Response to reviewers:

Reviewers comments are in italic font, authors' comments/responses start with (AC), and revised text is shown in red font

Anonymous Referee #1

Received and published: 15 November 2019

General comments:

This paper summarizes a study in which the finely resolved (2.5x2.5 km) GEM-MACHPAH model was employed to investigate contributions of motor vehicles to benzene and several PAHs in ambient air across northeastern North America. I found this paper to be a significant contribution to the field and of scientific merit, and had relatively few critical comments. I was particularly interested in the combined effects of removing benzene/PAHs at the same time as removing air quality criteria pollutants (precursors of compounds that degrade benzene/PAHs), and the differences in these effects in rural versus urban locations. The study addresses several interesting questions on a very fine spatial scale, including:

-How much do vehicles contribute to ambient benzene and PAH concentrations, and how does that differ between the warm and cold seasons and across urban versus rural locations?

-How do reductions in vehicle emissions play out in actual ambient concentrations?

-What are the combined impacts of removing benzene/PAH oxidant precursors and benzene/PAH emissions themselves on ambient benzene/PAH concentrations?

-How does particulate fractioning respond when all vehicular emissions are removed?

-How do benzene/PAHs respond in general to changes in oxidant concentrations?

-How sensitive is the model to doubling and halving vehicular emissions?

-How does human health risk change when vehicular emissions are removed?

(AC) Thank you for your detailed and positive review! We have addressed each of your comments below.

Specific comments:

Line 121: Can examples of "off-road mobile sources" be provided?

(AC) Yes, we have updated the manuscript to include examples of off-road mobile sources, which include trains, boats, snowmobiles, aircraft, and others.

Line 135: It would be helpful to have "close to unity" qualified so readers don't have to dig back through the previous Whaley paper. Plus or minus what on average?

(AC) Thank you for the suggestion. We have quantified our statement as shown below,

Ratios of modelled to measured concentrations were generally within an order of magnitude of unity, with median values in spring-summer being lower for BENZ and PAHs with molecular weight 178-202 g mol^{-1} (0.31-0.86) than for PAHs with molecular weight 228-252 g mol^{-1} (1.8-8.4). Fall-winter values were modestly higher (1.5-9.9) though still within an order of magnitude of unity. Further details can be found in Whaley et al. (2018).

Line 155: Lower temperatures also increase partitioning to particles for PAHs. Does the decrease in degradation rates and decrease in dilution outweigh these effects?

(AC) Indeed, lower temperatures are generally related to increased PAH partitioning to particles. However, our statement about ambient concentrations being higher in winter than in summer refers to total (gas + particle) concentrations, and applies equally to particle-bound compounds and to those that are found exclusively or predominantly in the gas phase. Earlier studies using different particle-gas partitioning parametrizations suggest that modelled lifetimes of gaseous and particulate study compounds are similar at the regional scale (e.g., Galarneau et al., 2014, Atmos. Chem. Phys. 14:4065-4077), though we have noted that further work examining partitioning effects is warranted for future studies, particularly if larger spatial scales will be employed (line 278+).

Line 180-ish: It was mentioned in the intro that the adoption of ZEVs was encouraged in a variety of jurisdictions. Are there differences in this "encouragement" between US and Canadian cities that could also account for the higher contributions from on-road vehicles in US cities?

(AC) Transportation policies in Canada and the US are generally closely aligned, but our model results are based on simulations using emissions and meteorology from 2009, and market penetration of ZEVs was very low at that time, thus we don't expect this to be the cause of differences between Canada and the U.S. in our simulations for this paper.
In the years since, both Canada and the US have increased their market share of EVs – for example from 2012 to 2016, the market share of EVs in both countries increased about 0.45% (from 0.15% to 0.59% in Canada, and from 0.44% to 0.91% in the US[1]). Note that these numbers include plug-in hybrid vehicles as well, not just ZEV.
[1]https://lop.parl.ca/staticfiles/PublicWebsite/Home/ResearchPublications/BackgroundPapers/PDF/2017-27-e.pdf

Figure S2. Is there a particular reason why the BENZ and BaP fall-winter plots are not shown? It would be handy to be able to compare seasonally for all four species chosen, or have an explanation as to why they are not shown. It is mentioned in the conclusions that future work aims to improve model representation of wintertime benzene and BaP, but (unless I missed it) I couldn't find a discussion about why their representation wasn't acceptable.

(AC) Fall-winter BENZ and BaP were not shown for separate reasons. For BENZ, estimates of releases from residential wood combustion had not been included in the model-ready emissions, and their absence reduced our confidence in reporting motor vehicle contributions (see page 5 of the supplement) – we have added a clearer reference to this in the revised main manuscript in the Model evaluation summary. Modelled fall-winter BaP concentrations were biased high relative to available measurements, similarly reducing our confidence in the BaP fall-winter predictions, and we did not discuss vehicle contributions as a result (see lines 136-139 in original manuscript, and more detailed discussion in Whaley et al., 2018, Geosci. Model Dev. 11:2609-2632).

Lines 189-192: Would be helpful to quantify, based on model results, how much lower concentrations would need to go to reach these criteria, and whether the complete removal of on-road vehicle sources reverses exceedances, or if additional sources would need to be removed (hard to tease out from the plots).

(AC) Thank you for the suggestion. We agree that our model could be used as a tool to examine options for reducing airborne concentrations to levels below health-based guidelines. Unfortunately, the simulations described in this study do not provide the necessary information to do so. Guidelines tend to be promulgated at daily or annual time scales; the two that we have cited for our target jurisdiction (Toronto, Ontario, Canada) are for BENZ and BaP on an annual basis. However, our simulations covered

two seasonal periods, and BENZ and BaP results were simulated with confidence only in spring-summer. Given that the latter period does not represent typical conditions at the annual scale, we feel estimating the necessary reductions based on our results to date would not be justifiable. For example, doing so may underestimate necessary reductions given that spring-summer concentrations are lower than those at other times of the year. We hope that future applications of the model (with recommended improvements) will be useful for the analyses that you have suggested, and we appreciate your confidence in the relevance of our work.

Line 235: This is probably discussed in previous papers, but would be handy to have a clarification here: BaP is the ONLY PAH to react with O3 on particles, even though partitioning to particles takes place for the other PAHs as well? Given the changes in O3 in rural and urban areas and the impact on BaP in the "no mobile" case, can the authors comment on how including O3 particle-phase oxidation for the other PAHs might impact their reductions? Would it be similar? How would the combination of changing OH and O3 concentrations play out for semi-volatile species? If it's easy to test this, I suggest adding it to the study.

(AC) Yes, we have included reactions with ozone for only one particulate PAH (BaP). The literature has historically demonstrated that only BaP is substantially degraded by on-particle reactions with ozone, and robust reaction rates have not been published for other PAHs. The other particle-bound PAHs in our study are semi-volatile, meaning that only a fraction is particle-bound, and they are thought to be relatively unreactive with ozone. As a result, on-particle ozone reactions for those compounds is expected to result in negligible changes to total concentrations, and we have therefore excluded such reactions. This is clarified in the revised manuscript.

Sensitivity to oxidant experiments shown in the Supporting Info: This is a very interesting section of the paper and it's too bad it can't be highlighted in the main text. I think it would be helpful if the authors put a section in the methods that describe how the sensitivity analyses were conducted for making the S5 and S6 plots.

(AC) Thank you for that suggestion. We have added the following text at the end of the Methods section:

The sensitivity of model results for partitioning and other parameters (e.g., oxidant concentrations) is examined in Section 3.7 and in the Supplement. Good overall performance of GEM-MACH-PAH has been demonstrated by comparison to measurements as discussed above (see Whaley et al., 2018 for further detail), and our sensitivity analyses further support the model's validity for calculating ambient concentrations and for assessing source contributions at its evaluated resolution (2.5 km grid size and seasonal time scale).

Technical Corrections:
The placement of the parentheses in the very first line of the Introduction (lines 29-31) makes the sentence difficult to read. I think it would help to have another descriptor after "air quality", like "degradation", or "problems".

(AC) Thank you. The sentence has been re-written as:

Emissions from motor vehicles have been linked to air quality degradation (e.g., WHO(2005); Han and Naeher(2006); Zhang and Batterman(2013); Farrell et al.(2016); Zimmerman et al.(2016); Gentner et al.(2017); Wang et al.(2017)) and greenhouse gas pollution (e.g., Sims et al.(2014); Zimmerman et al.(2016); Boulton(2016); US EPA(2002)).

Line 124: Again, parentheses are oddly placed. I suspect automated citation management software was used, so suggest combing back through the paper and removing those interrupting parentheses.

(AC) Thank you. The sentence has been re-written as:
Detailed model descriptions and evaluations of GEM-MACH have been published for pollutants other than benzene and PAHs (Moran et al.,2010,2013;Makar et al.,2015b,a;Gong et al.,2015;Whaley et al.,2018a).

Line 165: Should be "show" instead of "shows"

(AC) Thank you. We have corrected that.

Line 183: Put a "to" between "concentrations" and "increase".

(AC) Thank you, we have added that.

Line 339: Should it read "91% PAH" instead of "91% PHEN"?

(AC) Yes, thank you. Both are correct, but 91% PAH is what was intended as a summary of the PAH results.

Anonymous Referee #2
Received and published: 20 December 2019

The introduction needs to be much clearer on why this reserach was undertaken. Additionally, the assertions need to be backed up with appropriate citations. In particular, Lines 33-35 do not seem true, so need citations to support them.

(AC) Thank you for your review. The need for high resolution, city-scale modelling of PAHs is clear because of previous research we cite in the paper (lines 63-66 in original) showing that human exposure to PAHs is concentrated in the cities and highways. Those were observational studies, but no modelling study has been done on this subject to date. The model has the ability to quantify this source contribution – whereas measurements alone cannot.

The text in lines 33-35 contained three references in the original manuscript: US EPA, 2012; Reid and Aherne, 2006; and Government of Canada, 2018. We are uncertain which part of that text you have found to be lacking credibility; that transportation policies between Canada and the U.S. are closely aligned, or that "Government and automobile manufacturers have both pledged to further reduce emissions".

Regarding the former, we have added another reference to the revised manuscript. The ECCC page (link [1] below) discusses the strategy to align with U.S. policies: "There is a long history of collaboration between Environment Canada (EC) and the U.S. Environmental Protection Agency (EPA) to reduce transportation emissions, largely fostered by the framework of Canada-U.S. Air Quality Agreement (AQA)."[1]
There is also further evidence from a new ECCC report[2] to support "transportation policies being closely aligned in Canada and the United States", where the market share of electric vehicles in both countries has increased by a similar amount (~0.45%) from 2012 to 2016.

[1]https://www.canada.ca/en/environment-climate-change/corporate/international-affairs/partnerships-countries-regions/north-america/canada-united-states-vehicle-engine-emissions.html
[2]https://lop.parl.ca/staticfiles/PublicWebsite/Home/ResearchPublications/BackgroundPapers/PDF/2017-27-e.pdf

Regarding the latter, we have modified the sentence to the following in our revision:
"The Canadian and US governments promote the benefits of zero emission vehicles (ZEV)[3,4], and several jurisdictions in both countries have adopted strategies to increase ZEV use (e.g., [5,6])."
Indeed, the Canadian government has "established light-duty zero-emission vehicles policy sales targets of 10% by 2025, 30% by 2030, and 100% by 2040"[7].
[3]https://www.tc.gc.ca/en/services/road/innovative-technologies/zero-emission-vehicles.html
[4]https://www.energy.gov/eere/electricvehicles/electric-vehicle-benefits
[5]http://www.environnement.gouv.qc.ca/changementsclimatiques/vze/index-en.htm
[6]https://www.c2es.org/document/us-state-clean-vehicle-policies-and-incentives/
[7]https://www.canada.ca/en/services/environment/weather/climatechange/climate-plan/reduce-emissions.html

We regret that the motivation for the study is not clear to you. The motivation can be summarized by the following research question:

What is the contribution of vehicle emissions to ambient air PAH & BENZ concentrations at the local (human exposure) scale?

We base our research question on the following known factors:

→ Vehicle emissions are associated with air pollution

→ Vehicle emissions represent a small fraction of total PAH & BENZ emissions in national inventories

However, the system is more complex, showing the need for advanced photochemical model capable of resolving emissions and concentrations at an urban scale:

→ Due to a number of physico-chemical processes, PAH & BENZ emissions are transformed between point of release and ambient air

→ Mobile PAH emissions, while small on a national basis, are emitted in a spatially heterogeneous manner (e.g., in cities and on major roadways), and the scale that is relevant to human exposure is therefore local rather than national.

We have walked through these points in our Introduction in order to set out the motivation for the work. The other reviewer for the manuscript, who found it to "be a significant contribution to the field and of scientific merit" has not indicated any such concerns, nor have colleagues who reviewed the manuscript in advance of its submission.

I cannot comment on how this model performs relative to its peers. However, I don't see the utility in turning various block-level emission estimates and county level emissions estimates into a geographical model. There does not appear to be any need of a 2.5km resolution for the type of analyses presented here.

(AC) Regarding your statements that you "cannot comment on how this model performs relative to its peers" and "I don't see the utility in turning…emissions…into a geographic model.": Three-dimensional chemical transport models, wherein a complete description of the processes that result in changes in concentration have been incorporated into model code, have a history in the air-quality modelling community stretching back to the late 1970's. 'Turning emissions into a geographical model' is an oversimplification of that entire field of research. The non-linearity of the connection between emissions and ambient concentrations is well-known, and has resulted largely because of the development and application of chemical transport models over the last 40 years. These models have been used for both research and policy purposes, helping to determine the relationship between pollution sources and receptors for important environmental issues such as acid deposition and smog pollution. The additional innovations in our work were to add benzene and PAH emissions and atmospheric processing to such a model (Galarneau et al., 2014; Whaley et al 2018b); and here, to use the model to determine the relative impact of a specific source sector on PAH concentrations, hence towards human exposure in populated areas.

Understanding the contribution of a potentially important pollution source such as vehicle exhaust to ambient air, where human exposure occurs, is the crux of the "need of a 2.5km resolution". Elevated pollutant concentrations tend to be found in urban areas where fine-scale modelling is required to properly represent spatial gradients. Measurements in ambient air, which are expensive for PAHs relative to other common air pollutants, are not available at such a fine scale over entire regions. Furthermore, determining source contributions from ambient air measurements is problematic, given the overlap in source signatures and differences in atmospheric processing that occur for these compounds. Hence, chemical transport models at fine spatial scale are tools of unparalleled utility for examining the importance of air pollution sources for the air to which humans are exposed.

In examining the referenced article Whaley et al 2018b, it is not clear that the GEMMACH-PAH model has the accuracy and precision to really describe the difference the authors say it is between the two scenarios. The variability across sites and seasons seems that it is larger than the observed difference. For example, the % reduction of the PF of FLRT in winter looks to be 20% in Figure 6f. In Whaley et al 2018b, the model to measurement ratio for FLRT varies across sites from -10 to 10. It seems that this
degree of uncertainty makes it hard to believe the model is able to tell the difference between a change of 20% and a change of 200%.

(AC) We agree that adequate performance from an atmospheric chemical transport model such as GEM-MACH-PAH must be demonstrated before it is used to answer questions about source contributions. At the same time, a predicted spatial variation in a simulated field such as the model to measurement ratio for FLRT should not be confused with the impact of an emissions scenario which results in a reduction in concentrations across the entire domain. The model-to-measurement ratio for the base case mentioned is a prediction of spatial variability in error, not a measure of uncertainty in the model predictions across the domain. For domain-wide impact predictions such as the % reduction of PF, the model's bias with respect to observations is the relevant metric of performance. As presented in the 2018 paper, and reiterated in the current manuscript, simulated seasonal concentrations were found to be unbiased relative to measurements for all reported compounds. This finding was based on measurements from locations associated with a variety of land uses (e.g., urban, industrial, rural, etc.) and concentration levels, and represents the most extensive assessment of model performance ever conducted for PAHs. We also note that the reviewer's cited rage is based on daily values (Figure 6b in Whaley et al., 2018b) whereas the vehicle contributions in the current manuscript are based on seasonal averages, which exhibit less inter-site variability.

Though atmospheric chemical transport models are not perfect, validated models such as ours are nevertheless useful for assessing source contributions. We used our validated model to examine vehicle contributions by taking the difference between two simulations ("base" with all emissions on, and "no mobile" with vehicle emissions off). Given that process representation and non-vehicle emission uncertainties will be the same in both simulations, the impact of those uncertainties are substantially reduced when estimating vehicle contributions. This is also the strandard "scenario emissions simulation" practice in use by the air-quality modelling community in providing advice on the impact of emissions over the last 40 years. As a result, we have high confidence in the resulting vehicle contributions that we have reported.

As an additional measure, we note that in our submitted manuscript we examined potential uncertainties in vehicle emissions, which do not cancel out in our difference scenario. Our tests showed that changes in simulated concentrations were sensitive to, but consistent with, the emission perturbations (see lines 287-296 of the original manuscript and Section V of the Supplement), lending further confidence to our mobile source contribution estimates.

I'm also not completely clear on what the difference is between the Whaley 2018 model and the model used in this paper.

(AC) The model used in both papers is the same, and is described in Section 2.1 of the manuscript. The Whaley 2018b paper provided the technical background of the model development and evaluation, and the current paper describes the application of the model to answer the research question noted above (viz., what is the contribution of vehicle emissions to ambient air concentrations of PAHs at the local (human exposure) scale?).

How much does traffic contribute to benzene and PAH air pollution? Results from a high-resolution North American air quality model centered on Toronto, Canada

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Abstract. Benzene and polycyclic aromatic hydrocarbons (PAHs) are toxic air pollutants that have long been associated with motor vehicle emissions, though the importance of such emissions has never been quantified over an extended domain using a chemical transport model. Herein we present the first application of such a model (GEM-MACH-PAH) to examine the contribution of motor vehicles to benzene and PAHs in ambient air. We have applied the model over a region that is centered on Toronto, Canada, and includes much of southern Ontario and the northeastern United States. The resolution (2.5 km) was the highest ever employed by a model for these compounds in North America, and the model domain was the largest at this resolution in the world to date. Using paired model simulations that were run with vehicle emissions turned on and off (while all other emissions were left on), we estimated the absolute and relative contributions of motor vehicles to ambient pollutant concentrations. Our results provide estimates of motor vehicle contributions that are realistic as a result of the inclusion of atmospheric processing, whereas assessing changes in benzene and PAH emissions alone would neglect effects caused by shifts in atmospheric oxidation and particle/gas partitioning. A secondary benefit of our scenario approach is in its utility in representing a fleet of zero emission vehicles (ZEV), whose adoption is being encouraged in a variety of jurisdictions. Our simulations predicted domain-average on-road vehicle contributions to benzene and PAH concentrations of 4-21% and 14-24% in the spring-summer and fall-winter periods, respectively, depending on the aromatic compound. Contributions to PAH concentrations up to 50% were predicted for the Greater Toronto Area, ~~with a domain maximum of~~ and the domain maximum was simulated to be 91%. Such contributions are substantially higher than those reported ~~in national~~ at the national level in Canadian emissions inventories, and they also differ from inventory estimates at the sub-national scale because those do not account for the physico-chemical processing that alters pollutant concentrations in the atmosphere. The removal of on-road vehicle emissions generally led to decreases in benzene and PAH concentrations during both periods that were studied, though atmospheric processing (such as chemical reactions and changes to gas/particle partitioning) contributed to non-linear behaviour at some locations or times of year. Such results demonstrate the added value associated with regional air quality modelling relative to examinations of emissions inventories alone. We also found that removing on-road vehicle emissions reduced spring-summertime surface O_3 volume mixing ratios and fall-wintertime PM_{10} concentrations each by $\sim$10% in the model domain, providing further air quality benefits. Toxic equivalents contributed by vehicle emissions of PAHs were found

to be substantial (20-60% depending on location), and this finding is particularly relevant to the study of public health in the urban areas of our model ~~area~~ domain where human population, ambient concentrations, and traffic volumes tend to be high.

1 Introduction

~~It is well known that vehicle traffic emissions cause significant air quality~~ Emissions from motor vehicles have been linked to air quality degradation (e.g., WHO (2005); Han and Naeher (2006); Zhang and Batterman (2013); Farrell et al. (2016); Zimmerman et al. (2016); Gentner et al. (2017); Wang et al. (2017)) and greenhouse gas pollution (e.g., Sims et al. (2014); Zimmerman et al. (2016); Boulton (2016); US EPA (2002)) globally. In North America, vehicle emission controls have gradually reduced emissions of many pollutants, and made vehicles more fuel-efficient (U.S. Environmental Protection Agency, 2012; Reid and Aherne, 2016), with transportation policies being closely aligned in Canada and the United States ~~. Governments and automobile manufacturers have both pledged to further reduce emissions over the coming decades with increased adoption of fully-electric and hybrid-electric vehicles and charging infrastructure (Government of Canada, 2018).~~(ECCC, 2019b). The Canadian and US governments promote the benefits of zero emission vehicles (ZEV) (Transport Canada, 2019; energy.gov, 2020) , and several jurisdictions in both countries have adopted strategies to increase ZEV use (e.g., Government of Quebec (2020); Center for clima). Additionally, the phase-out of high emission electricity generation has already begun, with Ontario's power generation ~~90~~95% emissions-free as of ~~2015 (58~~2017 (61% nuclear, ~~23~~27% hydro, ~~9~~7% wind and solar; ~~Ontario (2019)~~ECCC (2019a)). With this rapidly approaching future in mind, atmospheric chemistry models are useful tools for predicting the expected changes in pollutant concentrations that will result from a continuing reduction in vehicle emissions.

Of particular interest are highly toxic pollutants such as benzene and polycyclic aromatic hydrocarbons (PAHs), which are ubiquitous in the environment and include compounds that are carcinogenic, mutagenic, and teratogenic. In Canada, both have been subject to risk management under the Canadian Environmental Protection Act (CEPA) with actions focused on emergency management, fuel composition, and emitting activities associated with the natural gas, aluminum, iron and steel, and wood preservation industries (ECCC, 2015, 2018b). Ontario, Canada's most populous province and home to the nation's largest city, Toronto, has developed health-based ambient air quality criteria for these pollutants, but these are exceeded at many locations throughout the country (Galarneau et al., 2016) despite the actions taken under CEPA. In the U.S., benzene and PAHs have been identified as contributors to excess cancer risk under the National Air Toxics Assessment (NATA) program (EPA, 2015).

National benzene emissions in Canada are compiled through the National Pollutant Release Inventory (NPRI) (NPRI, 2016) but only for major industrial, commercial, and institutional sources. Previous model-based estimates (Stroud et al., 2016) suggest that 40-54% of benzene in the ambient air of major Canadian cities is due to mobile sources (e.g., cars, trains, ships), which are not included in the NPRI. In the U.S., the most recent National Emissions Inventory (NEI) (US EPA, 2018) includes benzene emissions estimates from a variety of natural and anthropogenic sources. At the national scale, 47% (90 kT) of benzene emissions in the U.S. are estimated to arise from mobile sources, of which 60% (54 kT) is from on-road vehicles (e.g.,

cars, trucks, motorcycles). Those on-road vehicle contributions range from 0-84% of total benzene emissions when reported at the county or tribal level.

Canadian emissions of four PAHs (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, and indeno[1,2,3-cd]pyrene) from all known anthropogenic sources are estimated through the comprehensive national Air Pollutant Emission Inventory (APEI) (ECCC, 2018a) whose major point source emissions are reported through the NPRI. Mobile source contributions in the APEI accounted for 8.3% (2,~~620~~ 629 kg) of the total anthropogenic emissions of benzo[a]pyrene (31,516 kg) in 2017, the most recent data year available, consistent with (Environment Canada and Health Canada, 1994; Galarneau et al., 2007). In the U.S., the 2014 NEI (US EPA, 2018) reports that on-road vehicle emissions are 20% (28,931 kg) of total national anthropogenic benzo[a]pyrene (BaP) emissions (145,102 kg). Relative mobile source contributions are expected to be greater in urban centres (Nielsen, 1996; Harrison et al., 1996; Dunbar et al., 2001; Shen et al., 2011; Pachón et al., 2013; Kuoppamäki et al., 2014; Miao et al., 2015) than they are at the national scale due to the spatial concentration of urban on-road vehicle use and the tendency of large industrial sources to be located outside those cities.

Here, we make use of a recently developed and validated high-resolution, on-line chemical transport model (GEM-MACH-PAH, Whaley et al. (2018b)) to study the impact of on-road vehicle emissions on ambient concentrations of benzene and a suite of PAHs in a regional domain centred over Toronto, Canada that includes much of sourthern Ontario and the northeastern U.S. (Figure 1). GEM-MACH-PAH was run with identical meteorology for two emissions cases: (1) a “base" case with all emissions of all species and sectors included; and (2) a “no mobile" case with emissions of all species from on-road vehicles set to zero (BENZ, PAHs, and criteria air contaminants (CACs) such as NO_x, CO, VOCs, PM, etc). The vehicle contributions are determined from the difference of the “base" and “no mobile" cases, and this strategy has permitted us to calculate vehicle contributions in a realistic way that incorporates not only the effect of benzene and PAH emissions, but also the effect of atmospheric processing caused by the changes to CACs emitted by motor vehicles. The “no mobile" scenario has additionally allowed us to quantify the impact of a hypothetical future ~~fleet of zero-emissions vehicles (ZEV)~~ZEV fleet, whose adoption is being encouraged in a variety of jurisdictions. We did not simulate biofuel emission scenarios, as those fuels have sometimes been shown to increase PAH emissions, rather than reduce them (Karavalakis et al., 2011), and further work is needed before they can be simulated with confidence.

These simulations provide consistent information about the spatial distribution of concentrations and on-road vehicle contributions for benzene and PAHs. While other PAH chemical transport models exist (Aulinger et al., 2007; Friedman and Selin, 2012; San José et al., 2013; Gariazzo et al., 2014, 2015; Thackray et al., 2015; Zhang et al., 2016, 2017), this is the first study to use such a model to evaluate traffic contributions to ambient air and assess the change in resulting airborne toxicity. Our simulations also have the highest resolution employed to date in a North American domain, and the largest high-resolution domain compared to other PAH modelling studies anywhere in the world.

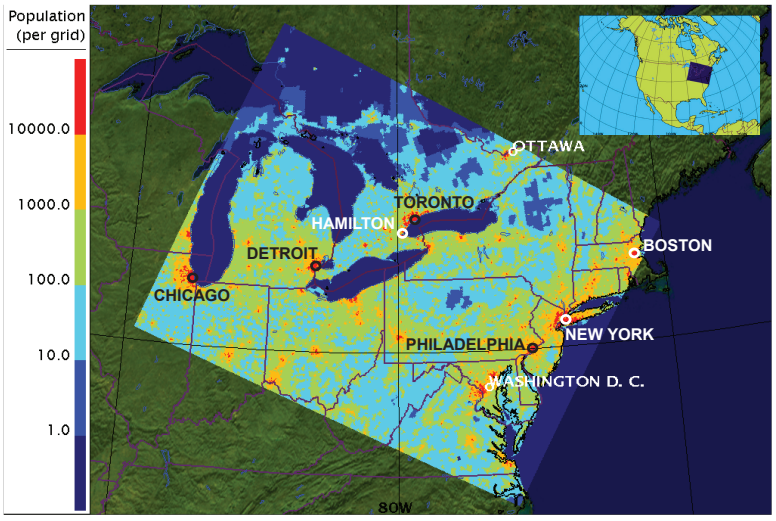

Figure 1. Model domain, coloured on a logarithmic scale by the human population per 2.5×2.5-km^2 model grid cell.

2 Methods

2.1 Model description

GEM-MACH (Moran et al., 2010) (Global Environment Multiscale Modelling Air quality and CHemistry) is an online chemical transport model driven by meteorological fields produced by the GEM numerical weather prediction model (Côté et al., 1998b, a). The model was recently adapted to include the emission, advection and diffusion, deposition, and chemical degradation of benzene (BENZ) and seven PAHs: phenanthrene (PHEN); anthracene (ANTH); fluoranthene (FLRT); pyrene (PYR); benz[a]anthracene (BaA); chrysene (CHRY); and benzo[a]pyrene (BaP) (Whaley et al., 2018b). While BENZ in ambient air is gaseous, PAHs are semi-volatile species, found in both the gas and particle phases. Their particle/gas partitioning in GEM-MACH-PAH is determined via the Dachs-Eisenreich scheme (Dachs and Eisenreich, 2000; Whaley et al., 2018b). Section I of the Supplement provides further information on PAH process representations within the model.

GEM-MACH-PAH was run at 2.5 km horizontal grid spacing on a domain that includes large North American urban areas such as Toronto, New York City, Chicago, Washington, D.C., Philadelphia, Boston, and Detroit (Figure 1).

Two time periods in 2009 were chosen (spring-summer, 13 May to 13 August; and fall-winter, 23 October to 5 January 2010) to balance the computational demands required for this model (IBM Power7 supercomputer) against the ability to examine seasonal differences and include evaluation data from a temporally coincident, high-density campaign conducted in 2009 west of Toronto (Anastasopoulos et al., 2012). Additional details about the model setup and run strategy are provided in the Supplement (Section I).

2.2 Emissions

Hourly, gridded, and speciated input emissions fields were prepared using the Sparse Matrix Operator Kernel Emissions system (SMOKE, https://www.cmascenter.org/smoke, ~~(Houyoux et al., 2002)~~Houyoux et al. (2002)) making use of criteria air pollutant emissions from Canada's 2010 APEI (Sassi et al., 2015) reported by province, and U.S. EPA 2011 NEI (Eyth et al., 2013) emissions reported at the county/tribal level. BENZ and PAHs were speciated relative to aggregate VOC emissions using VOC speciation profiles from the Canadian Emissions Processing System (Moran et al., 1997) for BENZ and special speciation profiles developed by Galarneau et al. (2007, 2014); Whaley et al. (2018b) for PAHs. PAH emissions from on-road mobile sources were calculated from VOC emissions generated using MOBILE 6.2C (EPA, 2002) and MOVES 2010b (https://www.epa.gov/moves/moves2014-and-moves2010b-versions-limited-current-use) for Canada and the U.S., respectively. PAH species emissions were estimated using PAH-to-VOC and PAH-to-organic carbon emission ratios from MOVES2014 converted to a total organic gas (TOG) basis. Note that reported emission factors (EFs) for PAHs in the literature are highly variable. Different EFs were tested in the model but those from MOVES2014 achieved the best results compared to observations (Whaley et al., 2018b).

SMOKE uses spatial surrogate fields to distribute vehicle emissions reported for each jurisdiction (e.g., provinces in Canada, counties in the U.S.) among model grid cells. Unlike the MOBILE 6.2C-based inventory for Canada, the MOVES2010b-based inventory for the U.S. explicitly includes an "off-network" road type that accounts for emissions when vehicles are stationary (e.g., idle, parked, starting or refuelling), and this road type contributes $\sim$60% of on-road emissions (NEI2011). The effect of this spatial-allocation difference between the MOBILE and MOVES inventories on the modelled on-road vehicle contributions of BENZ and PAH is presented later in this work.

To construct the emissions fields for the "no mobile" case, emissions from all area sources, off-road mobile sources ~~,~~(e.g., trains, boats, snowmobiles, aircraft, etc.), and minor point sources present in the "base" case were retained, but all on-road vehicle emissions (of all species) were removed.

2.3 Model evaluation summary

Detailed model descriptions and evaluations of GEM-MACH ~~appear in (Moran et al., 2010, 2013; Makar et al., 2015b, a; Gong et al., 2015; V~~ have been published for pollutants other than benzene and PAHs (Moran et al., 2010, 2013; Makar et al., 2015b, a; Gong et al., 2015; Whaley . The GEM-MACH-PAH base simulation used for the current study was previously evaluated in the most rigorous comparison to measurements yet published for such a model at fine spatial resolution (Whaley et al., 2018b). That evaluation compared GEM-MACH-PAH output to benzene and PAH measurements from 121 and 35 network sites, respectively, from Canada's National Air Pollution Surveillance program (NAPS), the U.S. National Air Toxics Trends Stations (NATTS), and the Canada-U.S. Integrated Atmospheric Deposition Network (IADN), which all record 24-hour integrated air concentrations every one in six days, at locations associated with a variety of population densities and land uses (e.g., urban, sub-urban, industrial and rural locations). Additional 2-week integrated PAH measurements from 46 sites in a high-spatial-density campaign conducted

in Hamilton, Ontario, Canada in spring-summer and fall-winter 2009 (Anastasopoulos et al., 2012) were also used to assess concentration variability within a city as well as within model grid squares (Supplement, Section I).

Ratios of modelled to measured concentrations were ~~close to unityfor the lowest molecular weight compounds~~ generally within an order of magnitude of unity, with median values in spring-summer ~~, and increased modestly in the fall-winter and with increasing molecular weight .~~ being lower for BENZ and PAHs with molecular weight 178-202 g mol-1 (0.31-0.86) than for PAHs with molecular weight 228-252 g mol-1 (1.8-8.4). Fall-winter values were modestly higher (1.5-9.9) though still within an order of magnitude of unity. Further details can be found in Whaley et al. (2018b). Modelled concentrations were found to be statistically unbiased relative to measurements (paired t-test with $t < 1$, $p > 0.01$) for all compounds and seasons except for BaP in fall-winter (Whaley et al., 2018b), which was biased high. Model output for the latter compound and season combination was therefore excluded from this study. Fall-winter BENZ was also excluded from this study because of an important missing sector discovered in the fall-wintertime BENZ emissions. Please refer to the Supplement, Section I for more information.

GEM-MACH-PAH's particle/gas partitioning parametrization was evaluated at six IADN stations and the results showed a substantial improvement over the previous AURAMS-PAH partitioning (Galarneau et al., 2014) due to an empirically-based update in partitioning parameters (Whaley et al., 2018b).

The good overall performance (Whaley et al., 2018b) of GEM-MACH-PAH demonstrates its validity for calculating ambient concentrations and for assessing source contributions at its evaluated resolution (2.5 km grid size and seasonal time scale).

The sensitivity of model results for partitioning and other parameters (e.g., oxidant concentrations) is examined in Section 3.7 and in the Supplement. Good overall performance of GEM-MACH-PAH has been demonstrated by comparison to measurements as discussed above, with more detail in Whaley et al. (2018b), and our sensitivity analyses further support the model's validity for calculating ambient concentrations and for assessing source contributions at its evaluated resolution (2.5 km grid size and seasonal time scale).

3 Results

Spatial distributions of modelled concentrations and vehicle contributions were similar for BENZ and the seven PAHs. As a result, we focus on a few representative species in this section, and show results for the remaining species in the Supplement.

3.1 Benzene and PAH concentrations from the base case

Modelled "base" case (all emissions activated) average airborne concentrations of BENZ, PHEN, PYR and BaP are shown in Figure 2 for the spring-summer and Figure S.2(a) for the fall-winter. The three PAH compounds exhibit a range of volatilities. PHEN and BaP are found predominantly in the gas and particle phases, respectively, whereas PYR, with a mid-range volatility, is typically found in both. The spatial distribution of concentrations is similar to the distribution of human population shown in Figure 1 as expected from the prevalence of anthropogenic sources in the study area.

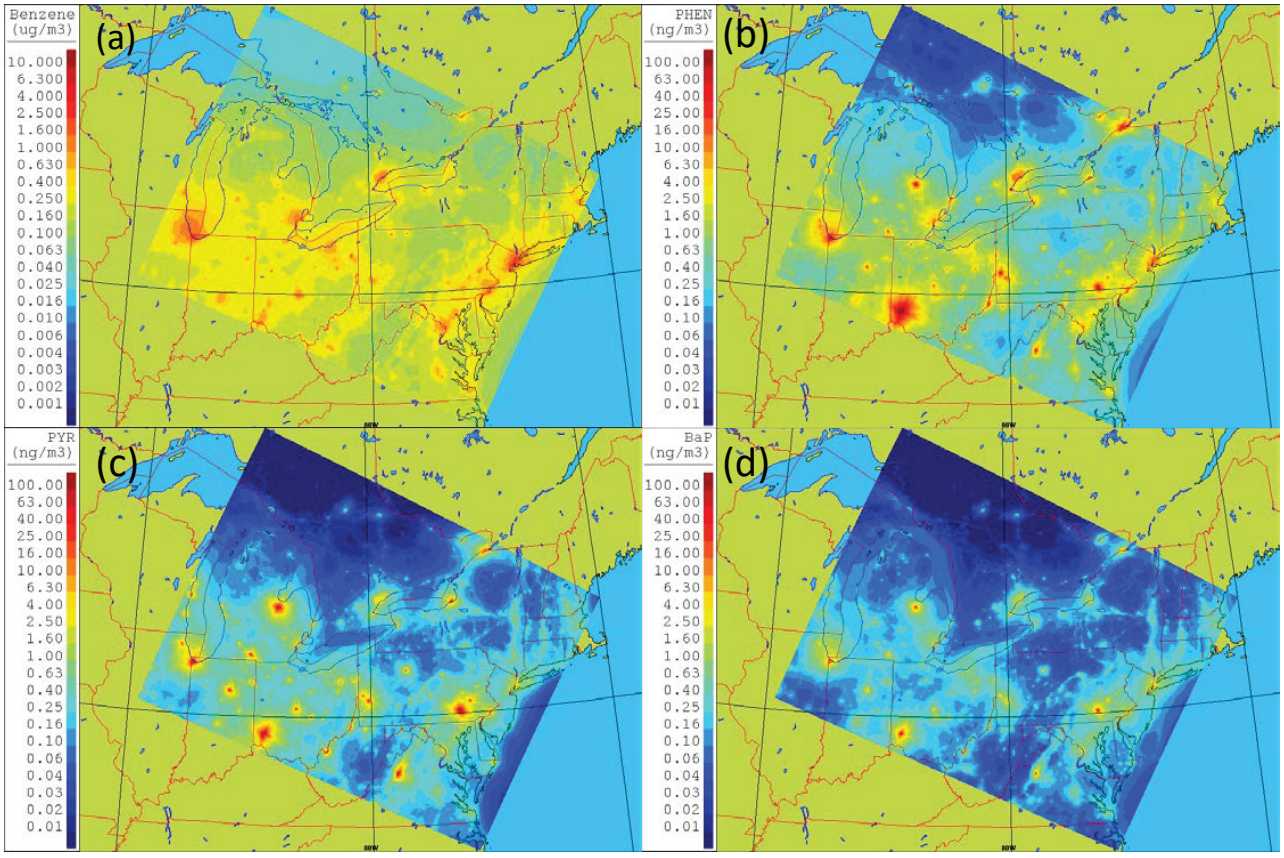

Figure 2. Modelled average airborne concentrations for (a) BENZ, (b) PHEN, (c) PYR, and (d) BaP in the spring-summer.

Modelled concentrations for BENZ and PAHs are higher in fall-winter than in spring-summer (Whaley et al., 2018b) due to lower fall-winter temperatures and solar radiation. These factors lead to to reduced photochemical degradation and increased vertical stability, which in turn induce less vertical mixing and dilution, and lower boundary layer heights. Thus, ambient concentrations are higher per unit emission in fall-winter than in spring-summer. Additionally, total emissions for PAHs are higher in fall-winter than in spring-summer (Figure S.3a) due to increased on-road vehicle emissions (e.g., cold starts) and combined area/off-road mobile sources (e.g., heating, snowmobiling). Note that different rates of PAH oxidation in the different seasons are expected to lead to different rates of production of secondary products such as oxy- and nitro-PAHs. These secondary products are not yet included in GEM-MACH-PAH due to uncertainties in their sources and properties, but they are under consideration for future addition to the modelling package given that some of these compounds are more toxic than their parent PAHs.

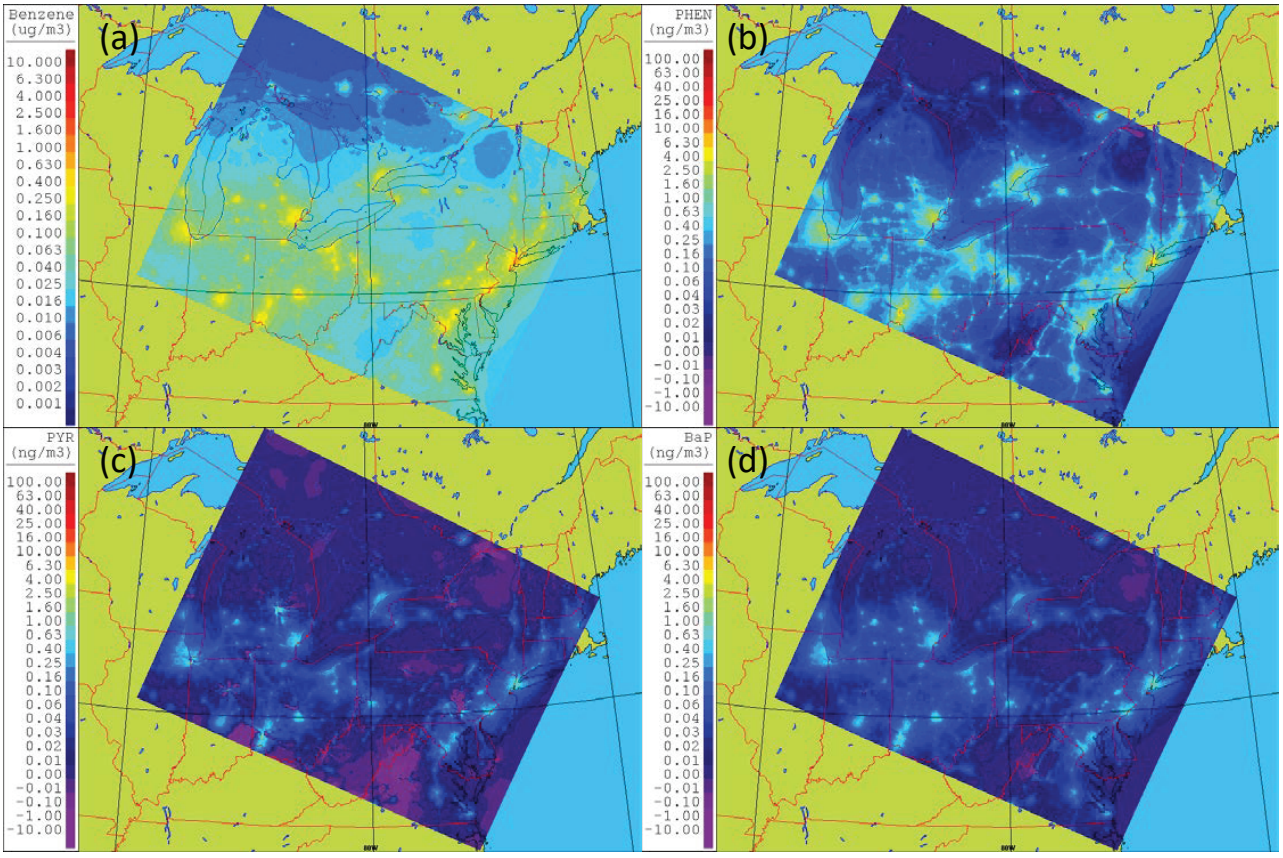

Figure 3. Seasonal-average absolute on-road vehicle contributions for (a) BENZ, (b) PHEN, (c) PYR, and (d) BaP in the spring-summer.

3.2 Absolute on-road vehicle contributions

Figure 3 and Figure S.2(b) ~~shows~~ show the contribution of on-road vehicles to ambient concentrations in the spring-summer and fall-winter, respectively, as represented by the absolute differences in concentrations between the “base" and “no mobile" cases. Concentrations in the “no mobile" case are significantly lower than those for the “base" case as expected from the lack of on-road vehicle emissions.

Major cities are prominent in Figure 3 for all species as expected given high urban traffic volumes. In the Greater Toronto Area (GTA), BENZ concentrations due to on-road vehicles in spring-summer are on the order of 0.1-0.3 μg m^{-3} (Figure S.4) and these values are similar to those of other urban centres in Ontario such as Hamilton. Spring-summer contributions up to 0.5-0.9 μg m^{-3} of BENZ are seen in the large urban centres of the U.S. such as New York City, Chicago, and Washington, DC (Figure S.4) as well as in several smaller U.S. cities (Figure 3).

Spatial distributions of absolute on-road mobile source contributions for the PAHs are similar to those for BENZ. Spring-summer contributions in the GTA for PHEN, PYR and BaP are approximately 2.0, 0.35, and 0.3 ng m^{-3}, respectively, and

slightly higher in fall- winter for the species reported in Figure S.2b. Absolute contributions from on-road vehicles are higher in the major U.S. urban areas than they are in the Canadian cities (examples for BENZ and PYR shown in Figure S.4). These cross-border differences arise in part because of differences in the spatial surrogates mentioned above and the different emissions inventories (see Section 2.2 and Supplement, Section IV). Furthermore, the cities in the U.S. portion of the study region have populations that are larger on average than the cities in the Canadian portion, and concentrations of PAHs have been shown to increase in direct proportion to human population (Hafner et al., 2005).

However, there are some geographically-limited exceptions where the removal of on-road vehicle emissions causes PAH concentrations to increase slightly (areas with negative values in Figure 3): in the spring-summer there are small concentration increases in the northeastern portion of New York State and along the border between Virginia and West Virginia. These apparent anomalies are located where base PAH concentrations are already relatively low, and are consistent with the impacts on oxidant chemistry discussed below, and in the supplement (Section V). In fall-winter, PAH increases in the "no mobile" case are confined to two small regions near the domain borders (Figure S.2b), where factors other than the emission change may be responsible (e.g., boundary effects, numerical issues, etc.).

Nevertheless, measurements show that Ontario's annual ambient air quality criteria for BENZ (0.45 μg m^{-3}) and BaP (0.01 ng m^{-3}), the latter of which is used by the province as a surrogate for PAHs, are exceeded in Toronto, Hamilton, and Windsor (Galarneau et al., 2016). The absolute contributions of on-road vehicles in those areas (Figure 3) suggest that reducing their emissions could assist in reducing those exceedances. Policies and programs seek to achieve air quality benefits with minimal socioeconomic cost, thus knowledge of the relative (e.g., percent) contributions of different sources is an important criterion for prioritizing possible management actions. The reduction of on-road vehicle emissions will only be effective in achieving meaningful reductions in ambient concentrations if their local contributions are significant relative to the total.

3.3 Relative on-road vehicle contributions

The relative contributions (expressed as the percentage of the "base" case concentrations) of on-road vehicles to BENZ, PHEN, PYR, and BaP concentrations are shown as maps and frequency distributions of domain-wide ranges in Figures 4 and 5, respectively, with maps for the remaining PAH species shown in Figures S.2c and S.8 of the Supplement. Domain-wide average and maximum values are also listed in Table 1 and shown in Figure 5. Relative on-road vehicle contributions to PAH concentrations in individual model grid squares had maxima as high as 64-91% in spring-summer. Maxima were slightly lower in fall-winter (49-72%) for the subset of PAHs reported for that period (Figures 5 and S.2c, and Table 1). Domain means, however, were higher in the fall-winter than in the spring-summer (Figure 5, and Table 1). The highest relative on-road vehicle contributions were observed in or near small cities such as North Bay, Ontario; Columbus and Toledo, Ohio; and Grand Rapids, Michigan, where major highways are found in areas of otherwise low ambient concentrations.

In the spring-summertime, domain-mean on-road vehicle contributions to ambient BENZ in the GTA were on the order of 14-37%, consistent with, though slightly lower than previously reported values (Stroud et al., 2016) due to the latter study including off-road mobile sources in their "mobile" category. PAH contributions in the GTA ranged from 5-50% depending on species, season, and proximity to major highways. Even greater contributions were seen in other Canadian cities, thus,

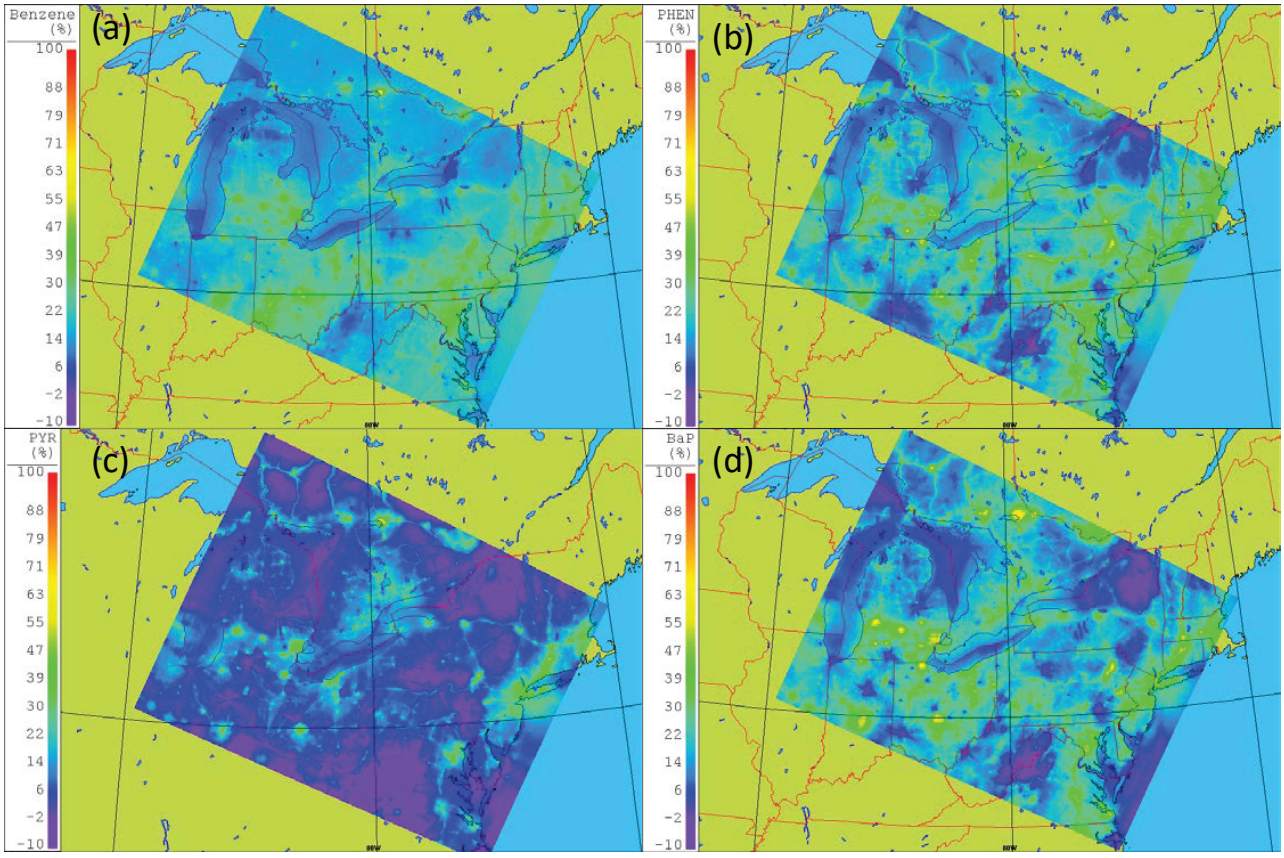

Figure 4. Seasonal-average relative on-road vehicle contributions to ambient concentrations of (a) BENZ, (b) PHEN, (c) PYR, and (d) BaP in the spring-summer.

Table 1. Domain-wide average and maxima on-road vehicle contribution to ambient concentrations. NR = not reported

	benzene	PHEN	ANTH	FLRT	PYR	BaA	CHRY	BaP
spring-summer avg	21%	21%	19%	4%	8%	16%	13%	19%
spring-summer max	74%	91%	86%	64%	76%	75%	74%	83%
fall-winter avg	NR	24%	24%	14%	18%	19%	19%	NR
fall-winter max	NR	72%	64%	52%	64%	49%	54%	NR

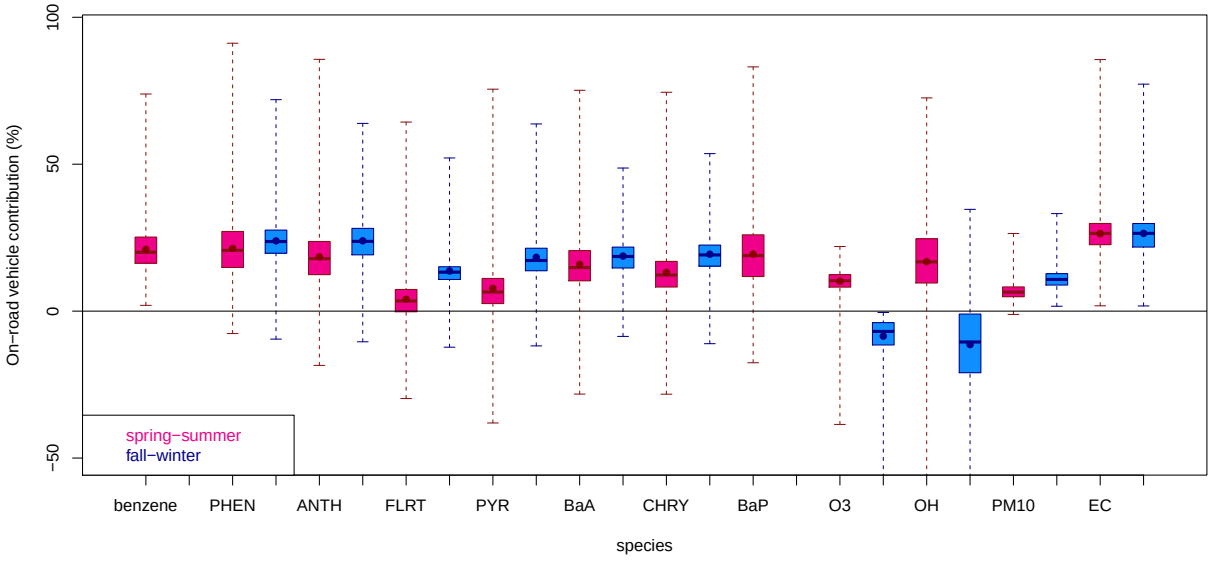

Figure 5. Seasonal-averaged relative on-road vehicle contributions to daily-average surface concentrations (in % of total) in the model domain for all pollutants studied. Whiskers extend to the maximum range of the data in the domain, the centre line is the domain-median, and the dots are the domain-average.

our results suggest that fewer and/or less extreme exceedances of provincial BENZ and PAH guidelines could be achieved by reductions in on-road vehicle emissions in cities within the model domain.

This finding is significant in the Canadian policy-making context and demonstrates the value of examining pollutant emissions and concentrations on fine geographic scales. The APEI and other Canadian efforts (Environment Canada and Health Canada, 1994; Galarneau et al., 2007) have estimated that PAH contributions from on-road mobile sources amount to ~~less than 10~~7-8% of total anthropogenic PAH emissions, at the national scale (provincial-scale estimates for BENZ and PAHs are not included in the APEI). Such minor relative contribution at the national scale could lead to the neglect of the on-road mobile source category in emissions reductions strategies, yet we have shown that this category is important at the local scale in terms of impacts of potential BENZ or PAH management actions.

In the U.S., NEI emissions are reported at the county or tribal level. On-road vehicle contributions in those reported emissions are closer to this study's high-resolution results in ambient air than are the contributions in emissions reported at the national scale. Nonetheless, on-road vehicle contributions of BENZ and PAHs differ between emissions and ambient air due to physico-chemical processing that occurs in the atmosphere. Such processing varies with time of year and levels of vehicle co-pollutants as described below.

3.4 Seasons' impact on on-road vehicle contributions to benzene and PAHs

Though PAH emissions from on-road vehicles are higher in fall-winter than in spring-summer (Figure S.3a), the relative contribution of on-road vehicles to total emissions is stable among seasons (viz., domain-average differences between fall-winter and spring-summer emission contributions from on-road vehicles are -0.6% and range from -1.8% to +2.7% for species reported for both time periods; see Figure S.3b).

In contrast, relative on-road vehicle contributions to ambient concentrations differ more between seasons than do their emissions, with differences of +3% to +10%, respectively between fall-winter and spring-summer (Figure 5). This suggests that a given relative reduction in on-road vehicle emissions may lead to greater concentration reductions in fall-winter than in spring-summer, and highlights the importance of conducting analyses that represent conditions at different times of year. The following analysis expands on factors that are potentially responsible for this temporal variability.

3.5 Oxidants' impact on on-road vehicle contributions to benzene and PAHs

GEM-MACH-PAH includes reactions of BENZ and PAHs with two oxidants: hydroxyl radical (OH, which reacts with BENZ and gaseous PAHs) and ozone (O_3, which reacts only with particulate BaP) (Galarneau et al., 2014; Whaley et al., 2018b). As noted earlier, the "no mobile" case zeroed on-road vehicle emissions for all emitted chemical species, including precursors to tropospheric OH and O_3, such as NO_x, CO, and VOCs. Thus, the removal of vehicle emissions impacts not only the concentrations of the pollutants of BENZ and PAH directly, but also modifies the concentrations of the oxidants responsible for their chemical degradation.

In the spring-summer, the removal of on-road vehicle emissions of criteria air pollutants leads to OH reductions in most parts of the study region (Figure 5 and red areas in Figure S.9a). Oxidative removal rates of BENZ and gaseous PAH are thus reduced in those parts of the domain as a result. This contributes to the finding that reductions of BENZ and PAH emissions of 10-27% associated with the removal of the on-road mobile emissions (Figure S.3b) result in domain-average concentration reduction to a lesser degree, of 4-21% (Table 1). The removal of all mobile on-road emissions decreases oxidant concentrations, hence BENZ and PAH from other sources is oxidized to a lesser degree, offsetting the reductions in BENZ and PAH associated with the mobile emissions removal itself. Conversely, OH increases by 10-50% in some urban cores (e.g., Toronto, Detroit, New York City; blue areas in Figure S.9a) in the spring-summer when on-road vehicle emissions are removed, in response to higher O_3 levels via reduced NO_x titration, with a similar result over large portions of the study area in fall-winter (blue in Figure S.9b). At these times and locations, a positive feedback is produced, whereby the degradation of BENZ and gaseous PAHs from other sources is accelerated in areas where their emissions from vehicles have been removed.

Similarly, on-road vehicles emissions in spring-summer contribute to a domain-wide median of $\sim$10% ($\sim$3.5 ppbv) to surface O_3 volume mixing ratios (Figure 5). Thus, when vehicle emissions are removed, airborne BaP is reduced less than expected from the emissions reduction because of reduced oxidation of BaP from O_3. However, in and around major cities, the changes in O_3 due to on-road vehicles are smaller than 10% and are often negative (see blue in Figure S.9c), viz., O_3 increases in response to the removal of NO_x from on-road vehicles in this hydrocarbon-limited regime (Sillman, 1995; Kleinman et al.,

2000; Sillman and West, 2009; Jing et al., 2014; Zhang et al., 2014), thus increasing oxidation of BaP from non-mobile sources. The "no mobile" case degradation of BaP is thus enhanced in urban areas. This leads to net urban BaP reductions that are greater than might be expected from the removal of urban BaP on-road vehicle emissions alone.

3.6 Effect of elemental carbon on on-road vehicle contributions to PAHs

PAHs are semivolatile and their mass is therefore partitioned between the gas and particle phases in ambient air. Particulate fraction (PF) (Junge, 1977), the ratio of the particulate concentration to the total (gaseous + particulate) concentration, is a common descriptor of particle/gas partitioning. Smaller, lighter PAHs have small PFs of about 0 (e.g., for PHEN), whereas larger, heavier PAHs, have PFs around 1 (e.g., for BaP), and semi-volatile PAHs like FLRT and BaA fall somewhere in the middle (Figure 6a,c). The extent of PAH partitioning varies with temperature and with the availability and composition of particulate matter (PM), where the latter is affected by the zeroing of on-road vehicle emissions as discussed below.

On-road mobile source contributions to domain-averaged PM were 7% in spring-summer and 10% in fall-winter (Figure 5 and S.9e and f), lower than those for total (gaseous + particulate) PAHs. This suggests that PAH PFs might rise, that is, a greater relative amount of the PAH might partition to the particulate phase, if on-road mobile source emissions were reduced because relatively more PM would be available per unit mass of remaining PAH. However, decreases in PAH PFs were observed in the "no mobile" case (Figure 6b, d-f). This was due to the nature of partitioning, which is specific to PM speciation. Elemental carbon (EC) is the prime sorbent for PAHs in the particle/gas partitioning parameterization in the model (Dachs and Eisenreich, 2000). The on-road vehicle contributions of EC averaged 26.5% of total EC mass in both seasons (Figures 5 and S.9g and h). Relative to the "base" case, EC in the "no mobile" case was thus reduced to a greater extent than PAH due to the high EC fraction of PM emissions from motor vehicles. This in turn, resulted in the particle/gas partitioning equilibrium being shifted toward the gas phase since less EC mass was available to sorb the remaining PAH. Shifts in particle/gas equilibrium in turn affect removal processes such as deposition and degradation, whose mechanisms differ for gaseous and particulate compounds (Bidleman and Foreman, 1987). Further analysis of the differences in PAH lifetimes that arise from a shift in particle/gas partitioning is beyond the scope of this paper, but it should be kept in mind for future analyses, particularly those that incorporate considerations of transboundary or long-range transport.

3.7 Sensitivity Considerations

The results described thus far have shown that on-road vehicle emissions contribute substantially to benzene and PAHs in ambient air at a variety of locations in our study area. Differences between seasonal vehicle contributions have been examined with respect to the atmospheric processing that transforms toxic pollutants after they have been emitted to the air. Potential sensitivities of our model results to the uncertainties in emissions and atmospheric chemistry are explored in this section, and are described in more detail in the Supplement (Section V).

We expect that the largest contribution to uncertainty in our results to be associated with the PAH mobile emissions. The on-road vehicle EFs for PAHs that underlay this study's inventory were taken from MOVES2014b (EPA, 2014). These factors were determined from two U.S. reports that examined gasoline and diesel emissions separately (Kishan et al., 2008; Khalek et al.,

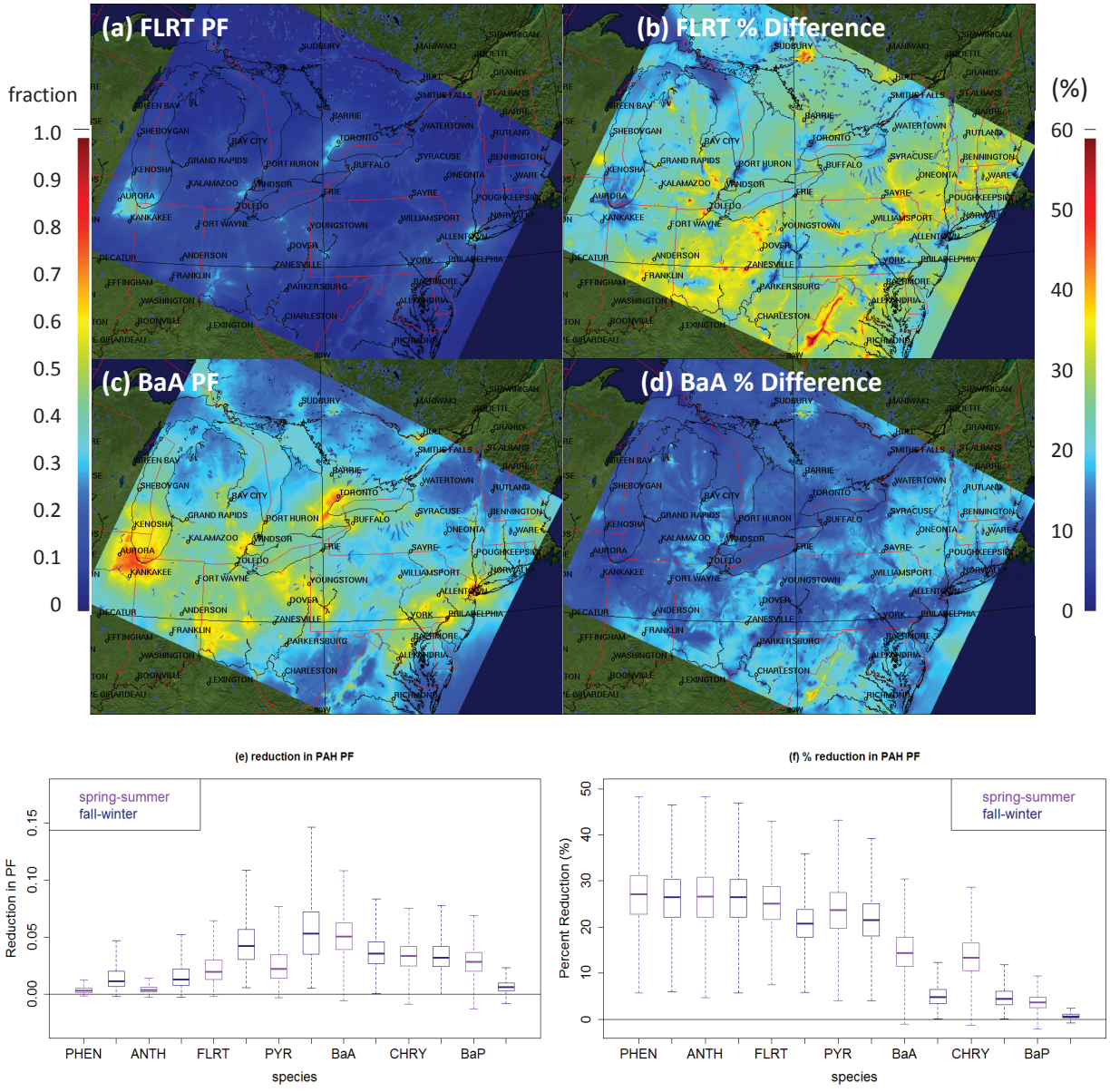

Figure 6. (a & c) Sample maps of particulate fraction (PF), and (b & d) its percent change due to the removal of on-road vehicle emissions. Spring-summer FLRT and BaA shown as examples. The spring-summer and fall-winter averages of absolute (e) and percent (f) reduction in PF for all PAH species.

Table 2. Domain-wide average on-road vehicle contributions to ambient concentrations, when on-road vehicle emissions of BENZ and PAHs are halved or doubled. NR = not reported

	benzene	PHEN	ANTH	FLRT	PYR	BaA	CHRY	BaP
spring-summer test with 0.5× emissions	11%	8%	9%	0.5%	2%	7%	6%	6%
spring-summer test with 2× emissions	42%	30%	33%	4%	10%	27%	21%	25%
fall-winter test with 0.5× emissions	NR	12%	4%	8%	10%	11%	11%	NR
fall-winter test with 2× emissions	NR	41%	41%	27%	34%	30%	30%	NR

2009). We carried out four sensitivity simulations with GEM-MACH-PAH with the BENZ and PAH emissions from on-road vehicles scaled by factors of 0.5 and 2 in both seasons. This range corresponds approximately to the 25th and 75th percentiles of the range of EFs reported in the recent peer-reviewed literature (Whaley et al., 2018b). The model responded consistently to on-road vehicle emission scaling with average changes to the vehicle contribution amount of -5 to -10% and +20 to +30%, depending on species, for halved and doubled vehicle emissions, respectively (Table 1 vs 2). This finding suggests that the relative importance of vehicle contributions when different EFs are used remains consistent with our current results across a broad range of emissions levels. This topic is described in more detail in the Supplement (Section V).

Whereas the effects of emissions perturbations are straightforward to evaluate, uncertainties that arise from atmospheric chemistry are complex to assess because they result from secondary formation processes for atmospheric oxidants. A reduction in precursor emissions yields a nonlinear change in oxidant concentrations that depends on chemistry and the physical state of the atmosphere at each location. The removal of on-road vehicle emissions induces a large range of changes in oxidant concentrations (Figures 5 and S.9). The resulting changes in BENZ and PAH concentrations as a function of changes in oxidant concentration are highly variable (e.g., Figures S.5 and S.6), and some geographic areas see a net increase in PAH concentrations because reduced atmospheric oxidation of PAHs overwhelms the effect of removing vehicle emissions. However, such results were uncommon throughout the study area. For a reactive PAH such as pyrene, for example, 88.3% and 99.9% of model grid squares in spring-summer and fall-winter, respectively, responded to the removal of vehicle emissions with reductions in ambient PAH concentrations. Relatively unreactive benzene, on the other hand, responded to emissions reductions with ambient concentration reductions in all model grid squares.

3.8 Human Health Implications

The removal of on-road vehicle emissions would lead not only to reductions in ambient benzene and PAH concentrations (as well as in other pollutants), as demonstrated by our model results, but also to reductions in human exposure. Proximity to roadways and traffic has been linked to elevated exposure outdoors, and this has led to particular concerns for commuters (Miao et al., 2015; Yan et al., 2015; Tan et al., 2017; Lovett et al., 2018; Miri et al., 2018). Further inhalation exposure to traffic pollutants occurs in indoor environments, where infiltration of outdoor air can contribute a substantial proportion of benzene

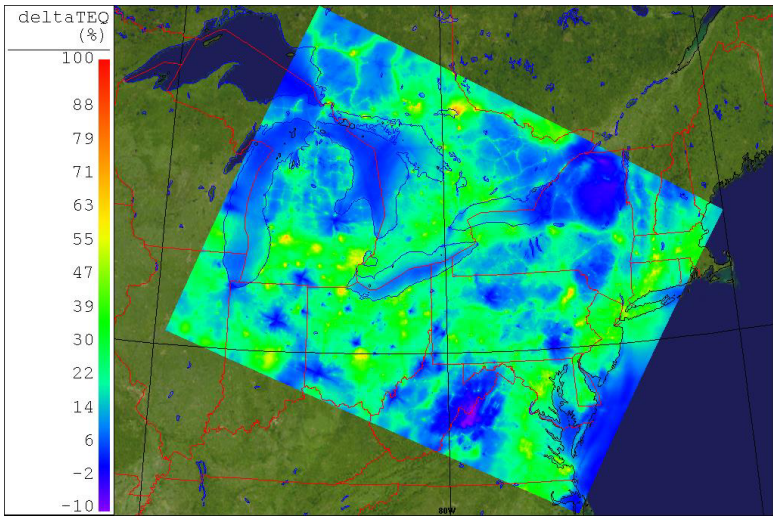

Figure 7. Average change in BaP toxic equivalents (TEQ) in ambient air during spring-summer 2009 when on-road vehicle emissions are set to zero.

and PAH exposure (Naumova et al., 2002; Xu et al., 2016), adding to concerns about residences, schools and workplaces that are situated near roadways.

PAH species vary in toxicity, and their mixture is often represented as a toxic equivalent concentration (TEQ) which is the sum of contributing compound concentrations that have been normalized by their carcinogenic potencies relative to BaP (Nisbet and LaGoy, 1992). The percent reduction in TEQ when on-road vehicle emissions were removed (Figure 7) averaged 18.9% across the domain. The magnitudes and geographic distribution of these TEQ reductions closely follow the reductions in simulated PAH concentrations, implying a direct toxicity benefit of mobile emissions reductions. For large urban areas and their suburbs, where both ambient concentrations and human population density are high, results herein suggest that TEQs could be reduced by values of 20-60% if vehicle emissions were removed. Maximum TEQ reductions of up to ∼80% were predicted for some rural and suburban locations near highways (e.g., North Bay, ON; Sudbury, ON; Grand Rapids, MI; and Maumee, OH).

Benzene has not been assigned a BaP toxic equivalency factor in the available literature. However, the combination of its modelled concentration and its human toxicity potential (Hertwich et al., 2001), which are approximately 1000 times larger and smaller than those of BaP, respectively, suggests that reductions in traffic emissions would lead to similar reductions in risk for benzene as for PAHs.

Further connection of the results of this study to potential human health benefits will require careful attention to the interplay between air toxics and criteria air contaminants, since these are not often considered together in air quality research. The

development, evaluation and first application of GEM-MACH-PAH makes such work possible. Another priority for future research is the improvement of emissions inventories and model process representations.

4 Conclusions

The previously validated GEM-MACH-PAH model was used to simulate benzene, PAH, and other pollutant concentrations for both ~~base case and~~ "base case" and "no-mobile" emissions scenarios for a densely populated region in north-eastern North America. Taking the difference of the two scenarios has allowed the on-road vehicle contribution to ambient concentrations to be calculated and this effect was 4-21% for benzene and PAHs, and 10% for both spring-summer O_3 and fall-winter PM_{10} on average in our southern Ontario/north-eastern U.S. model domain (variations for season and compound). Maxima seasonally-averaged vehicle contributions were 74% for BENZ, 91% for PHEN, and 22% for spring-summer O_3 and 33% for fall-winter PM_{10} within the model domain. These can additionally be interpreted as the relative reductions in pollutant concentrations expected with the introduction of a ZEV fleet. The chemical transport modelling of benzene and PAHs presented in this study is unprecedented in terms of combined domain size and spatial resolution, and it has demonstrated that vehicular sources of these toxic species make substantial contributions to ambient concentrations (expressed on the basis of both mass and toxic equivalents) at the urban scale. This suggests that meaningful decreases in BENZ and PAH concentrations can be achieved through on-road vehicle emission reductions. Such reductions could be achieved through a number of potential management actions, including increases in ZEV use, and greater use of active transportation modes such as walking and cycling. Future work aims to include more PAH species, including secondary reaction products such as oxy- and nitro-PAHs, and to improve model representation of wintertime benzene and BaP.

Code availability. The MACH-PAH (chemistry) code is available here: https://zenodo.org/record/1162252#.Wm9DtK1lJZQ, DOI:10.5281/zenodo.1162252, and the GEM (meteorology model) code is available here: https://github.com/mfvalin?tab=repositories. The executable for GEM-MACH-PAH is obtained by providing the chemistry library (MACH-PAH) to GEM when generating its executable.

Author contributions. EG is the principal investigator for this project. EG, PM, and CHW designed the model experiment and CHW and EG developed the model code. JZ, MDM, and CHW created the emissions files for the model simulations. CHW performed the model simulations and analysis and CHW and EG wrote the manuscript with support from all co-authors.

Competing interests. We have no competing interests.

Acknowledgements. The authors acknowledge funding from the Government of Canada's Program of Energy Research and Development (PERD; ALMITEE Project led by Jeffrey R. Brook) and from Environment and Climate Change Canada's Climate Change and Air Pollution program. The authors also acknowledge the contributions of Ayodeji Akingunola, Sylvie Gravel, Wanmin Gong, Craig Stroud, and Qiong Zheng for their assistance in setting up GEM-MACH-PAH (Whaley et al., 2018b). All maps were created using CMC software, SPI.

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