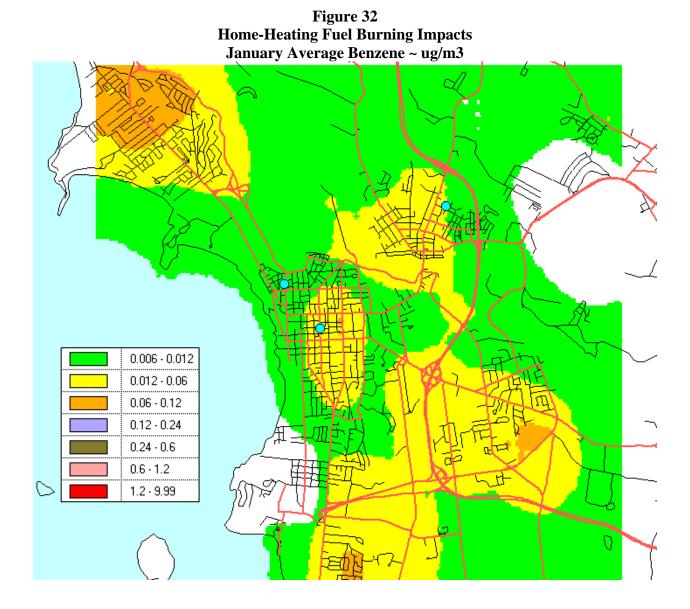
January Average Benzene ~ ug/m3 Approx. 12 Kilometers 0.006 - 0.012 0.012 - 0.06 0.06 - 0.12 0.12 - 0.24 0.24 - 0.6 0.6 - 1.2 1.2 - 9.99 O

Figure 30

70a

Figure 31
Exxon/Mobil Bulk Terminal & McNeil Plant Impacts
January Average Benzene ~ ug/m3





72a

Figure 33 Non-Urban Road Vehicle Impacts January Average Benzene ~ ug/m3

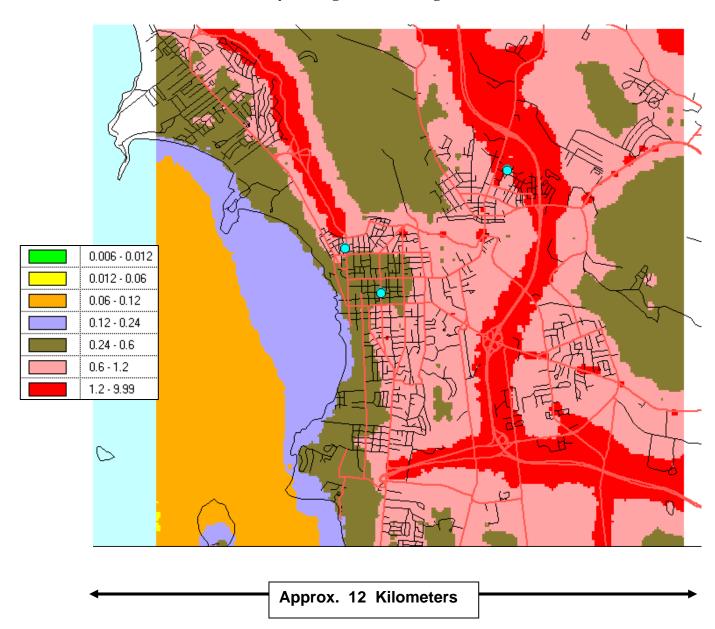
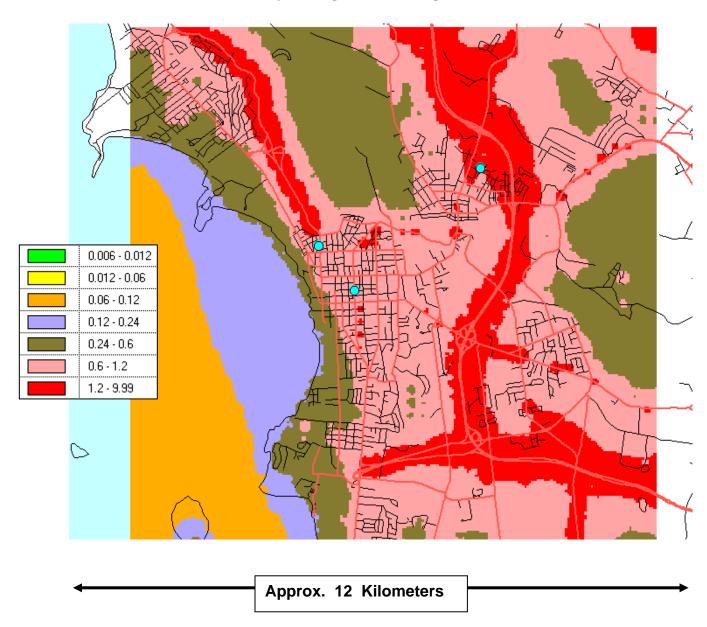
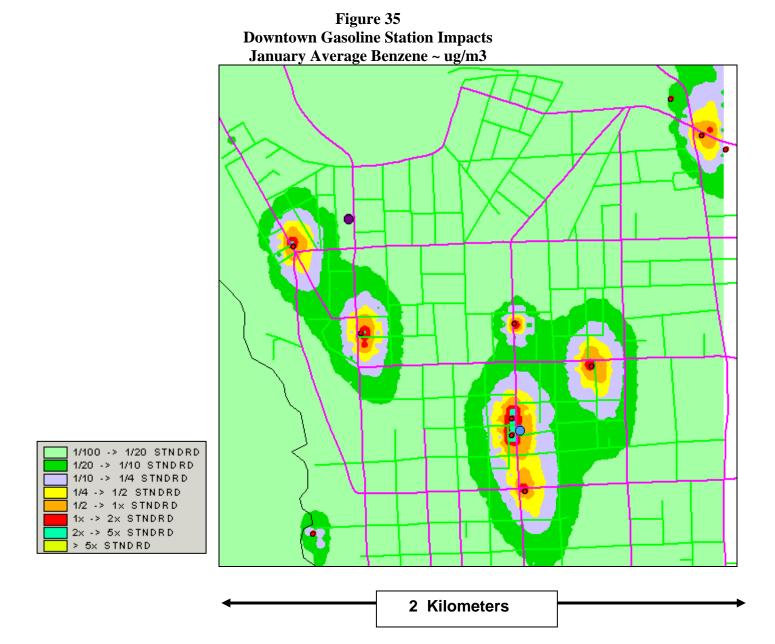


Figure 34
ALL LOCAL SOURCE CATEGORY Impacts
January Average Benzene ~ ug/m3



Refined Spatial Influence of Selected Sources on Monthly Average Ambient Benzene Concentration: <u>50 meter spacing of Gridded Receptors</u>



90 Meter Length of Park Street / On-Road Traffic Impacts January Average Benzene ~ ug/m3 1/100 -> 1/20 STNDRD 1/20 -> 1/10 STNDRD 1/10 -> 1/4 STNDRD 1/4 -> 1/2 STNDRD 1/2 -> 1× STNDRD 1× -> 2× STNDRD 2x -> 5x STNDRD > 5x STNDRD

2 Kilometers

Figure 36

Figure 37
Monthly and Annual average benzene concentration patterns due to emissions from the Exxon/Mobil Bulk Gasoline Terminal:

JANUARY

1/19 STNDRD 9,912 Ug/m3

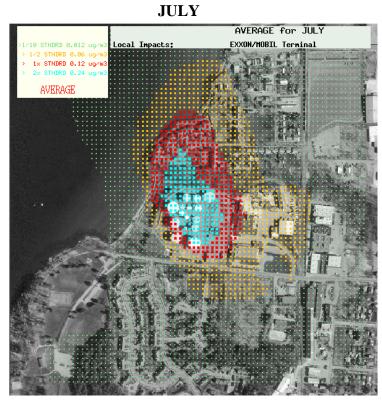
> 1/2 STNDRD 0.96 Ug/m3

> 1x STNDRD 0.12 Ug/m3

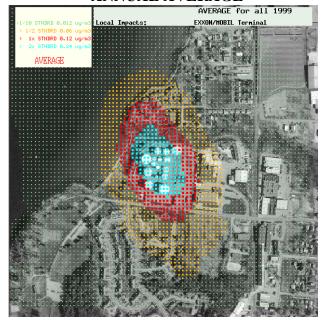
AVERAGE

AVERAGE

AVERAGE



ANNUAL AVERAGE



SHORT-TERM Modeling Results:

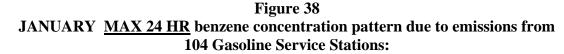
Although short-term ambient concentration impacts of benzene from the local source categories modeled are not directly compared to the Vermont hazardous ambient air standard for benzene (because the standard is a long-term annual average concentration), it is useful to look at gridded model results which show both <u>average daily</u> (24-hr) scale impacts as well as <u>maximum daily</u> impacts.

24-Hr Average Daily Results:

In the case of the 24-hr average, the patterns produced illustrate the extent of influence on an average day. These gridded short-term modeling results for the whole Burlington domain are currently only available for January 1999. A number of subsets of sources have been modeled with gridded daily output for other months of the year. These gridded results are centered on specific locations such as Essex Five Corners and may include only a limited number of nearby gasoline stations as modeled sources for example. The average daily gridded results may be best interpreted visually using snapshot maps created sequentially for an entire month which are then put together into a movie which sequences through the daily maps. A number of these movie sequences have been created to date. They are being placed on an internet accessible Web Site with the following URL.

24-Hr Maximum Daily Results:

In the case of the maximum daily plots shown below, the pattern represents the maximum 24-hour average benzene experienced during the month of January at each location in the domain. These maximum impacts do not necessarily occur at the same time everywhere. The time (day) of maximum impact at any particular location is to a great extent determined by the meteorological conditions which are most conducive to high ambient benzene concentration at that location, which is a function of which way the winds were blowing on each day and the wind speed as well. If on a particular date winds happen to be persistent for the whole 24 hour period from a particular direction transporting benzene from an emission source to the location, it is likely that that date will show a period of maximum impact there. The maximum daily impact patterns show the highest benzene concentrations at each location relative to other locations, but they are not a snapshot in time since these maximum at various locations do not necessarily occur during the same hour or day. They are useful in identifying locations with absolute maximum short-term ambient benzene concentration potential.



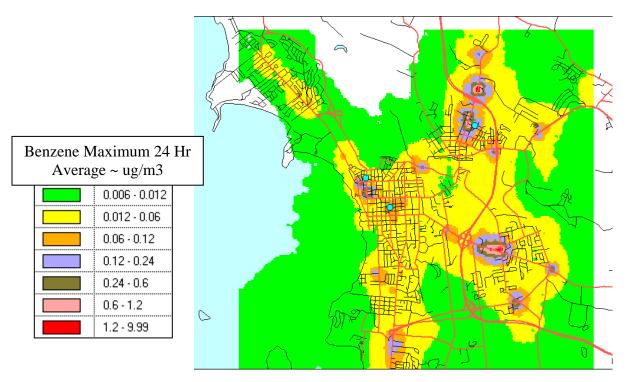
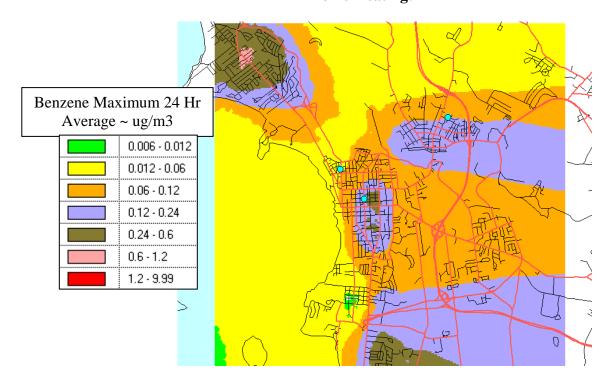
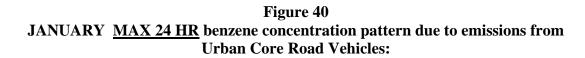
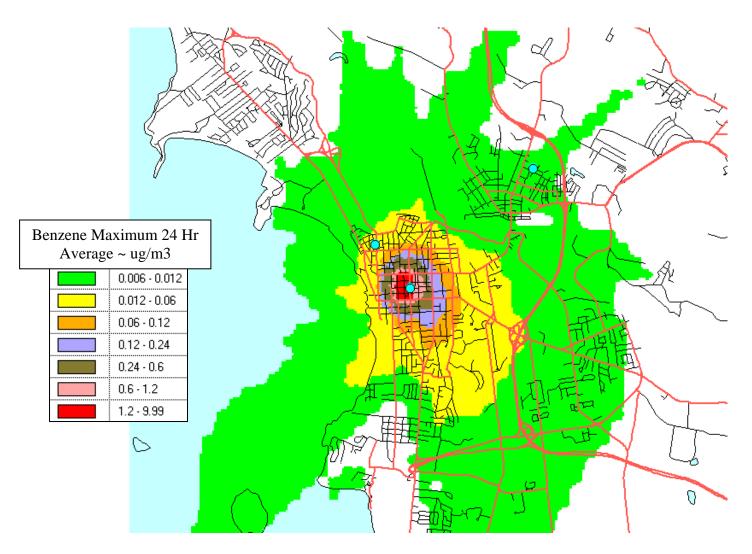


Figure 39

JANUARY MAX 24 HR benzene concentration pattern due to emissions from All Home Heating:







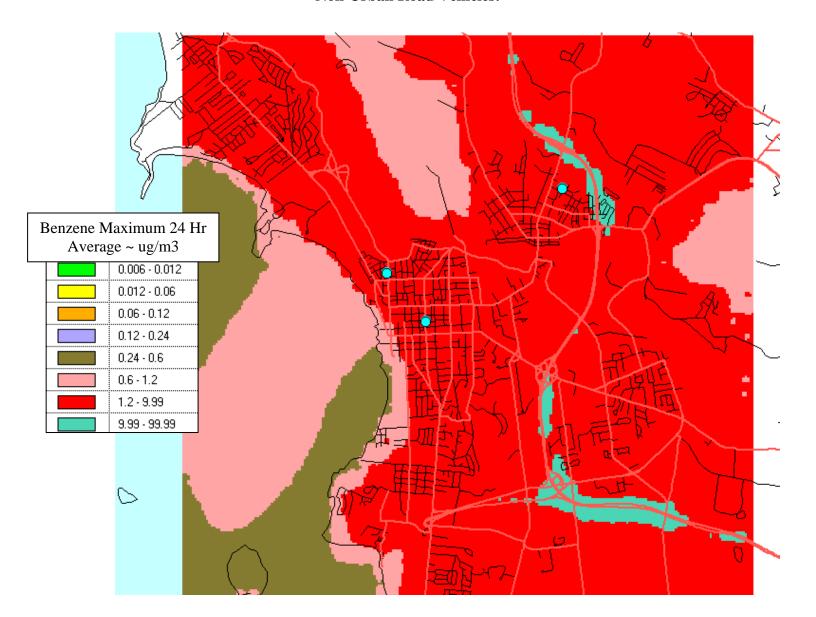


Figure 41

JANUARY MAX 24 HR benzene concentration pattern due to emissions from Non-Urban Road Vehicles:

Future Extensions of this Modeling Study:

Modeling with the platform developed so far will continue. The meteorological inputs are applicable to other sets of emission inputs. For example, other motor vehicle related air contaminants may be examined. Levels of fine particulate matter (particles in the air with size less than 2.5 micrometers in diameter) across the domain may also be examined. The model may also prove useful in forecasting periods of elevated air pollution in Burlington. Forecasting

could only be developed with additional local-scale meteorological wind field development capabilities based on National Weather Service prognostic model data.

Completion of the full year of gridded benzene outputs will be the primary first objective of the use of the CALPUFF Model now available for the Burlington urban area in Chittenden County.

References:

- (1) "Toxicological Advisory Committee Air Toxics Report", prepared for State of Vermont Agency of Natural Resources, February, 1998.
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- (3) "Mobil Oil Corporation Burlington, Vermont Gasoline Terminal Air Toxics Modeling Analysis Report", 12 April 1999, Radian International
- (4) "Benzene, Toluene and Xylene Measurements in the Vicinity of Petrol Stations", P. Perez Ballesta and E. De Saeger, European Commission Joint Research Centre Environment Institute publication EUR 16309 EN, 1995.
- (5) "Urban Benzene and Population Exposure", brief communication, Cocheo, Sacco, et. al. NATURE, Vol 404, March 9, 2000, www.nature.com, 2000 Macmillan Magazines Ltd.
- (6) "Human Exposure to Traffic Pollution, Experience from Danish Studies", Hertel, Jensen, Andersen, et.al., Pure Appl. Chem., Vol 73, No. 1, pp. 137-145, 2001, 2001 IUPAC.
- (7) "Motor Vehicle-Related Air Toxics Study", Technical Support Branch, Emission Planning and Strategies Division, Office of Mobile Sources, Office of Air and Radiation, U.S. Environmental Protection Agency, April 1993.

Appendix B

Production of Meteorological Fields for the Ambient Benzene Modeling Study in Burlington, Vermont.

May 19, 2009

Daniel Riley, Air Pollution Meteorologist

Air Pollution Control Division (APCD)
Department of Environmental Conservation
Vermont Agency of Natural Resources

Introduction

A previously completed modeling study of benzene in Burlington ("Ambient Benzene Modeling Study CHITTENDEN COUNTY, Final Report, July 2005"), occurred which was closely related to the current Benzene modeling study, especially in some of the fundamental aspects of the preliminary meteorological fields production. For purposes of clarification, hereafter the preliminary 2005 study will be referred to as 'Phase I' of the current ambient benzene modeling study.

The ambient benzene modeling study utilized the CALPUFF modeling system to model the transport and dispersal of benzene emissions. Therefore this report focuses on proper set up and usage of CALMET, the meteorological preprocessor fundamental to the CALPUFF modeling system.

The CALMET meteorological processor is a key component of the CALPUFF modeling system. Its primary purpose is to prepare meteorological inputs for running CALPUFF, consisting nominally of three-dimensional wind fields, two-dimensional gridded derived boundary layer parameter fields (e.g. mixing depth, friction velocity, Monin Obukhov length, etc.), and two-dimensional gridded fields of surface measurements and precipitation rates (for use in calculating wet deposition fluxes).

The wind field generated by CALMET is based on a diagnostic wind field model. An initial guess wind field is adjusted for the effects of terrain to produce a step 1 wind field. Observations are then used to adjust the step 1 wind field to produce a final step 2 wind field based on interpolation that is written to the CALMET output data file. The CALMET model differs from the family of prognostic meteorological models, such as the Penn State/NCAR Meteorological Model (MM5), that solve basic conservation equations to generate a modeled atmosphere and which can be used in a forecast mode.

Inputs to CALMET consist of geophysical data (land use, terrain) and observations in the form of surface measurements, precipitation rates, and upper air rawinsonde soundings.

The first fundamental step in the procedures necessary for CALMET usage in the Ambient Benzene Modeling Study in Burlington involved establishing the modeled domain. With respect to meteorological fields, the decision involved horizontal and vertical resolution sufficient to handle local-scale effects on surface wind field production. The next primary step in the process to produce valid meteorological fields involved rerunning CALMET for various switch settings that are known to effect surface wind field production and comparing modeled predictions to measured meteorological fields for a site within the domain. This effort, termed the progressive model validation procedure (PMVP), should allow generation of the best possible wind fields across the Burlington modeling domain. After the two preliminary steps above were carried out in Phase I., further, more specific validation of the meteorological quantities of most importance for this application were performed.

For this study, another important aspect of the meteorological field development involved proper wind field representation for the downtown Burlington area. This was achieved by relying on the Vermont Air Pollution Control Division (VTAPCD), measured wind data in this vicinity and using a CALMET option to control production of the spatially varying wind field with 'barriers' to spatial interpolation in a manner that limited the VTAPCD measurements to the downtown area only.

Determination of Horizontal Model Resolution

Because this modeling effort involves local scale transport (i.e., transport within the surface layer), inspection of the geographical characteristics of the domain is essential so that the model runs may properly simulate atmospheric flow in the situation at hand. Primary characteristics of the Burlington domain include: Lake Champlain, and the terrain gently sloping downwards to the lake (westwards), over about 10 kilometers distance.

In stable conditions at the surface slope flows will affect wind speeds and lifting or wrapping phenomena will affect wind direction. For less stable and more well-mixed conditions (i.e., during the daytime at higher wind speeds), the geographical effects on the surface windfield are much less significant. Therefore this evaluation to determine sufficient horizontal grid resolution for geographical effects is based on stable conditions. Examination of the annual frequency distribution of winds for Burlington reveals that for wind speeds less than 3 meters/second greatest directional frequency occurs from the easterly sectors (i.e., downslope flows toward the lake, usually occurring overnight).

Burlington, VT - Measured Windfield Stable Conditions

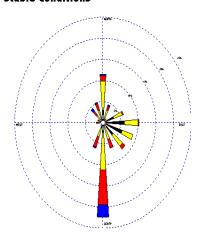
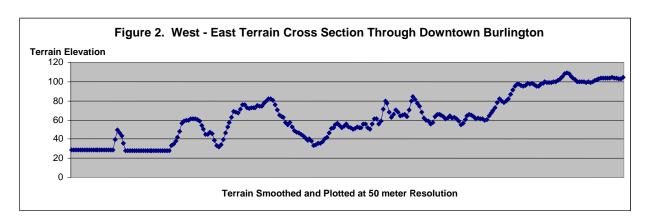
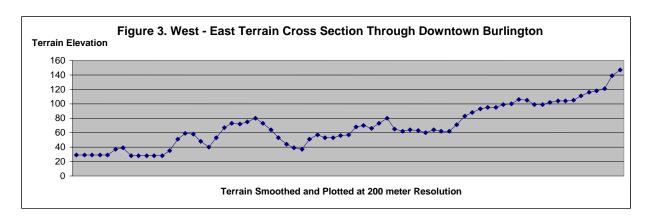
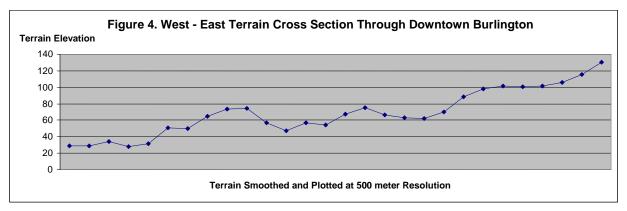


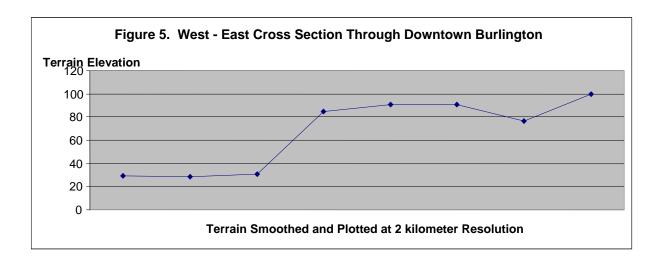
Figure 1. Burlington, Vermont Windrose - stable conditions only

Therefore it is essential that significant terrain features be sufficiently represented for modeled flow from the east downslope to the lake. Sufficient representation must allow two different physical phenomena to be properly simulated: 1). actual average slope over distances sufficient to cause slope flows. And, 2) actual height of terrain undulations that Figures 2. through 5. are cross section plots of terrain may causing wrapping of flow. elevations from west to east across the domain, where lowest elevations to the left represent the lake surface. Note that these plots do not represent terrain slopes accurately, but demonstrate the effect of terrain smoothing at larger horizontal resolution from the finest resolution, 50 meters. From these figures it is evident that at 200 meter resolution some of the finer features of the terrain evident at 50 meters resolution are still represented, but at 500 meters resolution they are not. Because the slope angles of the more significant features are retained at 200 meter resolution it is likely the slope flows and wrapping situations will be properly simulated. Test runs at 200 meter resolution for this domain indicate that computing power is sufficient for annual runs in a reasonable time frame, therefore the 200 meter horizontal resolution will be used.









After the proper horizontal model resolution was established (at 200 meter horizontal resolution), the geographical fields for land used and terrain elevations were produced with data from the U.S. Geographical Survey. Figures 5 through 6 depict the CALMET output fields produced for the 200 meter horizontal resolution Burlington Domain. Figure 7. depicts the surface roughness calculated as a function of both land used and terrain elevation across the domain.

Figure 6. Terrain Heights for the Burlington Domain.

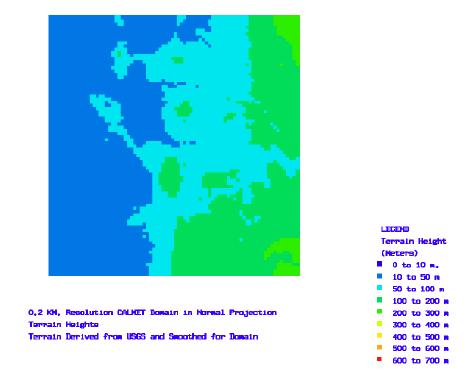
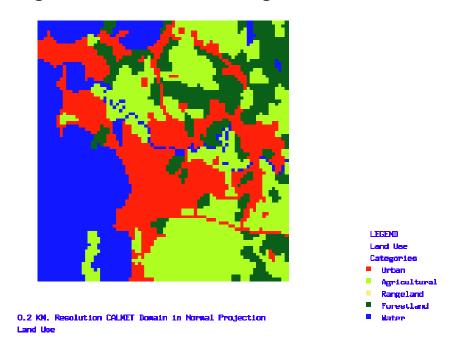


Figure 7. Land Use for the Burlington Domain.



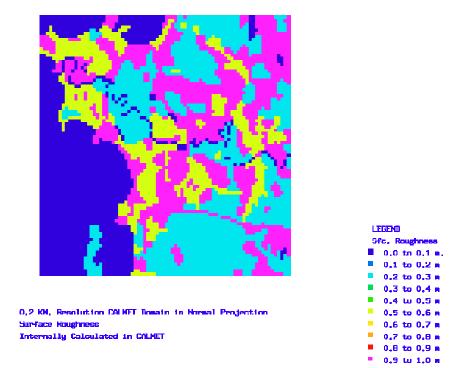


Figure 8. Surface Roughness for the Burlington Domain.

Meteorological Observations Used for the Burlington, Vermont Domain

After the initial domain and the geographical representation is compiled, further significant data processing efforts are necessary to produce the CALMET meteorological fields necessary to run CALPUFF. Essentially these efforts involve the meteorological observations necessary for input into the CALMET model. The proper combination of observations and format preparation must occur.

Surface Observations

For the Burlington domain meteorological conditions over water (Lake Champlain), and over land must be represented, because of significant differences in temperature, moisture, and winds in some situations. Over land, there are no significant orographic barriers or other geographical variations within the domain requiring more than one surface station for adequate coverage except in the downtown Burlington area. Therefore, at the surface, the Colchester Reef station represents over water conditions, and the Burlington Airport automated surface observing station (ASOS), represents over land conditions. The VTAPCD meteorological monitoring site co-located with the hourly Benzene BETEX measurements at 150 South Winooski was utilized to represent winds within the downtown area, where wind speeds are usually lower than areas of the domain with less obstruction to surface wind flows.

Wind Field Representation Within the Downtown Burlington Area

In production of the CALMET wind fields, the region influenced by an observation can be limited by user-specified "barriers." These barriers consist of line segments which define the boundaries of the region of the grid which can be influenced by a particular observation. Any time a barrier exists between a grid point and an observation site, the observational data are omitted for the interpolation. Using this approach, the downtown Burlington area, as identified by land use classification, was "barriered" away from the rest of the Burlington domain with the intent of representing the VTAPCD winds within the downtown area and the Burlington airport winds throughout the rest of the modeled domain. Note that final windfield production domain wide was still corrected to account for localized geographical effects.

In using barriers and examining wind fields produced by CALMET it was determined that the Burlington airport winds had to be represented at additional points on the domain so the interpolation procedures primarily in areas of the domain outside the barriered downtown area but 'shadowed' by the downtown area from the airport location still produced a windfield solely from the Burlington airport wind measurements. Figure 9 is a plot of the barrier locations and the points on the domain where the meteorological observations were represented, including the pseudo locations for the Burlington airport immediately surrounding the barriers.

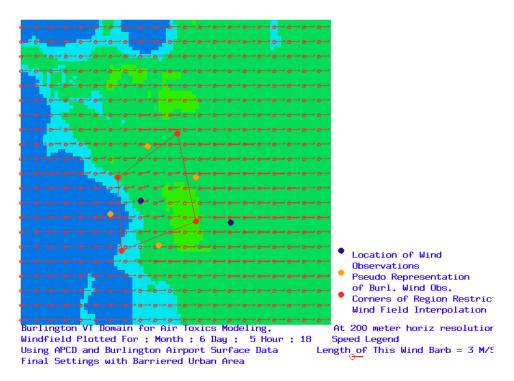


Figure 9. Example snapshot of the wind field produced with the barrier locations depicted, and all the points on the domain where the meteorological observations were represented, including the pseudo locations immediately surrounding the barriers.

In figure 9, on June 5, hr 18, a cold front has just passed through the domain, with low pressure to the north. The deviation in speed and direction of the VTAPCD winds from the Burlington airport is consistent with the greater frictional drag in the downtown area causing a greater directional component of surface wind flow inwards to low pressure to the north.

Figure 10. is a similar plot for a different hour, for which there is very little difference in the winds at the VTAPCD winds within the downtown area and the Burlington airport winds covering the rest of the domain. This lack of variation for some hours is likely the result of the variation in obstacle to surface wind flows for some directions of the compass due to the building orientations in the vicinity of the VTAPCD measurement location.

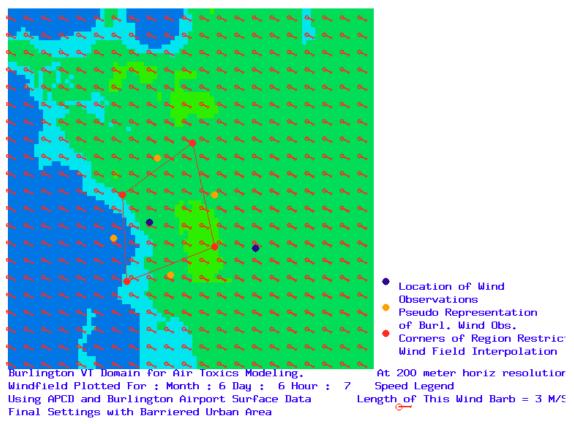


Figure 10. Another example snapshot of the wind field produced with the barrier locations depicted, and all the points on the domain where the meteorological observations were represented, including the pseudo locations immediately surrounding the barriers.

Representation of ASOS 'Calm' hours

The ASOS data sets for the Burlington Airport include about 1500 hours annually with a zero entry for wind speed, because the measured wind speed was less than 2.1 meters per second (M/S), for that hour. For dispersion modeling, having a lack of wind data for low wind speeds such as occurs with the 2.1 meters per second threshold will not permit simulation of dispersion during conditions with low wind speeds when elevated impacts may occur as a result of pollutant stagnation. The VTAPCD wind data has a much lower threshold, with measured wind speeds registering down to 0.1 M/S. Because of this lower threshold, if the zero M/S wind speed is retained in the ASOS data an unreasonable variation of the wind field across the domain is represented where the effect is to represent higher wind speeds in the downtown area. Therefore it was decided that substitution of the VTAPCD winds for the CALM and VAR WDIR hours defined in the ASOS data set would occur. In following this procedure, it is not expected that the VTAPCD wind data will be valid at points on the domain outside the downtown area, but the VTAPCD measurements used in this manner will allow the CALPUFF puff dispersion calculations to be performed with minimal, but non zero puff transport to approximately simulate the amount of dispersion occurring during more stagnant conditions. Figure 11. is an example of the CALMET windfield produced for an hour with zero M/S wind speed at the Burlington airport without substitution of the VTAPCD winds.

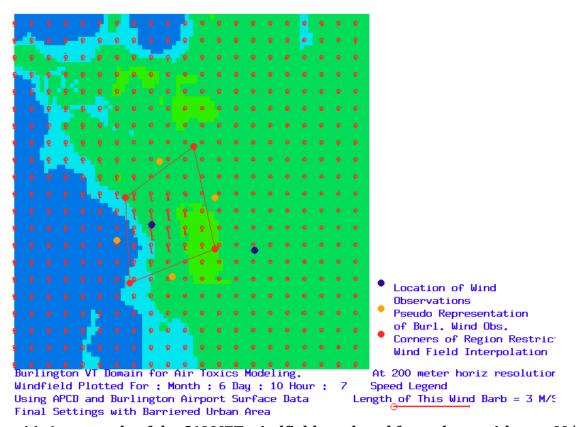


Figure 11. An example of the CALMET windfield produced for an hour with zero M/S wind speed at the Burlington airport without substitution of the VTAPCD winds.

The variation in wind speed across the domain appears more reasonable after the VTAPCD winds are substituted at the Burlington airport observational location and calmet is rerun (figure 12).

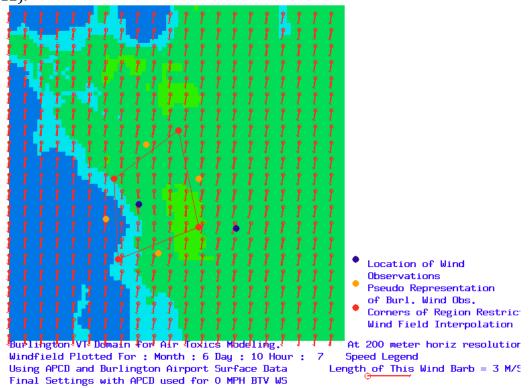


Figure 12. An example of the CALMET windfield produced for an hour with zero M/S wind speed at the Burlington airport with substitution of the VTAPCD winds at the Burlington airport observational location.

Upper Air Observations

Two alternatives currently exist for upper air representation for this domain: 1) utilization of radiosonde data from a remote location (Albany, NY), or extraction of prognostic windfields from the NAM model for locations within the domain. Because of the distance from Albany, New York to Burlington, the NAM upper air meteorological fields, if accurate, are obviously preferable. Further the NAM model output is available at a 3 hour interval.

In Phase I of the Benzene Modeling effort, the ETA prognostic model output was utilized for the CALMET runs. In the phase I. modeling, examination of the CALPUFF predictions indicated possible wind field discrepancies in isolated instances using the ETA model output. Therefore verification procedures of the CALMET output for crucial quantities, such as the mixing height and stability classifications, were performed.

Most of the following verifications of model performance for CALMET output were made using the ETA model for the Phase I. modeling. It has been assumed that *the evaluations*

using ETA are valid for use of the NAM output in phase II. Modeling. This assumption has been made for the following reasons. 1). The prognostic model output extracted for both ETA and NAM is similarly located at a location centered within the Burlington domain. Therefore in comparison to the measured data from Albany, NY the differences should be similar. 2). The NAM model is the National Weather Service's successor to the ETA model, and should be more accurate than the ETA model when significant variation occurs. 3). For the benzene modeling effort, we are primarily concerned with modeling dispersion and transport for pollutants emitted at ground level and predicting impacts at nearby, ground level receptors. In this situation most of the model-simulated dispersion and transport occurs in the lowest layer of the CALMET model defined as 0 through 20 meters in the vertical. Therefore the upper air wind fields are usually not relied on, but the surface data wind fields are.

Upper air windfield evaluation

A series of runs examining the wind fields produced at 370 meters elevation with the ETA upper air meteorological fields was compared to runs using the Albany, NY, upper air meteorological fields to look for differences in the two methods. For reference, figures 13 through 16 depict CALMET wind fields using the ETA upper air meteorological fields for two dates where the CALMET fields compare favorably to the real wind fields, as determined from a national weather service map, both in direction and speed..

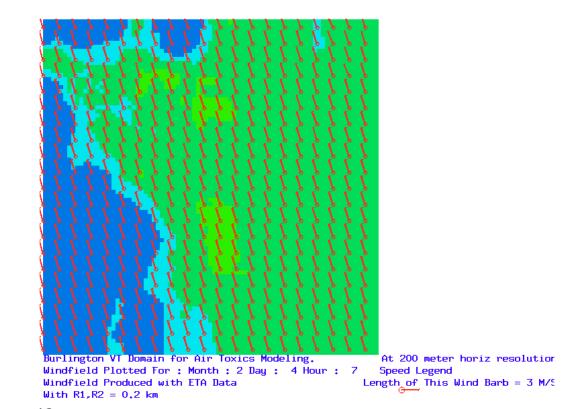


Figure 13.

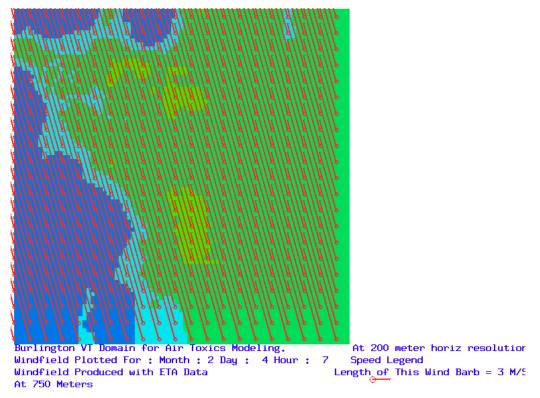


Figure 14.

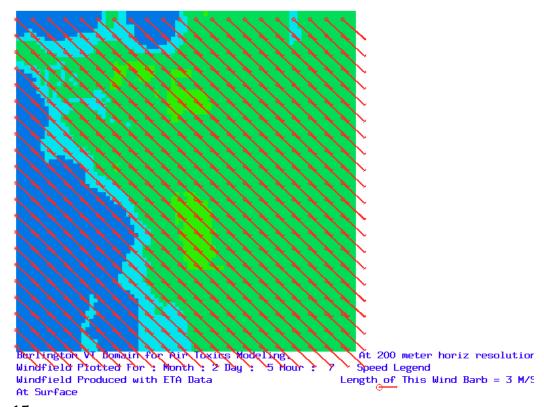


Figure 15.

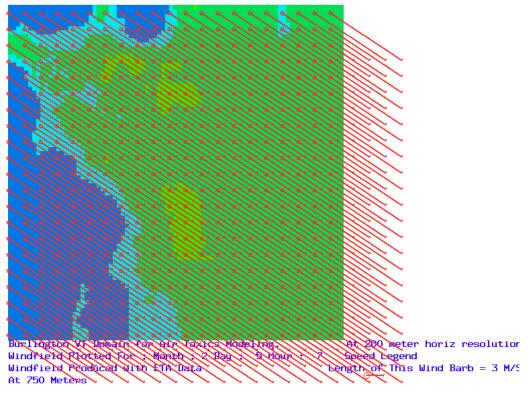


Figure 16.

Figures 13 through 16. CALMET wind fields using the ETA upper air meteorological fields for two dates where the CALMET fields compare favorably to the real wind fields, as determined from a national weather service map.

In figures 17. and 18., a comparison of the wind fields at 370 meters produced with the ETA upper air meteorological fields and the Albany radiosonde data is depicted for which the results are similar. In figures 19. and 20., a comparison of the wind fields at 370 meters produced with the ETA upper air meteorological fields and the Albany radiosonde data is depicted for which the results are dissimilar.

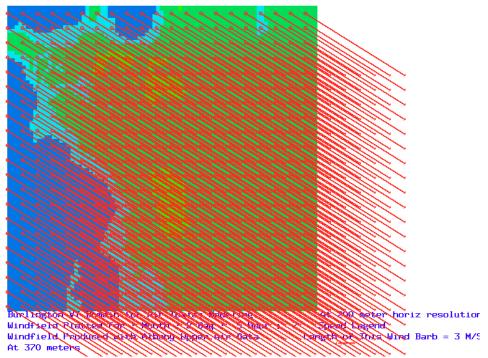


Figure 17.

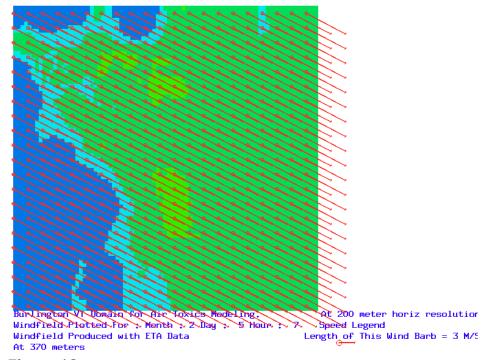


Figure 18.

Figure 17. and 18. A comparison of the wind fields at 370 meters produced with the ETA upper air meteorological fields and the Albany radiosonde data is depicted for which the results are similar.

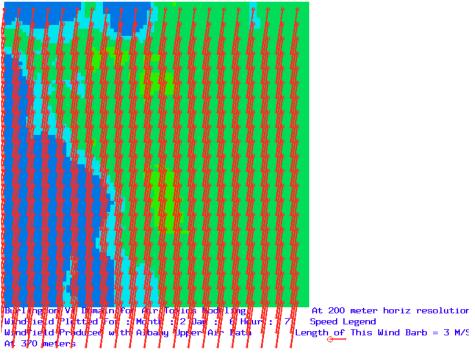


Figure 19.

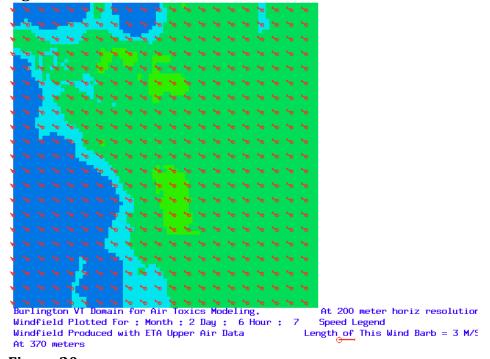


Figure 20.

Figure 19. and 20. A comparison of the wind fields at 370 meters produced with the ETA upper air meteorological fields and the Albany radiosonde data is depicted for which the results are dissimilar.

Examination of the national weather service maps for the February 6 plots indicated that the difference in upper air representation in the two cases was because of significant differences in the upper air windfield over the New England area. Albany, New York, several hundred kilometers distant from Burlington to the southwest, was experiencing higher wind speeds above the surface resulting from stronger pressure gradients aloft. The February 6, ETA representation at 370 meters height agreed with expectations of regional variations in the wind fields and was probably more accurate for the Burlington area than the Albany radiosonde derived wind fields.

Because the ETA derived fields appeared more accurate than the Albany radiosonde derived wind fields for the case examined where they differ, and because the ETA derived fields generally appear realistic for other times, the ETA derived fields will be used for the final wind field production.

In this study, further evaluation of the acceptability of the ETA fields has been performed as the CALMET output fields are examined for accuracy in the overall data validation procedures comparing modeled to measured wind predictions at Essex Junction.

These validation procedures examine wind fields separately from other output fields, such as mixing heights and stability classifications effecting pollutant dispersion. For output fields dependent on vertical temperature profiles, such as the mixing height, evaluation of the ETA fields used in combination with the measured surface temperature is especially critical. In the past, there has been some concern in the air quality modeling community that possible bias exist in the ETA temperature fields.

For the Phase II Benzene modeling it was assumed that the determination of acceptability for the ETA data would be valid for the NAM data as well, since the NAM windfields should represent an improvement to the ETA windfields when they vary significantly.

Evaluation of Mixing Heights and Stability Classification

Mixing Heights

For the Phase I. Benzene Modeling a series of CALMET runs were performed using three basic combinations of the meteorological inputs available and examining mixing heights and stability classifications produced by CALMET. These fields were compared and evaluated for reasonableness for winter and summer episodes, for day and night time conditions.

Figures 21. through 23. below depict mixing heights produced by CALMET for the Burlington domain where in figure 21. upper air data from Albany, New York, is used in conjunction with measured surface data from the Burlington Airport, in figure 22., ETA upper air data is used in conjunction with measured surface data from the Burlington Airport, and in figure 23, ETA upper air data is again used in conjunction with the surface ETA temperature field.

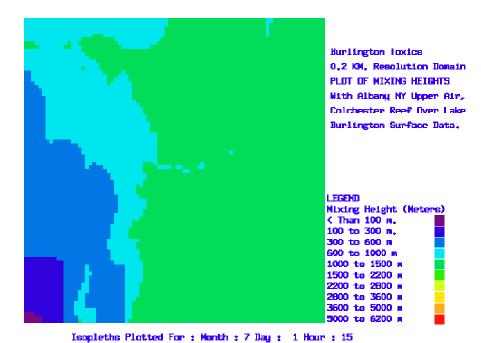


Figure 21.

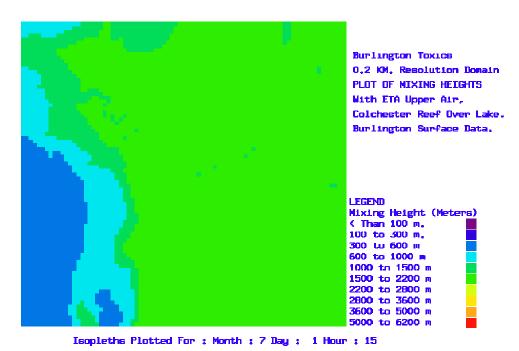


Figure 22.

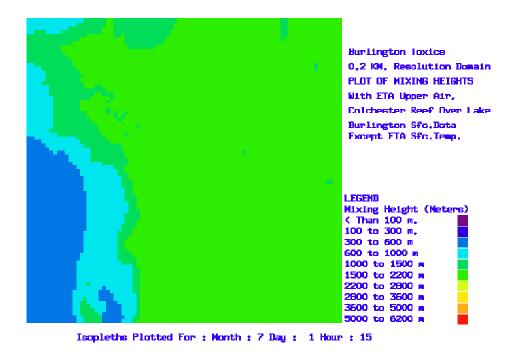


Figure 23.

Figure 21. - 23. Daytime Summer time Mixing Heights.

In comparison of figures 21 through 23, note very little difference between figures 22 and 23, which, in their production, differed in the usage of the ETA surface temperature for figure 23. and the measured Burlington surface temperature for figure 22. Prior examination of these two sets of surface temperature fields had revealed significant differences on an hourly basis, although no long term averaging was performed to evaluate a possible bias in the ETA surface temperature. Regardless, its effect on the mixing height estimates appears to be negligible. This also held true for mixing height estimates overnight. The ETA surface temperature was originally included in this comparative analysis because it was thought that the combination of ETA upper air with measured surface temperature would result in possible significant discontinuities in the thermal profile. In comparison of figure 21 and 22, it is apparent that overland daytime mixing heights for the ETA upper air run are significantly greater. It was concluded that these height were not unreasonable, and the differences between figures 21 and 22 occurred because the ETA upper air fields, being representative of atmospheric features 300 km north of Albany, New York, were usually colder, resulting in greater potential for thermal mixing, and represented in the greater modeled mixing heights.

Figures 24. and 25. below illustrate comparisons for nighttime, or early morning, mixing heights.

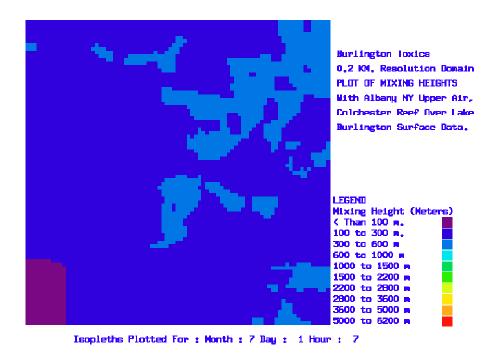


Figure 24. Night time Summer time Mixing Heights

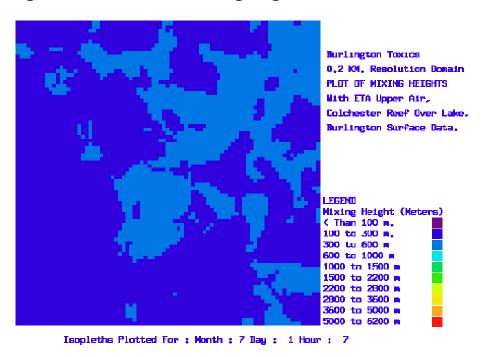


Figure 25. Night time Summer time Mixing Heights

Note that mixing heights in figure 24 tend to be lower than in figure 25. for this hour. In the other night time mixing height fields examined this usually held true. As for the daytime mixing heights, this variation may be attributed to the generally colder temperatures for the ETA upper air, where , overnight, the colder air tends to weaken the strength of

simulated thermal inversion trapping air at the surface and represented by a very low mixing height.

Therefore, for both day and night time conditions, it appears the primary effect on mixing heights estimates in utilizing the ETA upper air data, is to increase their values, thereby decreasing predicted ground level concentrations for emission scenarios near ground level.

For the Phase II. Benzene modeling it was assumed that the determination of acceptability for the ETA data would be valid for the NAM data as well, since the NAM meteorological fields should represent an improvement to the ETA meteorological fields, when variation occurs.

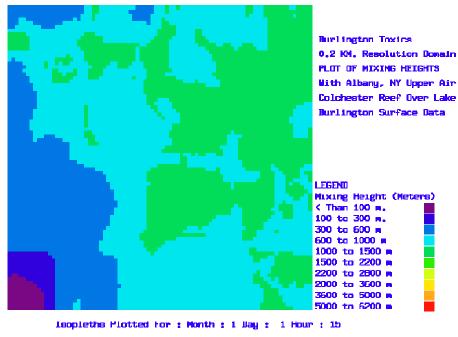


Figure 26. Day time Winter time Mixing Heights

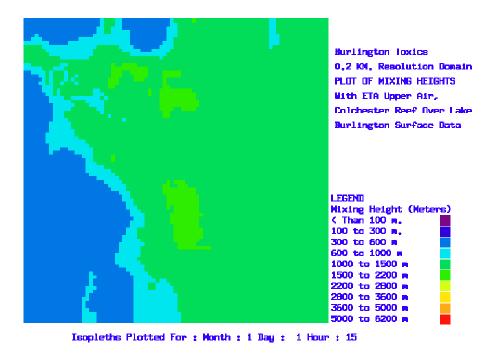


Figure 27. Day time Winter time Mixing Heights

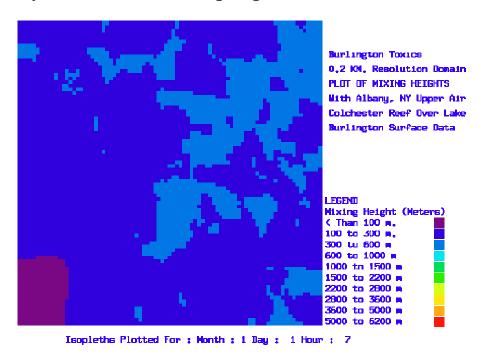


Figure 28. Night time Winter time Mixing Heights.

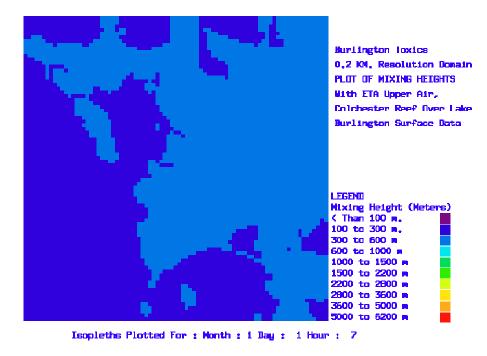
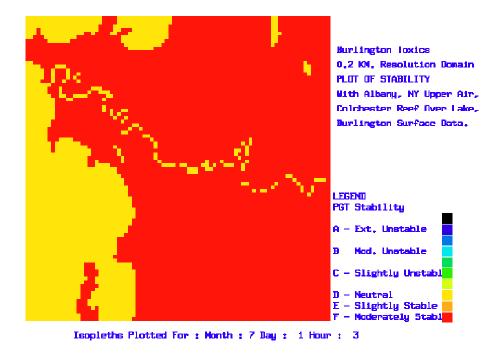


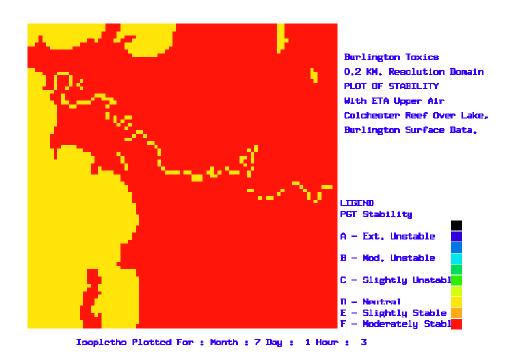
Figure 29. Night time Winter time Mixing Heights.

Stability Classification

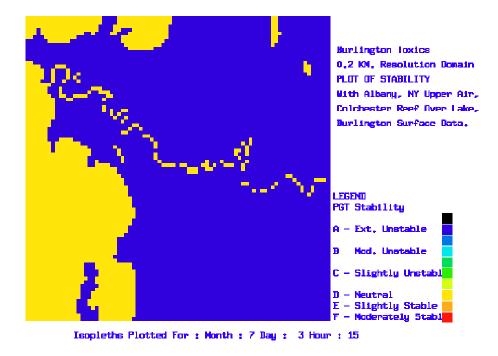
Of primary importance to the rate of lateral Gaussian dispersion in Calpuff's predictive efforts is the PGT stability classification derived by CALMET.

For the mixing heights modeled estimates examined prior to this it has been established that utilization of measured surface temperatures in combination with ETA upper air fields is acceptable. The PGT stability calculations are directly dependent on surface temperatures and other observations of surface weather conditions, such as cloud cover. Therefore, it was anticipated that the most accurate PGT stability calculations would occur using measured surface data, and very little difference in the PGT stability calculations would occur for the two alternative upper air wind field input data sets, Albany upper air and ETA fields. Examination of figures 30 through 33 verify this.

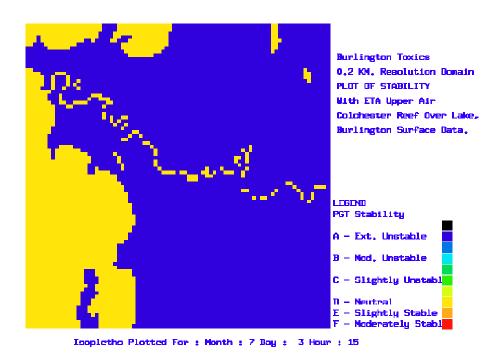




Figures 31. Night time stability classifications predicted by CALMET for the Burlington Domain.



Figures 32. Day time stability classifications predicted by CALMET for the Burlington Domain.



Figures 33. Day time stability classifications predicted by CALMET for the Burlington Domain.

The PGT stability calculations appear reasonable, and this verification completes the inspection of potential problems in CALMET output when utilizing the ETA fields and allows us to conclude that, with respect to CALMET's predictions of dispersion parameters, usage of the ETA upper air fields in combination with the measured surface meteorological fields is acceptable.

Choosing the Best CALMET Settings for the Burlington, Vermont Domain

In examining the accuracy of the CALMET wind fields in this study the intent was to make a domain wide assessment. After deciding that inclusion of the ETA data for upper air representation will occur, there are many parameter settings in the CALMET model that affect the model's handling of surface terrain effects. For certain meteorological conditions these settings may be varied to allow proper physical handling for a specific location, such as a sensitive receptor near a terrain feature. Location of an meteorological observation point in close proximity to a sensitive receptor will also improve windfield accuracy at that specific location. It is not the intent of this study to evaluate how the model performs for specific locations such as these, but rather how it performs on a grid-wide average, such as a prognostic model would be evaluated. The parameter settings that allow improvement of a localized windfield subject to certain conditions always apply gridwide and may result in a misrepresentation of the windfield elsewhere.

In the CALMET runs occurring in this study most of the parameter settings (i.e., those not associated with terrain representation in the model physics), were held constant for the runs and set to default mode. For the horizontal scale of this study, 16.6 km by 16.6 km, it was considered appropriate to use only one station as an observation data point. When the CALMET model is applied over an area of highly complex terrain, the linear interpolation of more than one observation point is only beneficial to gridwide accuracy if synoptic-scale variation is represented by the observation point windfields. Otherwise, usage of a domain-constant windfield at levels just above the surface layer to subject to the terrain physics is the most physically consistent approach. For long range transport applications the average spatial density of observations included for runs in a larger domain may typically be less than that occurring in this study. Several trial runs were made using different stations as the meteorological observation inputs in CALMET and that station resulting in the most accurate domain-wide results was chosen (Burlington, Vermont). It must be emphasized that the intent of this study is primarily to discern any *relative* improvements in the model's handling of terrain effects as sensitive parameter settings are varied.

For a domain wide model validation it is necessary to rely on a set of meteorological observations *not* used as input to run the CALMET model. The station used in this evaluation was Essex Junction, Vermont. In utilization of this local site care was taken to ensure that the sensors were accurate. This data was collected and archived for the summer of 1999.

The comparison between the temporally and spatially matched sets of wind vectors involved quantification of two error measures for both the wind speed and wind direction

(Wishinski,2000). The **Bias** was computed as the average of the difference between modeled and measured values for each data pair accounting for the sign, where a positive value means that the direction of the predicted wind is clockwise of the observed. The **Error** measure is an absolute (i.e. sign independent), measure of the average difference between modeled and measured data pairs. Hence the bias can be considered a measure of error for domain wide transport, i.e., whether the average direction of puff transport is off by 15 degrees, or the average windspeed is 3 knots too low. The error measure better addresses the degree the wind is mispredicted at any time, quantifies the ultimate predictability of the atmosphere by the model, and may effect the rate of lateral dispersion as the effect of the directional error is compounded over a puff's travel in the CALMET windfield.

The error measures described above were compared for a multitude of CALMET runs, where for each run the parameter settings most affecting terrain handling were altered with the intent of improving overall grid accuracy of the surface windfield.

RESULTS

Table 1. Below lists the varied parameter settings for each of the 10 final runs that occurred.

Run	1	2	3	4	5	6	7	8	9	10
Number										
R1	0.2	0.2	0.2	0.2	0.2	0.5	2.0	0.5	10.0	2.0
TERRAD	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
FROUDE	1.3	1.0	1.0	0.7	0.7	1.0	1.0	1.0	1.0	1.0
ALPHA	Off	Off	Off	Off	On	Off	Off	Off	Off	Off
					(0.1)					
IOBR	On	On	Off	On						
X,Y	72,51	72,51	72,51	72,51	72,51	72,51	72,51	73,50	72,51	72,51
CALMET										
Grid										
Location										
IEXTRP	1	1	1	1	1	1	1	1	1	-4

Table 1. CALMET Parameter settings used for Runs in the Modeled to Measured CALMET Wind field Validation.

Table 2. below provides plotted measures of CALMET's accuracy between runs for comparison for each of the four measures of error. For each of these runs the results are based on approximately 230 observation to model prediction data pairs.

As these trial and error attempts to combine the parameter settings for greatest gridwide accuracy progressed strategies eventually became apparent regarding the inter-related

effects of the variable settings. Subsequent runs would then alter the parameters of most promise to gridwide accuracy further. For this domain, it was apparent that the greatest effect on model accuracy involved varying the Relative weighting of the first guess field and observations in the SURFACE layer (R1). R1 is the distance from an observational station at which the observation and first guess field are equally weighted. For such a high resolution domain, improvement of model accuracy as R1 is decreased indicates that the application of the CALMET physics altering surface wind flows based on geographical effects are having a positive influence on final predicted wind fields. The runs are ordered corresponding to their overall accuracy combining both the bias and error measures for wind speed and direction with run 1 having best results.

	Summer	ummer Measured					CALMET
Run	or	Met.	WD	WD	WS	WS	x,y grid
Number	Winter	Location	Bias	Error	Bias	Error	point
					_		•
1	summer	Essex	-8.44	52.36	2.81	3.12	72,51
2					-		
	summer	Essex	-8.45	52.36	2.81	3.12	72,51
3					_		
	summer	Essex	-8.45	52.37	2.81	3.12	72,51
4					-		
	summer	Essex	-8.53	52.28	2.81	3.12	72,51
5					-		
	summer	Essex	-8.66	51.25	2.85	3.15	72,51
6			-				
	summer	Essex	14.12	48.38	-3	3.29	72,51
7			-				
	summer	Essex	14.12	48.38	-3	3.29	72,51
8			-				
	summer	Essex	14.13	48.35	-3	3.29	73,50
9			-				
	summer	Essex	14.12	48.38	-3	3.29	72,51
10			-		-		
	summer	Essex	16.57	49.99	4.45	4.68	72,51

Table 2. Results for Runs in the Modeled to Measured CALMET Wind field Validation.

Note that the kinematic effects (ALPHA), and the critical froude number (CRITFN), are the parameters most directly associated with the terrain physics. Prior to this study it has been established that exclusion of kinematic effects improves gridwide accuracy for most applications. Variation of the critical froude number value seems to hold more promise for improvement of model accuracy. Values set higher than the default, approximately at 1.3, marginally improved results. Figure 34 through 36 illustrate the minimal effect of the froude number variations tested on the wind field for this domain for overnight drainage flows.

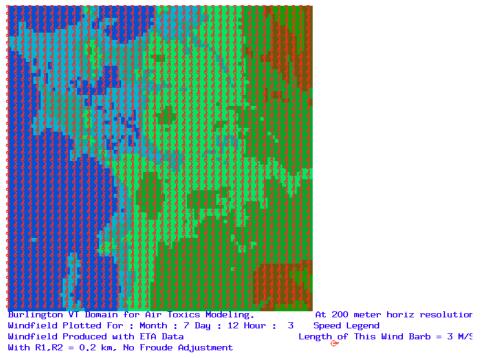


Figure 34. Comparison of Froude Number Adjustment - with no froude adjustment.

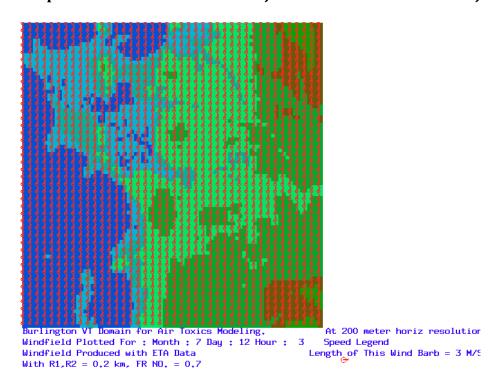


Figure 35. Comparison of Froude Number Adjustment - Froude number = 0.7.

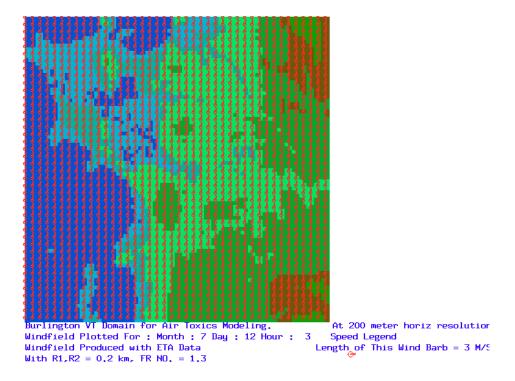


Figure 36. Comparison of Froude Number Adjustment - Froude number = 1.3.

Because there was only a very minimal improvement in model accuracy by utilizing the critical froude number of 1.3, it was decided to perform final model runs using the default setting of 1.0 (run number 2).

Conclusion

The findings in this study allow us to conclude that utilization of the prognostic windfields is acceptable for this application of CALMET. Initially, there was some concern regarding the combination of the upper air NAM – derived meteorological fields with measured surface data. Reasonable values for mixing height and stability classification by CALMET, however, allay these concerns. Examination of the CALMET wind field predictions for this high resolution domain, by comparing modeled to measured values in Essex Junction, indicate generally good model performance and allow us to choose the option settings for the final runs that will be used by CALPUFF.