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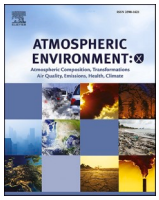

Modeling county-level benzene emissions using transportation analysis zones in the Denver metro area

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ABSTRACT

The link between exposure to benzene (an important toxic air pollutant) and physical health is well-documented as benzene is a known carcinogen. Understanding benzene concentration distributions in urban areas is very important and can be done using air dispersion models. An essential input requirement for dispersion models is the spatial and temporal allocation of emissions. Since most county-level benzene emissions come from gasoline powered motor vehicles, the goal of this work was to develop a new method of county-level benzene emission allocation using transportation analysis zones (TAZs) commonly used in travel demand models. The high spatial resolution provided by the TAZ allocation method helped visualize different flux patterns generated from five emission sectors and identified where more effort is needed to reduce benzene concentrations. The new allocation method was also tested using the AERMOD dispersion model to estimate benzene concentrations in the Denver metropolitan area. The model performance was assessed using 2014 morning benzene measurements from a monitoring station located in downtown Denver; results showed an acceptable model-to-monitor ratio. The model was also used to investigate the effect of temperature inversions on morning benzene concentrations. As expected, predicted benzene concentrations were higher during temperature inversions and model-to-monitor ratios during investigated days were within a factor of two. The TAZ allocation modeling methodology demonstrated in this work can improve the estimation of air pollution exposure in future health-related studies.

1. Introduction

Benzene is a major health concern in the Denver Metro/North Front Range in Colorado (DDPHE, 2006). It is a hazardous air pollutant classified as a known human carcinogen for all routes of exposure under the proposed revised Carcinogen Risk Assessment Guidelines and is one of the top 20 most common industrial chemicals in the U.S. (Smith, 2010).

The National Air Toxics Assessment (NATA) is the United States Environmental Protection Agency's (EPA) ongoing review of air toxics in the United States. EPA developed NATA as a screening tool for state, local and tribal air agencies (United States E PA, 2022). NATA's results help these agencies identify which pollutants, emission sources and places they may wish to study further to better understand any possible risks to public health from air toxics. The NATA is driven by county level (for mobile and area sources) and point source emission inventories (by EPA region and US state) in the National Emissions Inventory (NEI) (EPA, 2014a).

Starting in 2000, and with subsequent updates after each NATA was updated, the Denver Department of Public Health and Environment (DDPHE) developed and refined a local air dispersion modeling system that used emissions data from the NEI, supplemented with emission inventory data provided by the Colorado Dept of Public Health and Environment (CDPHE). For all sources except point sources, emissions data were provided at the county level. DDPHE apportioned the county level emissions into more discrete grid cells using surrogate data that was found to best align with the type of emission source (e.g., vehicle miles traveled for on-road mobile sources) (DDPHE, 2006). Emissions, in the form of annual totals, were also temporally allocated by season, day of week, and hour of day using a variety of methods (DDPHE, 2006). Emissions were spatially processed using a series of spreadsheets and a geographic information system (GIS) with layers that included vehicle miles traveled from a travel demand model and population data. The resulting emissions that were spatially and temporally allocated were then run in either the EPA ISC3ST dispersion model prior to 2007 or AERMOD after that. AERMOD was selected an appropriate model for this work and focused mainly on inert criteria pollutants and air toxics in

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the Denver metropolitan area (e.g., carbon monoxide, BTEX, and black carbon). Lastly, dispersion model results were post-processed and compared with comparable air monitoring data, where it existed.

Comparison of Denver's dispersion modeling work to NATA was conducted (DDPHE, 2006) which showed general similarities in terms of the spatial distribution of pollutants, but produced finer spatial resolution and used more detailed local level data (e.g. population and density, local vehicle miles traveled) as surrogates to disaggregate county level emissions. Over the past twenty years, EPA regions in partnership with states and universities have conducted similar types of comparisons at the metropolitan scale (Isakov et al., 2014; Texas A&M Transportation Institute College Station, 2020).

When Denver first started this work, analysis of ambient concentration estimates of benzene in EPA's 1996 National Air Toxics Assessment showed that benzene was ubiquitous and prevalent in all states ranging from 0.5 to 2.9 $\mu g/m^3$. Local air monitoring data in Denver at the time showed benzene routinely in excess of 3.25 $\mu g/\ m^3$ (1 ppb), hence the desire to better understand the spatial and temporal differences in benzene. Benzene is mostly emitted from motor vehicle exhaust and has a strong diurnal emission pattern (Cook et al., 2008; Fujita et al., 2011). Other sources of emissions are gasoline service stations, oil, and gas (O&G) exploration and production activities, and combustion emissions such as coal and oil burning (Dehghani et al., 2018). At the time DDPHE started this work in the early 2000's, 70% of the benzene inventory was estimated to come from on-road mobile sources, mostly from gasoline vehicles, 20% from off-road engines and 10% from point sources. That has obviously changed over time as motor vehicles and the fuels used to power them have gotten cleaner.

Colorado has traditionally had only a few monitoring sites that provide valuable and accurate information about toxic air pollutants because the upfront cost of installing such stations is quite high in addition to operation and maintenance expenses. These sites only provide information about the monitored pollutants in the location of the site, and during the monitoring period. Therefore, air quality models are often used to estimate the ambient concentrations of air pollutants in the absence of monitoring data. Air quality models are important for many reasons: 1) they can provide spatial and temporal visualization of air pollution concentrations, 2) they are used to assess air quality strategies and improve policies, and 3) they can be used to estimate air pollution exposure in health-related studies (Stein et al., 2007).

Air quality models can be classified into dispersion models and chemical transport models. Dispersion models are source-based models that estimate the downwind ambient concentrations of pollutants on a network of receptors providing a spatial distribution of those pollutants. Under specific scenarios, dispersion models can be used for future prediction and can also be used to estimate inert, chemically non-reactive or slow-reacting chemical species. The maximum distance for these models is 50 km and their temporal resolutions range from an hour to one year (Touma et al., 2006), yet they are still computationally efficient comparing to chemical transport models (Stein et al., 2007).

Chemical transport models (CTMs) are photochemical grid-based (Eulerian) or trajectory (Lagrangian) tools that simulate chemically reactive pollutants. CTMs often demand high computational time and are more complex than dispersion models in terms of mathematical equations, input parameters, etc. (Stein et al., 2007; Johnson et al., 2010; Daly and Zannetti, 2007). One of the commonly used Eulerian models is the three-dimensional Community Multi-scale Air Quality (CMAQ) model, used to simulate a wide range of pollutants including ozone, particulate matter, and toxic air pollutants.

When modeling reactive air toxic pollutants, it would be desirable to use a hybrid model combining a dispersion model and a chemical transport model (Touma et al., 2006). AERMOD is a steady-state Gaussian plume dispersion model that is widely used for estimating local-scale concentrations of nonreactive pollutants. Using AERMOD to predict reliable air toxic concentrations requires accurate model inputs and careful selection of modeling settings. Many parameters and model inputs could impact the model performance such as emissions, receptor selection, temporal and spatial allocation factors, meteorological data, and background concentrations (Touma et al., 2006). Ideally, AERMOD would be used to estimate the air toxic concentrations due to emissions from local sources. Then the regional background concentrations from outside the modeled region and chemical reactions of secondary products are accounted for using a chemical transport model such as CMAQ. The estimated concentrations from the transport model coupled with the AERMOD concentrations provide total ambient concentration estimates (Stein et al., 2007; Touma et al., 2006). However, relying only on dispersion models to estimate air toxics is not entirely uncommon. For example, benzene is a stable, and slowly reactive air toxic and therefore, can be modeled using AERMOD (Stein et al., 2007; Touma et al., 2006; E.P.A, 2002).

Emission inventories are an essential input for dispersion models. The National Emission Inventory (NEI) (EPA, 2014a)provides county-level emissions (the total mass per time of a pollutant that was emitted from one county) of benzene as well as volatile organic compounds (VOCs). In dispersion modeling, the county-level emissions are typically allocated to uniform grids using emission surrogates. In this work an alternative method is used to generate spatial and temporal surrogates and allocate county-level emissions to high resolution grid cells based on transportation analysis zones (TAZs), as used in travel modeling by the Denver Regional Council of Governments (DRCOG) (Denver Regional Council of Governments). A TAZ is a geographic unit that is typically used in transportation planning models (Martinez et al., 2009). Each TAZ, which could consist of one or multiple census blocks (street-to-building scale), usually includes population, socio-economic and traffic-related data. This data is particularly useful for developing spatial surrogate data and for eventual health risk assessment.

The Denver Department of Public Health and Environment (DDPHE) has used dispersion modeling for more than 20 years to estimate both air toxics and criteria pollutant concentrations. In the Denver Urban Air Toxics Assessment: Methodology, Results and Risks study (DDPHE, 2006), DDPHE applied the Industrial Source Complex Model (ISC3ST) that showed good prediction capabilities of inert air toxics and some criteria pollutants in the Denver region. Benzene air monitoring data were not widely available in the urban area; therefore, the predictions for carbon monoxide were used to evaluate the performance of the model, since both pollutants are expected to come from fossil fuel combustion and had similar proportions in the emission inventories (e.g. 65–70% of benzene and carbon monoxide came from on-road motor vehicles). A goal of this current work is to update and build upon the previous work by DDPHE using a TAZ allocation method with AERMOD as a replacement tool of ISC3ST, more recent meteorological data, and recent benzene measurement data for model evaluation.

Poor air quality days in Denver are often associated with temperature inversions (Reddy et al., 1995; Malek et al., 2006; Kukkonen et al., 2005). Denver experiences near-surface temperature inversions in winter more than many southwestern cities (Bailey et al., 2011). Temperature inversions occur when a layer of warm air lies atop a layer of cooler air near the ground. Due to its topography and climate, Denver sometimes experiences poor air quality that coincide with temperature inversions, especially during wintertime (Reddy et al., 1995; Whiteman et al., 1999; Doesken and Bliss, 2007). This work also investigates whether benzene concentrations are enhanced during temperature inversions in the Denver area.

The objectives of this work were to: (1) demonstrate an alternative method of county-level emission allocation using TAZs versus census tracts or census block groups; (2) predict using AERMOD morning benzene concentrations using the TAZ allocation method; (3) evaluate the model performance using measurements of morning benzene concentrations from a Colorado Department of Public Health and Environment (CDPHE) site; and (4) investigate the impact of temperature inversions on benzene concentrations.

2. Methods

2.1. County-level benzene emissions allocation to transportation analysis zones

A reliable estimation of benzene concentrations using dispersion models requires an accurate method of generating spatial surrogates. In addition to providing the necessary inputs to air quality modeling, spatial allocation methods by which the emissions are distributed from a larger area to small areas, are also important in identifying key emission sources where more effort is needed to reduce pollution (Zheng et al., 2009). Typically, county-level emissions are allocated to uniform grid cells ranging from 1 to 16 square kilometers (DDPHE, 2006; Touma et al., 2006; Brandmeyer and Karimi, 2000). However, this traditional method spreads the emissions evenly throughout a grid cell instead of concentrating them near the actual location of the emission sources, which could lead to underestimation of concentrations near local sources such as highways (located up to 1 km from the receptor). In addition, the spatial allocation surrogates are often developed based on parameters such as population and/or density that are obtained from themed polygons such as census tracts, census block groups, or census blocks (Dai and Rocke, 2000). Since these themed polygons mostly are not uniform, an overlap in surrogate parameter information could happen between the uniform cell-grids and the TAZs. This overlap makes exact calculation of surrogates difficult (DDPHE, 2006; Kinnee et al., 2004). In this section an alternative method of county-level emission allocation is presented. The allocation surrogates are developed based on information in the TAZs obtained from the Denver Regional Council of Governments (DRCOG) travel demand model (Denver Regional Council of Governments). These allocation surrogates are used to apportion a fraction of the county-level benzene emissions to the TAZs. The use of the TAZ layer in our GIS also maintains discrete boundaries within each city and county. In other words, each county level emission total is 100% allocated to TAZs within that county.

When we explored the data we could use to apportion county level emissions to grid cells, a major challenge was that economic data are rarely provided below the county level. Highway data can be calculated by TAZs using GIS which makes for efficient spatial allocation of on-road mobile source emissions. Common data for TAZs are population, income, demographics, and average home values. For off-road motor

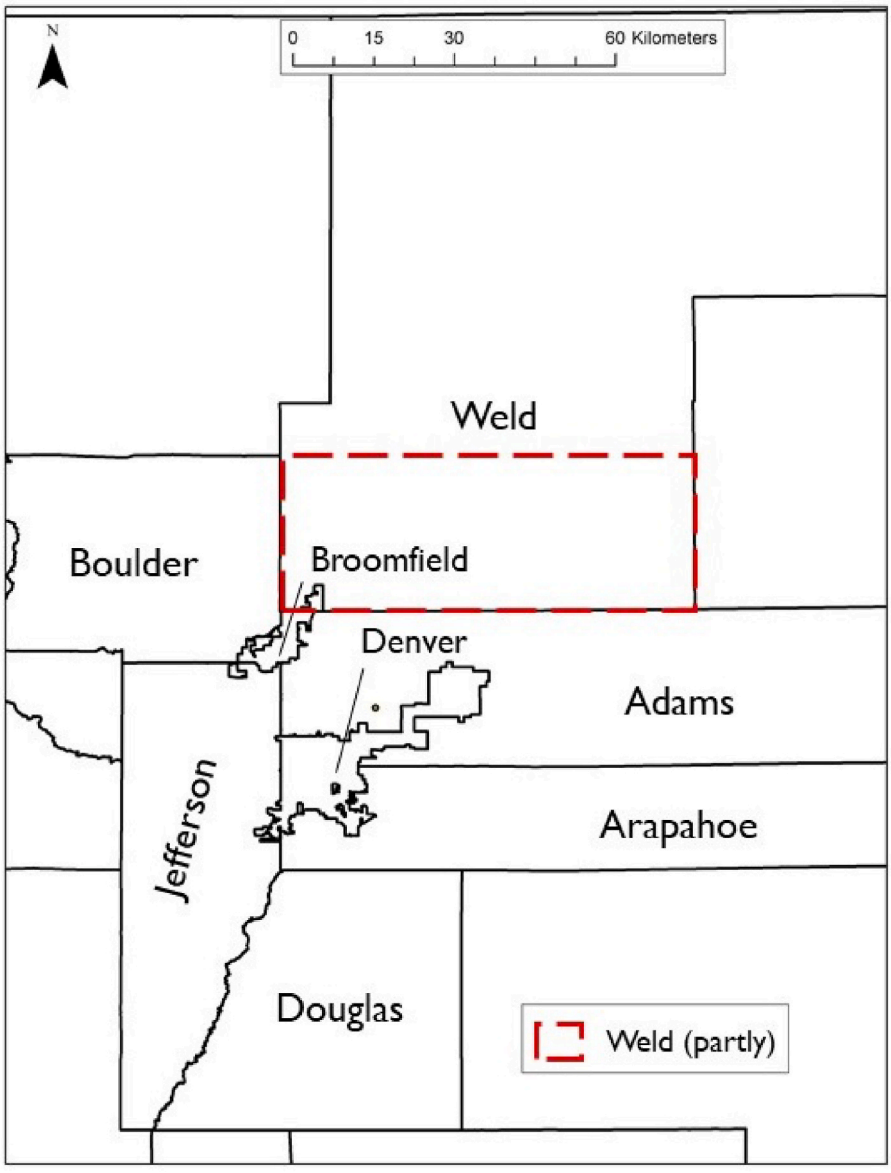

Fig. 1. Denver Metro/North Front Range study area.

vehicles, we developed spatial surrogates that combined vehicles miles traveled (construction happens more frequently on highly traveled roadways), population (lawn and garden equipment), and inverse population density (for undeveloped areas that might experience more construction) (DDPHE, 2006). Similar spatial allocation methods were employed for area source emissions.

Temporal emission factors relied more on real world observations for various activities. For example, lawn and garden emissions are limited to daylight hours, diurnal vehicle volumes are modeled in the travel/VMT model, construction related emissions and commercial business emissions mainly occur in the daytime and on weekdays. Temporal emissions profiles in AERMOD were applied by season, day of week, and hour of day (DDPHE, 2006).

The study focuses on the Denver Metro/North Front Range region and includes seven counties: Adams, Arapahoe, Boulder, Broomfield, Denver, Douglas, and Jefferson (Fig. 1). These counties represent most of the Denver Metro/North Front Range (DMNFR) area, with the largest population in the state of Colorado. The DMNFR has major on-road emissions including interstate 25, which carries an average of 250,000 vehicles per day and interstate 70, which carries an average of 150,000 vehicles per day (DDPHE, 2014). In addition to these seven counties, the southern part of Weld County is also included in the study. The boundaries of the included part of Weld County extend from 40° 15′ 42″ N, 105° 03′ 18″ W to 39° 59′ 59″ N, 104° 09′ 06″ W (shown by the red dashed rectangle in Fig. 1). According to Denver Regional Council of Governments (DRCOG) data (Quality Division, 2015), this part of Weld County contains 47% of the total number of oil and gas wells in Weld and 38% of the total length of Weld's railroad tracks. Oil and gas related emissions became a more significant source of benzene and other air toxics in state emission inventories with the advent of horizontal drilling and fracking in post-2005 inventories, so spatially apportioning them correctly took on added importance.

Fig. 2 shows the TAZs in each county in the study area. More information about county ID, area and number of TAZs in each county is provided in the Supplemental Material, Section S1. In this study, TAZ spatial surrogates were calculated and used to allocate county-level emissions. For the entire domain, the average TAZ area is 5.0 square kilometers and in Denver the average TAZ area is about 2.2 square kilometers. Some of the advantages of using TAZs are (DDPHE, 2006):

- they have information such as population and traffic counts that can be used to develop spatial surrogates and conduct risk assessments;
- because TAZs are used as emission sources in the model as well as for developing the surrogates, there will not be an overlap in information between TAZs or between counties; and
- in a densely populated urban area, the sizes of TAZs are quite small (less than 1 square kilometer) therefore the spatial resolution provided by the TAZ allocation method is equal or higher than the resolution provided by traditional uniform grid cells. A disadvantage is mostly computational (a greater number of sources requires additional processor time for each model run). However, modern computers can handle this number of sources with few problems and proper planning.

Total benzene emissions from a TAZ source were calculated as the summation of emissions from five sectors: on-road, off-road, O&G, area, and railroad. The county-level emissions for each sector were obtained from the 2014 US EPA National Emission Inventory (NEI) (EPA, 2014b) and then allocated to the TAZs using surrogates that were generated from DRCOG data. The two sets of data (NEI & DRCOG) were combined and the total emissions flux of benzene for every TAZ was calculated. Benzene emission fluxes were calculated for 2780 TAZ sources that represent benzene emissions in the study urban-scale domain (Touma et al., 2006). Despite the straightforward application of the TAZ approach for emission allocation, it has limitations regarding the selected information of allocation surrogates. For example, O&G surrogates were entirely developed based on the number of active wells in each TAZ. However, there are many factors that impact emissions from O&G section including the chemical composition of the product, well age and production rates. Also, the presence or absence of control equipment, design of equipment, and maintenance can significantly impact the emissions from the O&G sector (Brantley et al., 2015). Similarly, the length-based railroad surrogates that were developed to allocation railroad sector emissions, assume equal emissions from all rail track segments. This can be improved by including more details about rail traffic and different types of trains but this data is not publicly available. Due to lack of location specific data about where off-road and area sector emissions occur, the allocation surrogates for the off-road sector were developed based on a combination of vehicle miles traveled (VMT) and different forms of population data while area sector surrogates were developed based primarily on population data.

2.2. *Benzene sources and impacts of temperature inversions in Denver*

To illustrate an application of the TAZ allocation method, a modeling demonstration was conducted for Denver, Colorado, where benzene has been a major public health concern (DDPHE, 2006). The study area for the modeling demonstration consists of the entire county of Denver. Denver, the capital of Colorado, had a population of 716,492 in July 2018 (United States Census Bureau, 2019). The main sources of air pollution in Denver are on-road (traffic), off-road, area, oil and gas, and point source emissions (Ramboll Environ, 2017). Hourly morning (6 a.m.–9 a.m.) benzene concentrations were predicted in the Denver area using the dispersion model AERMOD. The predicted morning concentrations were compared with the available benzene air measurements that were also collected during the 6 a.m.–9 a.m. sampling period.

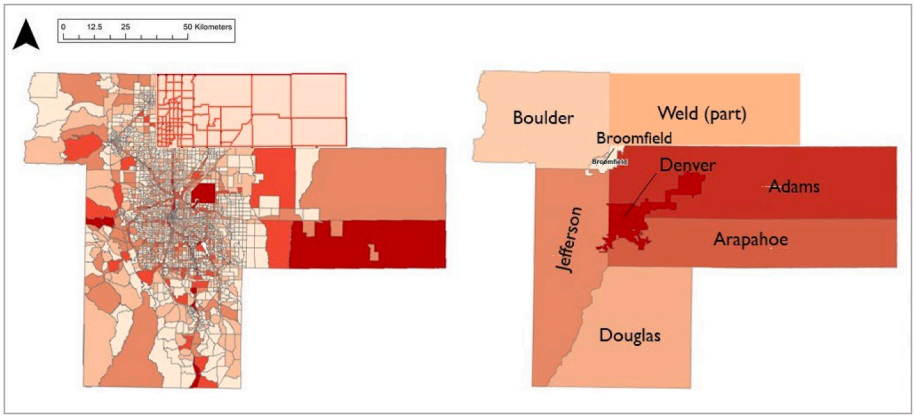

Fig. 2. Transportation analysis zones (TAZs) per county in the Denver Metro/North Front Range.

Fig. S1 illustrates this modeling process.

The impact of temperature inversions on benzene concentrations was also investigated in Denver area. Morning temperature inversions, which are usually accompanied by light winds and a stable atmosphere, leads to higher concentrations of traffic-related pollutants such as benzene. Taking advantage of upper air sounding data availability in the mornings, benzene concentrations during temperature inversions were compared with those without morning temperature inversions. Fig. 3 shows the geographical location of Denver County, the meteorological station (Denver International Airport, DIA), upper air sounding station (Weather Forecast Office), and the benzene measurement station (Consolidated Air Monitoring Program, CAMP) that are used in this study. CAMP station is an EPA funded monitor that is maintained and operated by the Air Pollution Control Division of the CDPHE and is located at 2105 Broadway near downtown Denver.

Meteorological data were collected at DIA located about 30 km northeast downtown Denver at latitude of 39° 50' 49'' N and longitude of 104° 39' 22'' W. The AERMOD-ready meteorological data, which are surface and upper air hourly measurements during the year of 2014 were obtained from the CDPHE (CDPHE, 2014). The data were processed using AERMET (version 16216). Supplementary material section S2 presents the model basic steps and input summary.

AERMOD estimates pollutant concentrations at pre-defined receptor locations. A network of 2628 receptors was used in the model covering the study area. The receptors were generated based on TAZ centroids in and around Denver County. In an urban area where emission sources are smaller and elevated levels of air pollution are expected a high-density network was used. Terrain elevations at each receptor were generated from AERMAP, which requires a Digital Elevation Model. The North American Datum of 1983 (NAD83) was used.

Benzene emissions were calculated from two major source categories: (1) point sources including major stationary sources such as refineries, large factories and numerous oil and gas wells; and (2) benzene emissions from polygon sources that are represented by emissions within TAZs. The point source inventory data used in our modeling was obtained from the Air Pollution Control Division of CDPHE and processed for quality assurance/quality control following the procedure described in DDPHE (2006) (DDPHE, 2006) for location accuracy (Environmental Quality Division, 2016). The emission fluxes for each of the 589 TAZs in Denver County, which are the summation of benzene emissions from the five sectors as described previously were also used in our modeling. The TAZ boundaries spatial coordinates (i.e., polygon vertices) were extracted using the Geographic Information System and the 2015 DRCOG TAZ data layer.

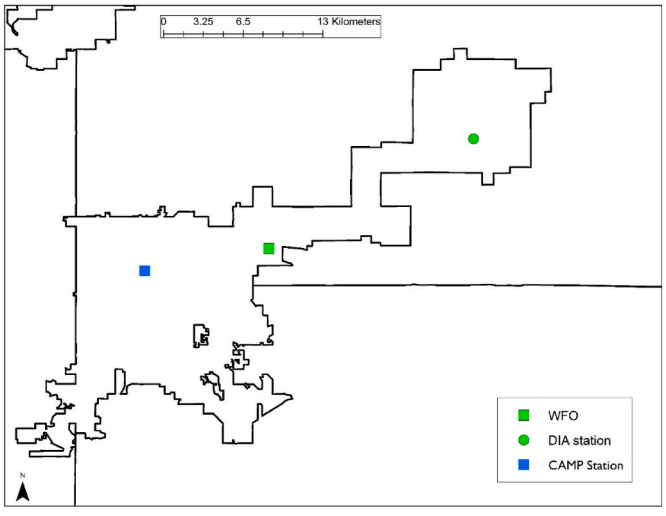

Fig. 3. Denver study area including the surface meteorological data station (green circle), the atmospheric sounding station (green square), and the benzene measurement station (blue square) that were used in the study. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

In this work we account for background benzene concentrations using the DDPHE air toxic assessment study (DDPHE, 2006) approach, which estimated that the 2002 average background benzene concentration in the Denver was of 0.48 $\mu g/m^3$ (0.15 ppbv), based on measurements from clean air locations. The background level is then added to our model estimates. It should be noted that this urban background value has likely decreased over time, as motor vehicle emissions have been reduced. If true, then the modeled concentrations shown here could be overestimated.

Fifty-eight benzene measurements were collected between 6:00 a.m. and 9:00 a.m. (morning) at CAMP between January 7th and December 25th' 2014 using a one-out-of-six-day air sampling campaign. The data were obtained from the CDPHE through a file transfer to the Environmental Quality Division in the DDPHE (Environmental Quality Division, 2014). The temperature inversion analysis focuses on these 58 days only.

Temperature profiles with elevation were generated from atmospheric sounding data collected by the Weather Forecast Office in Denver. They release radiosonde balloons twice every day at 00Z and 12Z. The site is located at latitude of 39° 46' 12'' N and longitude of 104° 52' 12'' W, about 10 km to the east of CAMP station as shown in Fig. 3. The data were accessed at http://weather.uwyo.edu/upperair/sounding.html. We used the data from the 12Z release (5:00 a.m. Mountain Standard Time/6:00 a.m. Mountain Daylight Saving Time).

In general, a negative upward temperature gradient is defined as no inversion present while a positive upward temperature gradient is defined as the presence of an inversion (Fochesatto, 2015). In this study, a temperature profile that shows a 6 °C increase or more was defined as a strong temperature inversion. On the other hand, a temperature profile that showed a temperature increase less than the 6 °C including a negative upward temperature gradient was defined as a not-strong inversion. It is important to mention that the data were first analyzed based on change in temperature per change in elevation (lapse rate). Only a small number of days showed a stable lapse rate compared to the dry adiabatic lapse rate. Therefore, the analysis in this work was carried out based on the 6 °C temperature difference and not based on lapse rate threshold.

3. Results

3.1. TAZ emissions allocation

According to the 2014 NEI, the on-road benzene emissions represented the largest contributor of the five sectors, (39%) followed by O&G (27%), off-road (18%), area (16%) and railroad sector (<1%). Fig. 4A shows that the highest benzene emissions fluxes in $\frac{mg}{hr.m^2}$ were distributed along highways followed by slightly lower emission fluxes distributed in urban areas corresponding to major traffic densities from non-highway roads. See Supplementary material: section S3-A for the equations used to calculate on-road benzene emission fluxes.

Fig. 4B presents the TAZ-based benzene emission fluxes from the off-road sector. The greatest emission fluxes were distributed in densely populated urban areas from non-diesel related benzene emissions, which were assumed to be associated with residential activities. On the other hand, the diesel benzene emissions, assumed to be proportional to agricultural and new development construction activities in rural areas and construction activities in heavy traffic areas, did not show clear patterns. This is probably due to the small contribution from diesel off-road emissions (only 11% of total off-road emissions). For more details see Supplementary section S3-B.

Emission fluxes from the area sector are shown in Fig. 4C. The populated-area related subsectors represented 75% of benzene

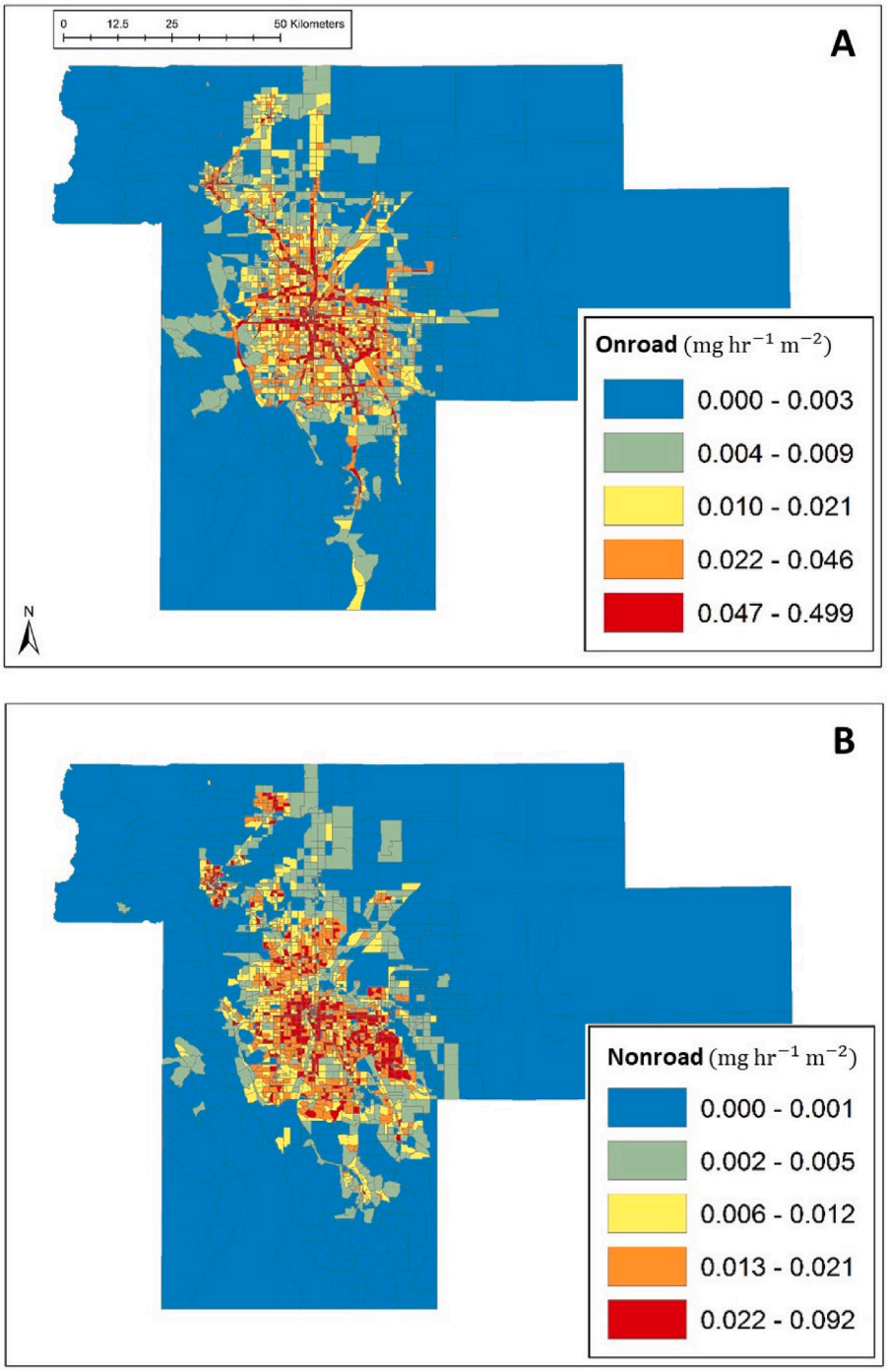

Fig. 4. Denver Metro/North Front Range benzene emission flux of five sectors using the TAZ allocation approach. (A) on-road; (B) off-road; (C) area; (D) oil and gas; (E) railroad.

emissions from total area sector emissions with highest emission fluxes in densely populated areas. Some rural TAZs showed relatively high benzene emissions presumably attributable to TAZ-specific inverse-populated-area activities. Supplementary section S3-C describes the equations that were used to calculate area benzene emission fluxes.

Ninety-seven percent of total O&G related benzene emissions in the model domain were in Weld County (Fig. 4D). Fig. 4E shows benzene emission fluxes from the railroad sector, which are highest along railroad tracks and at railyards. See Supplementary section S3-D and E for more details.

Another way of exploring the benzene emission flux results is to compare the on-road sector flux to another sector one at a time (i.e., compare on-road to O&G, on-road to off-road, on-road to area, on-road to railroad). In Fig. 5, the total fluxes in each TAZ are shown as the summation of on-road fluxes and the O&G fluxes. The figure shows the percentage of on-road benzene contribution to this total flux (on-road and O&G). Dark colors indicate that the contribution was mostly from the on-road sector. While on-road fluxes dominate most of the study area TAZs, the O&G fluxes dominate the TAZs in Weld County due to the presence of O&G production activities. Fig. S2(A-C) in the supplementary section shows similar contribution comparisons between on-road and (A) off-road, (B) area, and (C) railroad benzene fluxes.

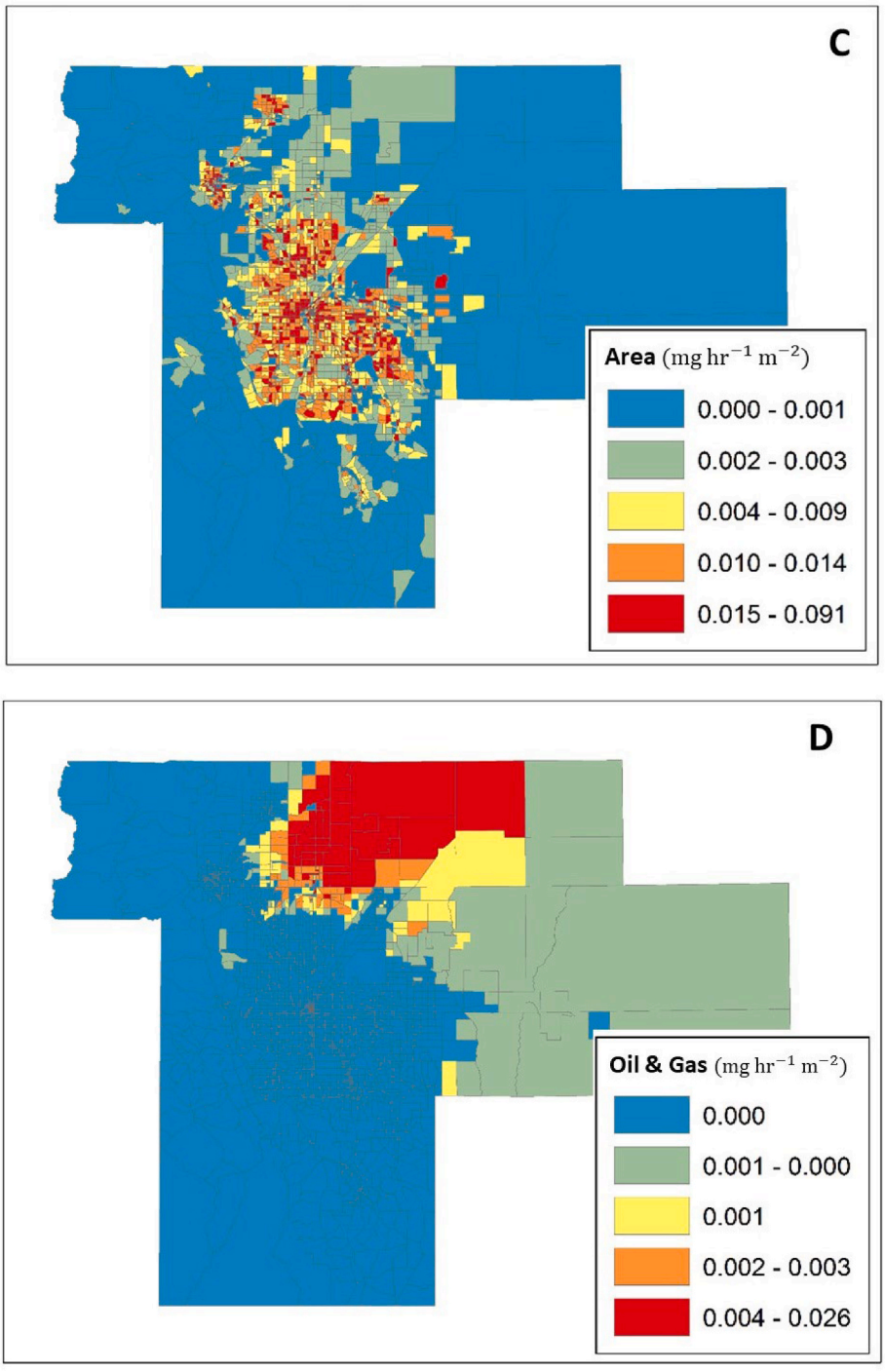

Fig. 4. (*continued*).

3.2. Morning benzene concentrations

The predicted annual average morning (6:00–9:00 a.m.) benzene concentrations for 2014 in the Denver area are shown in Fig. 6. The ratio of model prediction-to-measurement is 1.34 suggesting that the model over-predicts by about 30% the concentration in this area. The Denver urban core experienced the highest predicted morning concentrations exceeding 1.50 $\mu g/m^3$; benzene concentrations outside the urban core range from 1.11 to 1.30 $\mu g/m^3$. It is also worth noting that the contribution of point sources compared to TAZ sources is very small, less than 3% in Denver area.

4. Temperature inversion impact on benzene concentrations

Based on the temperature with elevation profiles generated from atmospheric data, the 58 study days were divided into strong inversions and not strong inversions. The strong temperature inversions occurred on the ten days (see Supplementary Fig. S3) in which the temperature profile showed at least a temperature increase of 6 °C with elevation. The elevation of the inversion associated with the 6 °C threshold increase ranged from 115 to 523 m during these ten strong inversion days. The remaining 48 days were considered "not-strong inversion days". During the ten strong inversions, the measured morning benzene measurements at CAMP exceeded 1 $\mu g/m^3$ for every single day and the

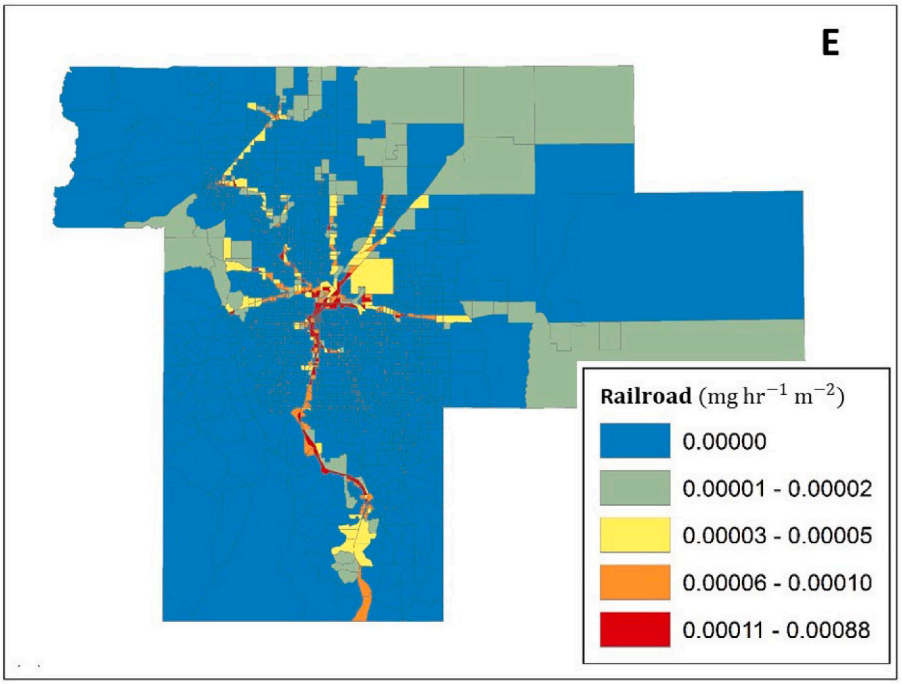

Fig. 4. (*continued*).

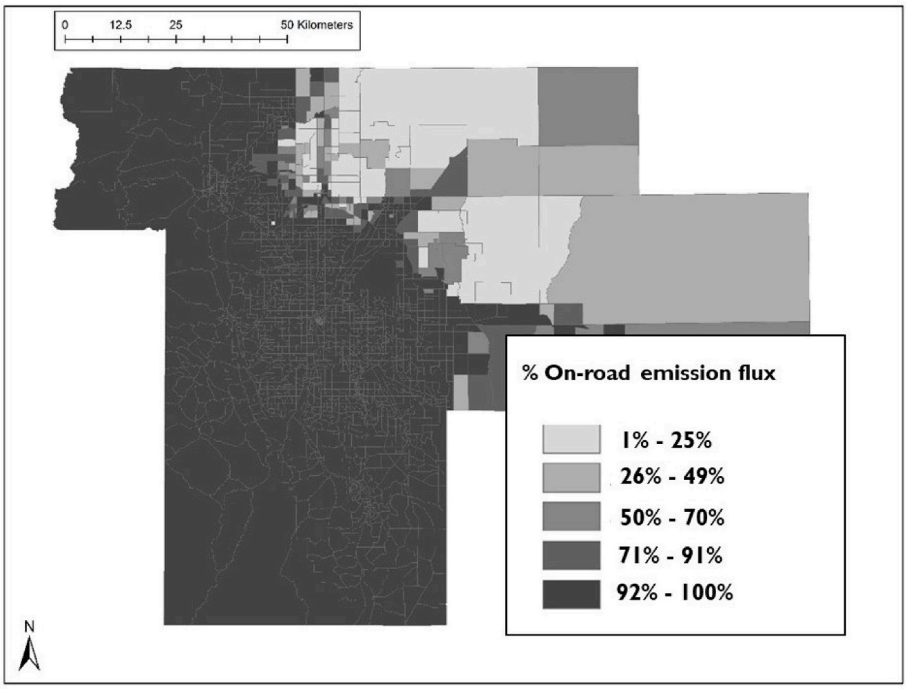

Fig. 5. Denver Metro/North Front Range benzene emission flux contribution using the TAZ allocation approach. On-road contribution to total on-road and oil and gas emission fluxes. Dark color indicates higher contribution from on-road fluxes.

average of morning benzene measurements was 1.89 $\mu g/\ m^3$. The average of benzene measurements during the remaining days (48 days) was 1.06 $\mu g/m^3$ (Fig. 7). A comparison between the two means using Welch's test for unequal variances resulted in a t-statistic of t (10.044) = 1.92, p = 0.08 indicating higher levels of benzene during the inversions but the difference in benzene levels was not statistically significant at the 0.05 level (Table S2). The assumption of normality underlying Welch's test was checked using normal probability plots.

Morning benzene concentrations were predicted for the same 58 days using AERMOD. The model results were examined for the receptor at the CAMP station. The average of the morning benzene predictions during the 10 days with strong inversions was 1.84 $\mu g/m^3$ while the average of the predictions during the rest of the days was 0.66 $\mu g/m^3$ as shown in Fig. 8. Welch's test for unequal variances showed statistically significant difference between the two sets (t (9) = 3.76, p = 0.004) and the assumption of normality was also checked using normal probability

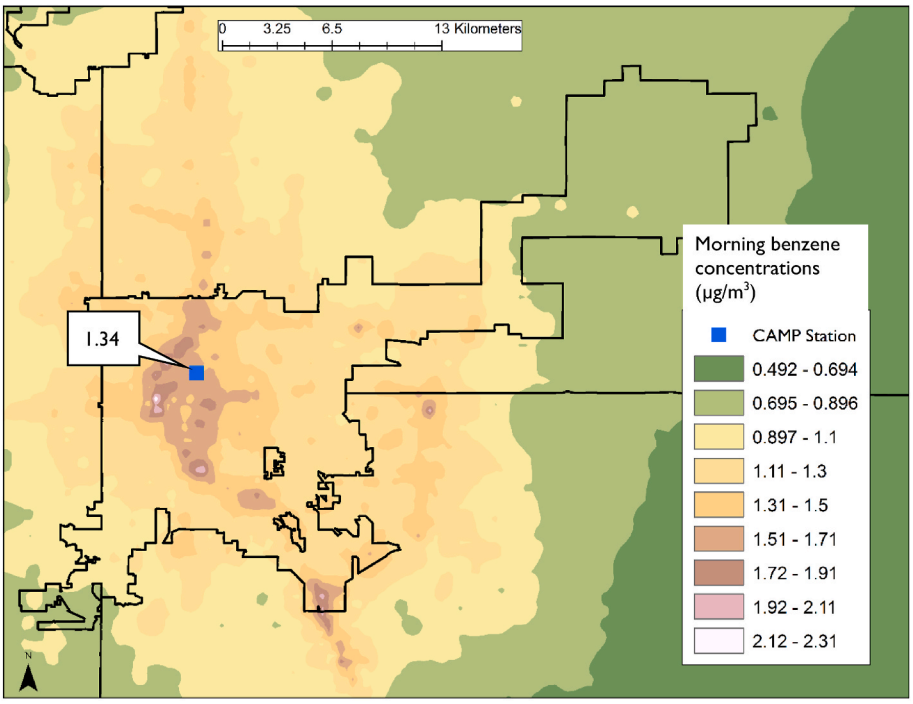

Fig. 6. AERMOD 2014 predicted annual average morning benzene concentrations in Denver area. The benzene concentrations are presented in $\mu g/m^3$. Model-to-monitor ratio at the CAMP monitor is shown on the figure.

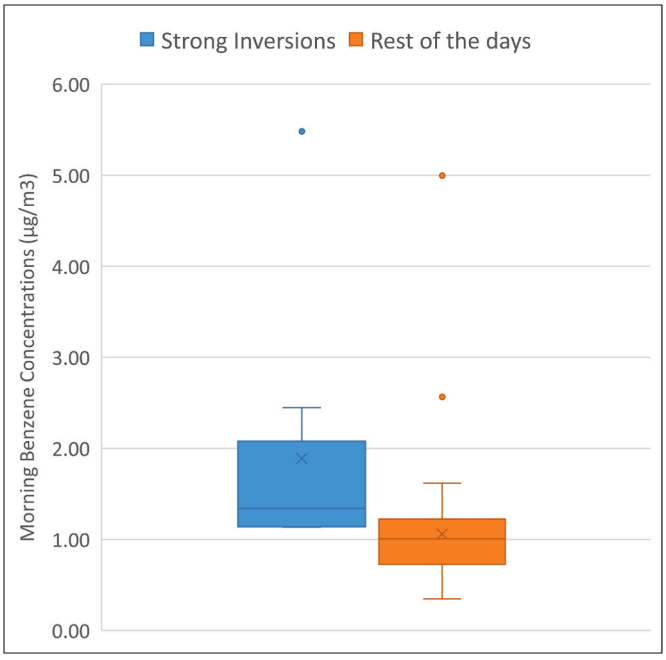

Fig. 7. Morning benzene measurements on the strong inversion days compared with morning benzene measurements on the remaining days.

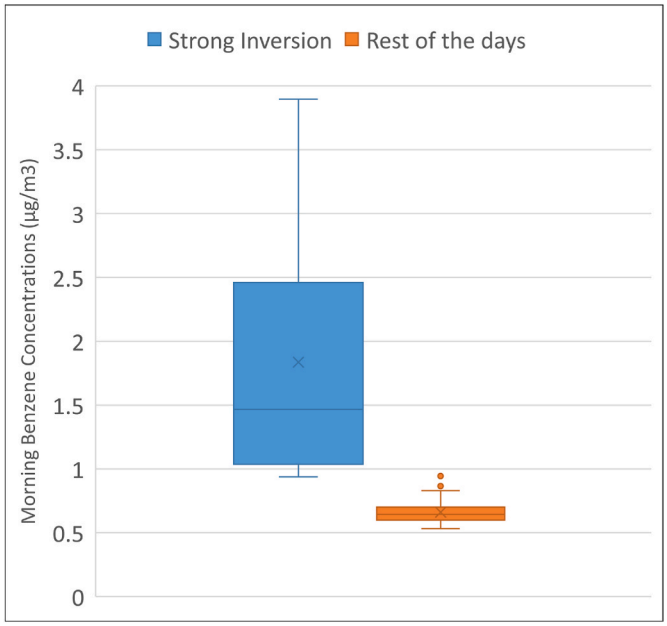

Fig. 8. Morning benzene predictions on the strong inversion days compared with morning benzene predictions on the remaining days.

plots (Table S3).

During these 58 days, the model-to-monitor ratio was 0.97 during the strong inversions, and 0.62 during the remaining days. A Pearson correlation coefficient was computed to assess the association between model and measurement benzene concentrations. There was a positive correlation between the two sets of benzene concentrations ($r = 0.31$, $n = 58$, $p = 0.016$). A closer look at Figs. 7 and 8 shows that the model overpredicts the role of inversions on benzene concentrations. It is also worth mentioning that the model's highest predicted concentrations happened on relatively cold inversion days, while on warmer days the model predicted lower benzene concentrations (see Supplementary Figs. S3, S4, and S5).

5. Discussions and conclusions

Accurate spatial and temporal allocation methods are expected to lead to good agreement between dispersion model estimates and measurements. As a result, more reliable and effective air pollution control strategies can be achieved. The county-level benzene emissions were

allocated to TAZs in the Denver Metro/North Front Range region. The TAZ method specifically provides fine spatial resolution near highways and in the densely populated urban areas. The resolution of this new TAZ allocation method helped visualize different flux patterns generated from the five emission sectors studied here.

Our TAZ allocation method showed that on-road emission fluxes were the highest followed by off-road and area sectors then O&G sector. Railroad sector had the least emission fluxes. High on-road emission fluxes were nearest to highways. Relatively high emission fluxes from off-road sectors were seen in urban areas most likely attributed to non-diesel benzene emissions. The highest emission fluxes from the area sector were associated with residential activities in the urban area while the highest emission fluxes from the oil and gas sector were noticed in rural areas in Weld County where many more oil and gas wells are present. The railroad sector did not have much of an impact on benzene emission fluxes in the study area. These emission flux results were different from results of the total emission contribution per sector. Based on the 2014 NEI, the largest contribution was from the on-road followed by the O&G sector. As mentioned before, most O&G emissions happened in Weld County where the TAZ size is relatively large resulting in an emission flux spread across a large area. This spatial emission distribution would help local authorities to prioritize certain locations for mitigation strategies. It is also an essential input requirement for accurate output from dispersion models.

An AERMOD dispersion model was used to provide a better understanding of the distribution of morning benzene concentrations in Denver. Model-to-monitor ratio was within a factor of 2, which is generally good for air quality model performance (Cook et al., 2008). Patterns along roadways, mainly highways, showed the most noticeable morning benzene concentration gradients in the Denver region. The general model performance and spatial patterns validate the effectiveness of the TAZ allocation method used in this model. This has also been documented in past research for earlier emissions years and/or for years where we did have additional monitoring data to compare with predicted concentrations (DDPHE, 2006).

The impact of temperature inversions on morning benzene concentrations was also investigated. The analysis showed that both measurements and modeled morning benzene concentrations on the strong temperature inversion days were higher than the remaining days. However, there was a difference in level of agreement between the model and measurement inversion results that is probably due to the limited number of strong inversion days. Another possibility of the agreement level differences is that the identification method of strong inversions was based on the 6 °C threshold increase in temperature magnitude. Selecting strong inversion days based on change in temperature with elevation would be an alternative method that can be used instead of the 6 °C threshold increase; this method, however, did not result in enough days for our analysis.

The model's performance changes during warmer days versus colder days. This seasonal change in model performance highlights the importance of investigating the temporal factors used in the model, in particular the assumptions and calculations underlying the seasonal differences.

The model results presented in this study should be interpreted with caution because the 2014 surface meteorological data were obtained from Denver International Airport (30 km miles to the NE of downtown Denver) and wind directions and speeds are frequently different than downtown, which is influenced by the South Platte River valley running through Denver. Meteorological stations that are located far from the emission sources in a complex terrain can lead to confounding factors in the model results (Tartakovsky et al., 2013). Other factors can lead to uncertainty in the dispersion model results such as the model input uncertainties (e.g., emission inventories, spatial and temporal allocation methods) (Touma et al., 2006). Also, the fact that AERMOD does not carry over emissions from hour-to-hour is another source of uncertainty and would cause the model to generally under predict. Some of that uncertainty can be reduced using a regional background concentration, as was done in this study. However, the background value of 0.48 μg/m3 is based on data from 2002, and is likely lower today.

The model results showed that the contribution from point sources was small; less than 3%. Most of the point sources used in the model were located far from the urban core where a relatively low-density receptor network was used. The model receptors did not capture much of the impact of these point sources. In addition, complex point sources were represented by a single emission point as determined from the point source inventory data. In the future, we recommend modeling the point sources (or at least the larger ones) using a network of polar receptors surrounding each source or modeling them as area or volume sources (especially sources with multiple emission points).

In this work, background benzene concentrations based on measurements from clean air locations were added to the model predictions in Denver area. A more detailed and modern method of estimating background benzene concentration estimation that is specifically applied to Denver area is recommended.

CRediT authorship contribution statement

Mohamed Eltarkawe: performed, Conceptualization, Methodology, Software, Validation, Formal analysis, Resources, Data curation, Writing – original draft, review and editing, Visualization. **Gregg Thomas:** performed, Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Shelly L. Miller:** performed, Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aeaoa.2022.100180.

References

Bailey, A., Chase, T., Cassano, J., 2011. Changing temperature inversion characteristics in the U.S. Southwest and relationships to large-scale Atmospheric circulation. J. Appl. Meteorol. Climatol. 50, 1307–1323.

Brandmeyer, J., Karimi, H., 2000. Improved spatial allocation methodology for on-road mobile emissions. J. Air Waste Manag. Assoc. 50, 972–980.

Brantley, H., Thoma, E.D., Eisele, A.P., 2015. Assessment of volatile organic compound and hazardous air pollutant emissions from oil and natural gas well pads using mobile remote and onsite direct measurements. J. Air Waste Manag. Assoc. 65, 1072–1082.

CDPHE, Meteorological Data 2014 from Denver International Airport, Contact info: Emmett Malone (emmett.malone@state.co.us).

Cook, R., Isakov, V., Touma, J.S., Benjey, W., Thurman, J., Kinnee, E., Ensley, D., 2008. Resolving local-scale emissions for modeling air quality near roadways. J. Air Waste Manag. Assoc. 58, 451–461. https://doi.org/10.3155/1047-3289.58.3.451.

Dai, J., Rocke, D., 2000. A GIS-based approach to spatial allocation of area source solvent emissions. Environ. Model. Software 15, 293–302.

Daly, A., Zannetti, P., 2007. Air Pollution Modeling - an Overview. Ambient air pollution, Fermont, CA.

DDPHE, 2006. Final Report: the Denver Urban Air Toxics Assessment Methodology Results and Risks. Denver Department of Public Health and Environment, Denver, CO, USA. Available online or upon request from DDPHE: https://www.denvergov.org/files/assets/public/public-health-and-environment/documents/eq/air-quality-reports/ddphe_air_toxics_report_final_update2006.pdf. May 31, 2022).

DDPHE, 2014. How Neighborhood Planning Affects Health in Globeville and Elyria Swansea. Denver, CO, USA.

Dehghani, M., Fazlzadeh, M., Sorooshian, A., Tabatabaee, H., Miri, M., Baghani, A., Delikhoon, M., Mahvi, A., Rashidi, M., 2018. Characteristics and health effects of BTEX in a hot spot for urban pollution. Ecotoxicol. Environ. Saf. 155, 133.

Denver Regional Council of Governments (DRCOG) – Travel Modeling. Available online: https://drcog.org/services-and-resources/data-maps-and-modeling/travel-modeling.

Doesken, N.; Bliss, O. Temperature Inversions in Colorado - What are they and what do they mean? Colorado State Univeristy. Available online: https://ccc.atmos.colostate.edu/pdfs/Nolan_TempInversions-Colorado(Jan9_2007)%20v2.pdf (accessed on 23 November 2018).

Environmental Quality Division, D.D.P.H.E., 2014. Benzene Measurement Data - CAMP Station, Contact Person. Gregg Thomas, Division Director (Gregg.thomas@denvergov.org), Denver.

Environmental Quality Division, D.D.P.H.E., 2016. Point Source Inventory, Contact Person. Gregg Thomas, Division Director (Gregg.thomas@denvergov.org), Denver.

E.P.A, 2002. Example Application of Modeling Toxic Air Pollution in Urban Areas. Office of Air Quality Planning and Standards, Reseach Triangle Park, NC.

EPA, 2014a–2019. National Emissions Inventory (NEI) Data. Available online: https://www.epa.gov/air-emissions-inventories/2014-national-emissions-inventory-nei-data. (Accessed 1 May 2018).

EPA, 2014b. National Emissions Inventory (NEI) Data - V2, 2019. Available online: https://www.epa.gov/air-emissions-inventories/2014-national-emissions-inventory-nei-data. (Accessed 1 May 2018).

Fochesatto, G.J., 2015. Methodology for determining multilayered temperature inversions. Atmos. Meas. Tech. 8, 2051–2060.

Fujita, E., Campbell, D., Zielinska, B., Arnott, W., Chow, J., 2011. Concentrations of air toxics in motor vehicle-dominated environments. Res. Rep. Health Eff. Inst. 156, 3–77.

Isakov, V., Arunachalam, S., Batterman, S., Bereznicki, S., Burke, J., Dionisio, K., Garcia, V., Heist, D., Perry, S., Snyder, M., Vette, A., 2014. Air quality modeling in support of the near-road exposures and effects of urban air pollutants study (NEXUS). Int. J. Environ. Res. Publ. Health 11 (9), 8777–8793. https://doi.org/10.3390/ijerph110908777.

Johnson, M., Isakov, V., Touma, J.S., Mukerjee, S., Ozkaynak, H., 2010. Evaluation of land-use regression models used to predict air quality concentrations in an urban area. Atmos. Environ. 44, 3660–3668.

Kinnee, E., Touma, J., Mason, R., Thurman, J., Beidler, A., Bailey, C., Cook, R., 2004. Allocation of onroad mobile emissions to road segments for air toxics modeling in an urban area. Transport. Res. D. 9, 139–150.

Kukkonen, J., Pohjola, M., Sokhi, R., Juhana, L., Kitwiroon, N., Rantamaki, M., Berge, E., Odegaard, V., Slordal, L., Denby, B., Finardi, S., 2005. Analysis and evaluation of selected local-scale PM10 air pollution episodes in four European cities: helsinki, London, Milan and Oslo. Atmos. Environ. 39, 2759–2773.

Malek, E., Davis, T., Martin, R., Silva, P., 2006. Meteorological and environmental aspects of one of the worst national air pollution episodes (January, 2004) in Logan, Cache Valley, Utah, USA. Atmos. Res. 79, 108–122.

Martinez, L., Viegas, J., Silva, E., 2009. A traffic analysis zone definition: a new methodology and algorithm. Transportation 36, 581–599.

Quality Division, Environmental, 2015. DDPHE, Denver Regional Council of Governments Data, Contact Person. Gregg Thomas, Division Director (Gregg.thomas@denvergov.org), Denver.

Ramboll Environ; Alpine Geophysics. Denver Metro/North Front Range 2017 8-Hour Ozone State Implementation Plan: 2017 Attainment Demonstration Modeling Final Report to the Regional Air Quality Council. https://views.cira.colostate.edu/wiki/Attachments/Source%20Apportionment/Denver/Denver_2017SIP_2017AttainDemo_Finalv1.pdf (Accessed on 28 February 2022).

Reddy, P.J., Barbarick, D., Osterburg, R.D., 1995. Development of a statistical model for forecasting episodes of visibility degradation in the Denver metropolitan area. J. Appl. Meteorol. 34, 616–625.

Smith, M.T., 2010. Advances in understanding benzene health effects and susceptibility. Annu. Rev. Publ. Health 31, 133–148.

Stein, A., Isakov, V., Godowitch, J., Draxler, R., 2007. A hybrid modeling approach to resolve pollutant concentrations in an urban area. Atmos. Environ. 41, 9410–9426.

Tartakovsky, D., Broday, D.M., Stern, E., 2013. Evaluation of AERMOD and CALPUFF for predicting ambient concentrations of total suspended particulate matter (TSP) emissions from a quarry in complex terrain. Environ. Pollut. 179, 138–145.

Texas A&M Transportation Institute College Station, 2020. Texas in Cooperation with the Federal Highway Administration and the Texas Department of Transportation, Evaluation of Air Quality Models with Near Road Monitoring Data: Technical Report. Available online. http://tti.tamu.edu/documents/0-6943-R1.pdf. Feb 22, 2022.

Touma, J., Isakov, V., Ching, J., Seigneur, C., 2006. Air quality modeling of hazardous pollutants: current status and future directions. J. Air Waste Manag. Assoc. 56, 547–558.

United States Census Bureau - Denver Colorado, Available online: https://www.census.gov/quickfacts/denvercountycolorado (Accessed on 25 April 2019).

United States EPA National Air Toxics Assessment, Available online: https://www.epa.gov/national-air-toxics-assessment (accessed on Feb 22, 2022).

Whiteman, C.D., Zhong, S., Bian, X., 1999. Wintertime evolution of the temperature inversion in the Colorado Plateau Basin. J. Appl. Meteorol. 38, 1103–1118.

Zheng, J., Che, W., Wang, X., Louie, P., Zhong, L., 2009. Road-network-based spatial allocation of on-road mobile source emissions in the pearl river delta region, China, and comparisons with population-based approach. J. Air Waste Manag. Assoc. 58, 1405–1416.