Interactive comments on "High-resolution quantification of atmospheric CO_2 mixing ratios in the Greater Toronto Area" by S.C. Pugliese et al.

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Response to Referee #1

We thank the reviewer for their consideration of our manuscript. Our responses to their comments are given below (their original comments are shown in small indented text).

General Comments

> 1. As I understand, there is provincial-level estimates of CO and CO2 that are reported by the Canadian National Inventory Report (NIR), with broad sectoral information (e.g., area, point, on-road, off-road). Then there is also a gridded inventory of CO emissions that is processed at 2.5 km x 2.5 km. The authors' reconcile the provincial-level CO2/CO estimates with the gridded CO inventory to arrive at a gridded CO2 inventory. My main critique with this approach is with the CO2/CO emission ratios reported. Some of these values seem unbelievable, which reflect potential problems in either CO2 or CO emissions reported by the NIR (more likely from CO). For example, the on-road CO2/CO emissions ratio reported here (Line 247) is 29.5 g CO2/g CO. This is equivalent to a CO emission factor of 33.9 g CO/kg CO2 or 110 g CO/kg fuel (using a carbon fraction of 0.85 g C/g fuel for gasoline). Roadway studies report tailpipe CO emission factors from gasoline cars at 10-20 g/kg fuel [McDonald et al., 2013]. The factors reported here appear too high. Also, based on the point source emission factor of 313.1 g CO2/g CO (Line 239), _0.5% of the carbon emitted is as CO and the rest from CO2. This is a very small number in the denominator from which to scale to CO2 emissions, introducing potentially large uncertainties in industrial CO2 emissions. Ultimately, I found the reporting of CO2/CO emission ratios distracting and not central to the inventory constructed. What I believe the authors' are really doing here is using the gridded CO inventory as spatial/temporal proxies for CO2 emissions, and downscaling CO2 emissions from the provincial-level to grid cells by sector. Rather than report CO2/CO emission ratios that are dubious, I suggest reframing inventory methods to emphasize the use of CO as spatial/temporal proxies for CO2.

We agree with the reviewer that the use of the CO inventory was to act as a spatial and temporal proxy for CO_2 emissions. We have added text to state this to the manuscript as well as a statement that the use of CO_2:CO emission ratios helps to produce realistic estimates of CO_2 emissions, despite uncertainties in CO emission estimates in lines 230-234. However, the reviewer's concern regarding the relevance of the detailed discussion of the sectoral CO_2:CO emission ratios also pointed out a lack of clarity in the manuscript concerning a key characteristic of the gridded CO inventory, which is that it contained separate emissions of CO for the seven primary source sectors discussed in Sections 2.4.1 to 2.4.6. Thus, there are in effect seven different spatial and temporal proxies for CO_2 emissions and the sectoral CO_2:CO emission ratios are used to weight these seven CO emissions fields. This is the explanation for the very different spatial distributions of sectoral CO_2 emissions evident in Figure 2. New text has been added to clarify this key aspect of the methodology in lines 207-213.

2. In Section 2.4, too many significant figures are reported in emission inventory estimates, which suggest a high degree of certainty in emissions that is unwarranted (especially for CO). Suggest using 2-3 significant figures at most.

The reviewer has raised a valid point, and we have reduced the number of significant figures used in Section 2.4 to 2-3 figures.

Specific Comments

3. Line 207. How are CO2 emissions from the Canadian National Inventory Report (NIR) estimated? Are these based on energy or fuel use statistics, or from engineering calculations? Since CO2 emissions is the focus of this paper, it would be helpful to include a few sentences on the basis for how CO2 emissions are estimated in national reporting.

We agree with the comment and have added a description of how CO_2 emissions are estimated in the Canadian National Inventory Report (lines 218-222).

4. Equation 1. The "total" subscript was confusing to me. I believe what the authors' mean is "sector" in the third term of the equation (e.g., total area, point source, on-road, etc.) and "sub-sector" in the first two terms.

We have changed the subscript of the third term to "Ontario sector" to indicate the value used is the NIR sector-wise provincial total for CO_2 (kt) and CO (kt).

5. Section 2.4.1. Typically when I think of area emissions they are dispersive sources that include residential, commercial, AND industrial sources. Suggest that this source category be renamed to something like "Area industrial emissions".

We think the reviewer raises an interesting point; however, because industrial emissions are included in both the Area and Point sectors in our inventory, we have left the term "industrial" out of the category name to minimize confusion.

6. Lines 232-234. The combustion efficiency is not actually that variable, it is just that CO emissions are almost negligible from point sources and hence why the CO2:CO ratio is variable due to a tiny denominator (see Comment 1). Suggest re-wording of this sentence.

We have re-worded the sentence to highlight that uncertainties associated with very small CO emissions are likely responsible for the variable CO_2:CO ratios for Point emissions (lines 253-254).

7. Lines 255-256. Lawn equipment and other small two- and four-stroke gasoline engines (e.g., snow equipment) have been shown to be a significant source of CO emissions [Gordon et al, 2013; Volckens et al., 2007; Bishop et al., 2001]. Where would they show up in the APEI, or are they included here? More importantly, how are off-road gasoline engines specifically accounted for in this study, which contribute high amounts of CO, but consume small amounts of fuel? Other off-road diesel equipment would consume significantly larger amounts of fuel than off-road gasoline engines, but have much lower CO emission factors. Not properly accounting for off-road emissions of CO between gasoline and diesel engines could affect the scaling of off-road emissions of CO to CO_2.

Four examples of the kinds of sources included in the "all off-road engines" subcategory in the Off-road sector of the APEI inventory have been added to the manuscript (lines 279-280).

We were not able to separate the contributions of gasoline and diesel engines because emissions from these different sources had been aggregated during SMOKE processing of the gridded CO inventory. We agree with the reviewer that this is a challenge and limitation to our inventory and we have added a statement in the manuscript that because of this, the CO_2 emissions from off-road sources are an approximation of a more complex situation (lines 296-299).

> 8. Lines 363-365. Some more description of the FLEXPART model is needed here, or could warrant a short paragraph in the methods section. Specifically, how many hours was the back trajectory simulated for? Was this run for each site? I'm guessing the emission inventories are then multiplied by the footprint to arrive at concentrations, and then compared with ambient CO2 measurements. Also, a reference to FLEXPART and some description of the model would be helpful to a reader unfamiliar with the model.

We agree more information is required about our use of the FLEXPART model. We have now outlined that footprints were generated for every third hour of the day (i.e., 00h, 03h, 06h, 09h, etc.) for the year 2014 for two sites, Downsview and TAO, and we have explained how the mixing ratio enhancements were calculated (lines 401-407). A reference has been provided to give a reader unfamiliar with FLEXPART a description of the model (line 402).

> 9. Line 365. This appears to be the first mention of the TAO site. It would be helpful to describe this location in more detail in Section 2.2. Also, it is not clear why looking at gradients between Downsview and TAO is a useful metric. Is it because TAO is a downwind site, whereas Downsview is downtown? In general, for a reader unfamiliar with Toronto, it would be helpful to describe locations as urban or rural more explicitly throughout Results and Discussion.

A description of TAO earlier in the manuscript in Section 2.2 was included (lines 124-126). We have also included a description why we looked at the gradient between Downsview and TAO (as an indication of CO_2 mixing ratios in the downtown core of the city, since Downsview and TAO are located just north and south of the city respectively) (lines 405-407).

> 10. Lines 492-494. Focusing on wintertime months, while easier from a modeling perspective, would bias our understanding of CO2 emissions towards wintertime sources. The sources and spatial patterns of emissions vary between winter and summer. For example, peaking plants could be important in summertime [Farkas et al., 2016]. Seems like we should try to understand both periods.

We agree with the referee that in some places there is a large variability in emissions between summer and winter months, so that peaking plants may be operational in the summer. However, 90% of the electricity generated in Ontario comes from nuclear, hydroelectric, or renewable sources so fossil-fuel peaking plants play a negligible role (http://www.energy.gov.on.ca/en/ontarios-electricity-system/ontarios-electricity-system-faqs/). Therefore, since such seasonal variability is not present in this jurisdiction, and since we are interested in understanding anthropogenic sources of CO_2, we have focused our study on the winter months so as to minimize the influence of the biosphere.

> 11. Figure 5. This plot could benefit from some uncertainty bands on the CO2 measurements, such as the standard deviation or 95% confidence interval of the mean. In this way, it will be easier to discern the variability in CO2 concentrations, as well as the significance of the model improvements.

We have added error bars representing the standard error of the mean to Figure 5.

> 12. Figure 7. I cannot see the line for the biogenic sources, though it is called out in the text (Line 490).

The Biogenic sources line is located on the zero line, underneath the Marine line. This is now explained in the text (lines 533-534).

Response to Referee #2

We thank the reviewer for their consideration of our manuscript. Our responses to their comments are given below (their original comments are shown in small indented text).

General Comments

1. The CO2 emission factor from natural gas combustion. I calculate by carbon balance that the value for pure methane should be 42 mol/m3 x 16 g/mol x 44 g CO2 / 12 g C = 2464 g CO2 / m3 of natural gas burned (assuming gas temperature of 15 deg C = 60 deg F). Real natural gas may include inert gases such as nitrogen and carbon dioxide. There may also be some incomplete combustion in the residential sector, though I expect those adjustments to be minor for the space heating sector in question. The cited emission factor (1879 g CO2/m3) may be too low, the authors should explain what assumptions underpin this emission factor, which dominates CO2 enhancements at night in their modeling.

The emission factor used in our study (1897 gCO_2/m^3) was estimated by the 2010 Canadian National Inventory Report, specific for the province of Ontario and based on data from a chemical analysis of representative natural gas samples and an assumed fuel combustion efficiency of 99.5 %. This information is now included in the manuscript to better explain the origin of the emission factor (lines 315-318).

2. The authors should say more about seasonality and diurnal patterns of emissions. Presumably many residential users turn down the heat at night, and some furnaces (esp. residential) run only during winter months. Have such effects been accounted for in formulating the CO2 emission inventory for southern Ontario?

In our study, the diurnal pattern of emissions was considered (Figure S2 shows the diurnal pattern of total CO_2 emissions estimated by the SOCE inventory). The temporal variability of natural gas furnaces or vehicles, for example, was including in the SMOKE emissions processing system (as outlined in lines 202-207 and 320-322).

3. It would be helpful to say more about how motor vehicle CO emissions were estimated, in

particular the spatial and diurnal distribution of traffic, and also the gasoline/diesel traffic split. The use of a single CO2/CO ratio is problematic for multiple reasons. (1) the mix of gasoline versus diesel-powered vehicles varies spatially (e.g., on highway/ city streets and in urban/rural areas). The diesel truck fraction tends to be much higher on major highways traveling through more sparsely populated rural areas (e.g., highway 401 outside of Toronto). The diesel CO2/CO ratio differs from the corresponding ratio for gasoline engines. Also (2) the emissions of CO are elevated during cold engine starting (and especially so during winter). Therefore the CO2/CO emissions ratio varies spatially and by time of day. The ratio should be higher on highways and lower in residential areas in the morning when vehicle engines are started under cold conditions. The method used in this study for estimating CO2 emissions from vehicles (by ratio to CO) is therefore questionable and only provides a rough approximation to a more complex reality.

We agree with the author that the use of a single CO_2:CO ratio is a limitation given (1) the spatial variability of diesel-powered and gasoline-powered vehicles and (2) the temporal variability of CO_2:CO for different driving-cycle phases such as cold starts in the morning. However, given that we used an existing and largely aggregated gridded CO inventory as a proxy for the spatial and temporal allocation of CO_2 emissions, and used the CO inventory as the basis for estimating the CO_2 inventory, we were unable to apply different emission ratios to different grid cells based on the presence of a highway or rural area nor were we able to apply a specific gasoline or diesel ratio to specific grid cells due to the lack of information on vehicle type in each grid cell. We have included some new text to the manuscript to state that based on these challenges, our estimate of On-road CO_2 mixing ratios is an approximation (lines 272-276).

Editorial Suggestions

4. Line 133, observational program Egbert: the word ‘site’ is missing

Fixed (line 136).

5. Watch sig figs in reporting emissions and calculating CO2/CO emission ratios. It is not reasonable to report emissions or emission ratios with 4-5 figures of accuracy.

All reporting of emissions and CO_2:CO ratios were reduced to 2-3 significant figures.

6. Line 224: CO2 emissions should be rounded to 23.5 Mt and CO emissions should be rounded to 219 kt (even that is optimistic precision) and the ratio should be reported as 107 kt CO2/kt CO.

The significant figures of the CO_2 and CO emissions were reduced.

7. The same excessive precision issue is again of concern at lines 239, 247, 274-75, 283, 311, 314, 318, and in Table 2

All reporting of emissions and CO_2:CO ratios were reduced to 2-3 significant figures.

8. The paper uses too many acronyms, which makes the paper harder to read. Suggest omitting some of the more obscure ones such as PIA, BBTCA, and NEE (the last one is defined on line 290 but not used anywhere else in the manuscript).

The acronyms PIA, BBTCA and NEE were removed from the manuscript.

9. Line 359: diel shoud be diurnal

Fixed (line 393).

10. Line 365: what does TAO stand for? Since the site was operational during the period of interest for the modeling, this site should be described as part of section 2.2 rather than suddenly appearing in the manuscript at this point.

TAO is now defined and included in Section 2.2 (lines 124-126).

11. In Figure 3, the resolution is coarse and it is not easy to discern differences among the three panels shown in this Figure. The first two panels (a) and (b) are almost indistinguishable. A legend showing the color scale is missing in this Figure.

Figure 3 was included to highlight the similarities of the FFDAS v2 inventory and the EDGAR inventory at the coarse 0.1^{o} x 0.1^{o} resolution, and to compare those inventories to the SOCE inventory scaled up to the same coarse resolution. The colour scale has been enlarged and moved to the bottom of the figure for easier readability.

12. In Figures 2 and 7, the marine contribution is negligible and should be omitted to simplify these figures. The point source panel in Figure 2 is not particularly helpful either.

The contributions of the Marine sector in Figures 2 and 7 are included to show its negligible contribution to CO_2 emissions in southern Ontario, in contrast to other areas where the influence of Marine emissions might be more significant. Consideration of this sector is also important given that two of the CO_2 measurement stations considered in the paper are in near-shore locations, and text noting this has been added to Section 2.4.5 (lines 306-308). Although the Point source panel in Figure 2 is not particularly helpful, emissions from this sector are significant and therefore it was included in the figure. Additionally, the Point source panel highlights the high emissions from Point sources on the western end of Lake Ontario, where the city of Hamilton, the main center for steel production in Canada, is located.

High-resolution quantification of atmospheric CO_2 mixing ratios in the Greater Toronto Area, Canada (with changes marked in red)

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Abstract

Many stakeholders are seeking methods to reduce carbon dioxide (CO_2) emissions in urban areas, however reliable, high-resolution inventories are required to guide these efforts. We present the development of a high-resolution CO_2 inventory available for the Greater Toronto Area and surrounding region in southern Ontario, Canada (area of ~2.8 x 10^5 km^2, 26 % of the province of Ontario). The new SOCE (Southern Ontario CO_2 Emissions) inventory is available at the 2.5 x 2.5 km spatial and hourly temporal resolution and characterizes emissions from seven sectors: Area, Residential natural gas combustion, Commercial natural gas combustion, Point, Marine, On-road and Off-road. To assess the accuracy of the SOCE inventory, we developed an observation-model framework using the GEM-MACH chemistry-transport model run on a high-resolution grid with 2.5 km grid spacing coupled to the Fossil Fuel Data Assimilation System (FFDAS) v2 inventories for anthropogenic CO_2 emissions and the European Center for Medium-Range Weather Forecasts (ECMWF) land carbon model C-TESSEL for biogenic fluxes. A run using FFDAS for the southern Ontario region was compared to a run in which its emissions were replaced by the SOCE inventory. Simulated CO_2 mixing ratios were compared against in situ measurements made at four sites in southern Ontario, Downsview, Hanlan's Point, Egbert and Turkey Point, in three winter months, January-March, 2016. Model simulations had better agreement with measurements when using the SOCE inventory emissions versus other inventories, quantified using a variety of statistics such as Correlation Coefficient, root mean square error and mean bias. Furthermore, when run with the SOCE inventory, the model had improved ability to capture the typical diurnal pattern of CO_2 mixing ratios, particularly at the Downsview, Hanlan's Point and Egbert sites. In addition to improved model-measurement agreement, the SOCE inventory offers a sectoral breakdown of emissions, allowing estimation of average time-of-day and day-of-week contributions of different sectors. Our results show that at night, emissions from Residential and Commercial natural gas combustion and

other Area sources can contribute > 80 % of the CO_2 enhancement while during the day emissions from the On-road sector dominate, accounting for >70 % of the enhancement.

1.0 Introduction

Urban areas are sites of dense population and the intensity of human activities (such as transportation, industry and residential and commercial development) makes them hot-spots for anthropogenic carbon dioxide (CO_2) emissions. While occupying only 3 % of the total land area, urban areas are locations of residence for 54 % of the global population and are the source of 53 – 87 % of anthropogenic CO_2 emissions globally (IPCC-WG3, 2014; WHO, 2015). When considering Canada alone, the urban population accounts for an even larger fraction of the total (81 % in 2011) (Statistics Canada, 2011) while urban areas cover only 0.25 % of the land area (Statistics Canada, 2009). Recognizing their influence on the global carbon budget, many urban areas are seeking methods to reduce their anthropogenic CO_2 emissions. The Greater Toronto Area (GTA) in southeastern Canada, for example, has committed to the *Change is in the Air* initiative as well as being a part of the *C40 Cities Climate Leadership Group,* both of which call to reduce CO_2 emissions 30 % below 1990 levels by 2020 (C40 Cities, 2016; Framework for Public Review and Engagement, 2007). However, in order to effectively guide anthropogenic CO_2 mitigation strategies, reliable inventories are needed, particularly at high spatial and temporal resolution, to gain a better understanding of the carbon cycle (Gurney et al., 2009; Patarasuk et al., 2016). To our knowledge, the only spatially disaggregated CO_2 inventories available for use in the GTA are the EDGAR v.4.2 (Emission Database for Global Atmospheric Research) CO_2 inventory (available at annual, 0.1^o x 0.1^o resolution) (EDGAR, 2010) and the FFDAS v2 (Fossil Fuel Data Assimilation System) CO_2 inventory (available at hourly, 0.1^o x 0.1^o resolution) (FFDAS, 2010), both which are limited in their spatial and/or temporal resolution and therefore are not well-suited for the quantification and understanding of CO_2 emissions at the urban scale. The Canadian national CO_2 inventory, on the other hand, is only available at the provincial level (Environment Canada, 2012).

Efforts to develop emission inventories at the fine spatial and temporal resolution required for urban-scale understanding of CO_2 emissions has been driven both by policy- and science-related questions (Gurney et al., 2009; Patarasuk et al., 2016). From a policy perspective, improving CO_2 emission quantification is essential to independently evaluate whether anthropogenic mitigation regulations are being effectively implemented. From a scientific perspective, gaining information about anthropogenic CO_2 emissions from urban areas has been primarily motivated by atmospheric CO_2 inversions, which are used to better understand the global carbon cycle (Gurney et al., 2009; Patarasuk et al., 2016). Regardless of the motivation, quantification of CO_2 source/sink processes currently uses two techniques: the bottom-up approach and the top-down approach. In the bottom-up approach, local-scale activity level information is combined with appropriate emission factors to infer emission rates. This method has been used widely to develop many inventories (EDGAR, 2010; FFDAS, 2010; Gurney et al., 2009) but is limited by the accuracy of the input parameters. Conversely, in the top-down approach, inverse modelling is used to exploit the variability in atmospheric mixing ratios of CO_2 to identify the source/sink distributions and magnitudes; this method is limited by insufficient mixing ratio data and uncertainties in simulating atmospheric transport (Pillai et al., 2011). Given current policy needs, a strategy using solely bottom-up or top-down approaches is likely insufficient to evaluate CO_2 emissions but rather a synthesis of the two methodologies is required (Miller and Michalak, 2016). Successful examples of high-resolution CO_2 inventory development are available on the urban scale, such as the Airparif inventory in Ile-de-France (publicly available at http://www.airparif.asso.fr/en/index/index) and in Indianapolis, Los Angeles, Salt Lake City and Phoenix through the Hestia project (Gurney et al., 2012), on the national scale, such as in China (Zhao et al., 2012), and on the global scale (Wang et al., 2013). However, to our knowledge, there are currently no studies that have quantified Canadian CO_2 emissions at the fine spatial and temporal resolution required for urban analyses in Canada.

In an effort to address this gap, this study was focused on quantifying CO_2 emissions at a fine spatial and temporal resolution in the GTA and southern Ontario (we expanded the inventory beyond the urban area of the GTA so we could exploit information on CO_2 mixing ratios collected at rural areas in central and south-western Ontario, proving additional sites for inventory validation). We present the new high-resolution Southern Ontario CO_2 Emissions (SOCE) inventory, which quantifies CO_2 emissions from seven source sectors (On-road, Off-road, Area, Point, Marine, Residential, and Commercial natural gas combustion) at 2.5 km x 2.5 km spatial and hourly temporal resolution for an area covering ~26 % of the province of Ontario (~2.8×10^5 km^2). The SOCE inventory was used in combination with the Environment and Climate Change Canada (ECCC) GEM-MACH chemistry-transport model to simulate CO_2 mixing ratios in a domain including south-eastern Canada and the northeastern USA (hereafter referred to as the "PanAm domain") for comparison with in situ measurements made by the Southern Ontario Greenhouse Gas Network. Until now, estimates of anthropogenic CO_2 emissions in the GTA were available only from the EDGAR v.4.2 (EDGAR, 2010) and the FFDAS v2 (FFDAS, 2010) inventories, which have very different annual totals for this region (1.36×10^8 vs. 1.05×10^8 tonnes CO_2, respectively). Therefore, we expect the results of this work will improve our ability to quantify the emissions of CO_2 in the entire domain as well as the relative contributions of different sectors, providing a more detailed characterization of the carbon budget in the GTA.

2.0 Methods

2.1 Geographic Domain

The geographic focus of this study was the GTA in southern Ontario, Canada. The GTA is the largest urban area in Canada; it comprises five municipalities, Toronto, Halton, Durham, Peel and York, which together have a population exceeding 6 million (Statistics Canada., 2012b). Although the GTA comprises only 0.07 % of Canadian land area, it represents over 17 % of the total population as a result of rapid urbanization over the past few decades (Statistics Canada., 2012b). Therefore, high-resolution characterization of CO_2 emissions can help integrate climate policy with urban planning. This region is home to a network of measurement sites providing long-term, publicly available datasets of atmospheric CO_2 mixing ratio measurements, *Section 2.2* (Environment Canada, 2011) which can be used to evaluate model outputs and inventory estimates. In 2016 the government of Ontario released a Climate Change Action Plan, which includes an endowment given to the Toronto Atmospheric Fund of $17 million to invest in strategies to reduce greenhouse gas pollution in the GTA (Ontario, 2016). Therefore this research can provide timely information on the carbon budget in the GTA and help to implement effective reduction strategies.

2.2 The Southern Ontario Greenhouse Gas Network

Measurements of ambient CO_2 dry air mixing ratios began in 2005 in southern Ontario at the Egbert station followed by the Downsview station (2007), Turkey Point station (2012) and Hanlan's Point station (2014), Figure 1. Measurements were also temporarily made at a site in downtown Toronto, the Toronto Atmospheric Observatory (TAO) (43.7^{o}N, 79.4^{o}W), but the instrument was relocated from this site in January 2016. Egbert is located ~75 km north-northwest of Toronto in a rural area, Downsview is located ~20 km north of downtown core of the city of Toronto in a populated suburban area, Turkey Point is located to the south-west of the GTA in a rural area on the north shore of Lake Erie, and Hanlan's Point is located on Toronto Island, just south of the city of Toronto on the shore of Lake Ontario. Site details and instrument types used can be found in Table 1. CO_2 measurements are collected as a part of ECCC's Greenhouse Gas Observational Program. The measurement procedure follows a set of established principles and protocols outlined by a number of international agencies through recommendations of the *Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques,* coordinated by the World Meteorological Organization (WMO) every 2 years.

The atmospheric CO_2 observational program at the Egbert site is based on non-dispersive infrared (NDIR) methodology and fine-tuned for high precision measurements (Worthy et al., 2005). A detailed description of the NDIR observational system can be found in Worthy et al, (2005). The atmospheric CO_2 observational programs at Turkey Point, Downsview, and Hanlan's Point are based on Cavity Ring-Down Spectrometer (CRDS). Each Picarro CRDS system is calibrated in the ECCC central calibration facility in Toronto before deployment to the field. The response function of the analyzer is determined against 3 calibrated standards tanks (Low, Mid, High). The working (W) and target (T) tanks assigned to the system are also included in the injection sequence and calibrated. At each site, ambient measurements are made using two sample lines placed at the same level. Each sample line has separate dedicated sample pumps and driers (~ -30^{o}C). Pressurized aluminum 30 L gas cylinders are used for the working and target tanks. The sample flow rate of the ambient and standard tank gases is set at ~300 cc/min. The injection sequence consists of a target and working tanks sequentially passed through the analyzer for 10 minutes each every 2 days. The ambient data from line1 is passed through the analyzer for 18 hours followed by Line2 for 6 hours. The Line1/Line2 sequence repeats one time before the target and working tanks are again passed through the system. The working and target tanks are calibrated on site at least once per year against a single transfer standard transported between the sites and the central laboratory facility in Toronto. The CO_2 measurements from both the NDIR and CRDS analytical systems have a precision of around 0.1 ppm based on one-minute averages and are accurate to within 0.2 ppm.

2.3 GEM-MACH chemistry- transport model

In this project, we used the GEM-MACH (Global Environmental Multi-scale–Modelling Air quality and CHemistry) chemistry–transport model (CTM) (Gong et al., 2015; Moran et al., 2013; Pavlovic et al., 2016; Talbot et al., 2008) to link surface emission estimates and atmospheric mixing ratios. GEM-MACH is an on–line CTM embedded within the Canadian weather forecast model GEM (Côté et al., 1998a; Côté et al., 1998b). The configuration of GEM-MACH used in our study has 62 vertical levels from the surface to ~1.45 hPa on a terrain-following staggered vertical grid for a log-hydrostatic pressure coordinate. The thickness of the lowest layer was 40 m. The PanAm domain used in our simulations, which includes central and southern Ontario, as well as western Quebec and the northeastern USA, is shown in Figure 1. The PanAm domain has 524 x 424 grid cells in the horizontal on a rotated latitude-longitude grid with 2.5-km grid spacing and covers an area of approximately 1310 km x 1060 km (total domain area is 1.39 x 10^6 km^2). A 24-hour forecasting period was used with a 60-second time step for each integration cycle. Meteorological fields (wind, temperature, humidity, etc.) were re-initialized every 24 hours (i.e., after each model integration cycle); chemical fields were carried forward from the previous integration cycle (i.e., perpetual forecast). Hourly meteorological and chemical boundary conditions were provided by the ECCC operational 10-km GEM-MACH air quality forecast model (Moran et al., 2015).

In our study, we simulated two scenarios of CO_2 surface fluxes, indicated by the sum of the following:

Scenario 1:

- Anthropogenic fossil fuel CO_2 emissions within the province of Ontario estimated by the SOCE inventory, available at 2.5 km x 2.5 km spatial and hourly temporal resolution, as described in *Section 2.4*

- Anthropogenic fossil fuel CO_2 emissions estimated by the FFDAS v2 inventory (FFDAS, 2010) outside of the province of Ontario (province of Quebec and USA), available at 0.1° x 0.1° spatial and hourly temporal resolution
- Biogenic CO_2 fluxes from the C-TESSEL land surface model, as described in *Section 2.5*

Scenario 2:

- Anthropogenic fossil fuel CO_2 emissions estimated by the FFDAS v2 inventory (FFDAS, 2010) for the entire domain, available at 0.1° x 0.1° spatial and hourly temporal resolution
- Biogenic CO_2 fluxes from the C-TESSEL land surface model, as described in *Section 2.5*

CO_2 is not a usual chemical species considered by GEM-MACH but a set of special inert tracer fields were added to GEM-MACH for this project to account for CO_2 concentration fields associated with difference source sectors and the lateral boundaries. The CO_2 boundary conditions set at the lateral and top edges of the domain were obtained from the Monitoring Atmospheric Composition and Climate (MACC) global inversion, v.10.2 (http://www.copernicus-atmosphere.eu/). Model simulated specific humidity (q, kg/kg) was used to convert estimated CO_2 mixing ratios to dry air mixing ratios. CO_2 dry air mixing ratios are hereafter referred to CO_2 mixing ratios.

2.4 High-Resolution SOCE inventory development

The high-resolution SOCE inventory was constructed primarily from a pre-existing carbon monoxide (CO) inventory developed by the Pollutant Inventories and Reporting Division (PIRD) of ECCC as part of the 2010 Canadian Air Pollutant Emissions Inventory (APEI). The CO inventory is a comprehensive national anthropogenic inventory that includes emissions from area sources, point sources, on-road mobile sources and off-road mobile sources, including aircraft, locomotive and marine emissions for base year 2010 (Moran et al., 2015). This annual inventory at the provincial level compiled by PIRD was transformed into model-ready emissions files using the Sparse Matrix

Operator Kernel Emissions (SMOKE, https://www.cmascenter.org/smoke/) emissions processing system for spatial allocation (distribution of non-point source emissions to 2.5 km x 2.5 km (roughly 0.02° x 0.02° resolution) using spatial surrogate fields) and temporal allocation (conversion of inventory annual emission rates into hourly values) (Moran et al., 2015). Because Ontario CO emissions in the 2010 APEI were processed in separate steps with SMOKE by primary source sector, files of gridded hourly CO emissions fields were available for seven different inventory sectors: area sources; point sources; on-road mobile sources; off-road mobile sources; marine sources; residential natural-gas sources; and commercial natural-gas sources. The spatial and temporal allocations applied to these seven sectors were different, so in effect they constitute a set of spatiotemporal emissions basis functions. More detailed information about the CO inventory compilation and subsequent processing has been provided elsewhere (Environment Canada, 2013; Moran et al., 2015; PIRD, 2016).

The objective of our work was to calculate CO_2 emissions based on this processed, sector-specific, model-ready CO inventory for Ontario grid cells using sector-specific emission ratios estimated by the Canadian National Inventory Report (NIR) (Environment Canada, 2012). The NIR estimates CO_2 and CO emissions using primarily bottom-up estimates; for example, emissions from industrial process are estimated using production data reported directly by facilities whereas emissions from road transport activities are estimated using vehicle population data, fuel consumption ratios, and vehicle kilometers travelled as reported by Environment Canada (2012). In the Ontario, model-ready CO inventory, emission sources are classified by SCC (Source Classification Code) and were mapped to NFR (Nomenclature for Reporting) codes for accurate cross-reference with the NIR CO_2 and CO estimates. Provincial totals for CO_2 and CO are estimated based on the NFR sources that are included in the sector, producing the following NIR sector-averaged CO_2:CO ratio:

$$CO_{2(sector,kt)} = CO_{(sector,kt)} * \frac{CO_{2(Ontario\ sector,kt)}}{CO_{(Ontario\ sector,kt)}} \quad \text{(Eq. 1)}$$

This sector-averaged CO_2:CO ratio is used to convert the APEI-based model-ready gridded CO emissions fields into CO_2 emissions fields at the same spatial and temporal resolution. Because the spatial and temporal variability of the sources of CO_2 are similar to those of CO, the fine-resolution gridded CO sectoral emissions fields for Ontario were primarily used as spatial and temporal proxies for CO_2 emissions; the use of NIR-based CO_2:CO ratios helps to produce realistic emissions estimates of CO_2 despite uncertainties in CO emissions estimates. A detailed outline of this conversion is presented for each of the seven CO emissions sectors in the following subsections. Unless otherwise noted, temporal allocation of emissions in each sector is based on estimates made available by SMOKE.

2.4.1 Area emissions

Area emissions are mostly small stationary sources that represent diffuse emissions that are not inventoried at the facility level. In the APEI CO inventory, the major emission sources in the Area sector include emissions from public electricity and heat production (1A1a), residential and commercial plants (1A4a and 1A4b), stationary agriculture/forestry/fishing (1A4c), iron and steel production (2C1), and pulp and paper (2D1). The NIR estimates an Ontario total from these (and other minor sources) of 2.3×10^4 kt CO_2 and 219 kt CO, producing a CO_2:CO ratio of 107 kt CO_2/kt CO. This ratio was applied to every Area sector grid cell belonging to Ontario in the domain to convert sector CO emissions to CO_2 emissions.

2.4.2 Point emissions

Point emissions are stationary sources in which emissions exit through a stack or identified exhaust. In the APEI CO inventory, the major emission sources in the Point sector include public electricity and heat production (1A1a), stationary combustion in manufacturing industries and construction (1A2f), chemical industry (2B5a), pulp and paper (2D1), iron and steel production (2C1) and other metal production (2C5). Unlike the Area sector, we found that applying a single CO_2:CO ratio to every facility did not produce realistic CO_2 emissions due to the negligible emissions of CO and therefore highly variable CO_2:CO ratios (because of a small denominator). Therefore, we used ECCC Facility Reported Data (Environment Canada, 2015) to identify the geocoded location and annual average CO_2:CO for 48 individual facilities in Ontario (Table S1) and applied the specific CO_2:CO ratios to the grid cells where the facilities were located. In addition, stack height of individual facilities were included in the emission model to optimize plume rise. All other point sources (minor facilities) were scaled by a sector average CO_2:CO ratio of 313 kt CO_2/kt CO, calculated from Ontario total CO_2 and CO point-source emissions from the NIR. Temporal allocation of emissions in the Point sector are based on facility level operating schedule data collected by ECCC.

2.4.3 On-road mobile emissions

On-road emissions include the emissions from any on-road vehicles (quantified by the Statistics Canada Canadian Vehicle Survey) (Environment Canada, 2013). In the APEI CO inventory, the major emission sources in the On-road sector includes gasoline and diesel-powered light- and heavy-duty vehicles (1A3b). The NIR estimates an Ontario total from these (and other minor on-road sources) of 4.4×10^4 kt CO_2 and 1.5×10^3 kt CO, producing a CO_2:CO ratio of 29 kt CO_2/kt CO. This ratio was applied to every On-road grid cell belonging to Ontario in the domain to convert sector CO emissions to CO_2. Temporal allocation of emissions in the On-road sector is estimated using data collected in the FEVER (Fast Evolution of Vehicle Emissions from Roadways) campaign in 2010 (Gordon et al., 2012a; Gordon et al., 2012b; Zhang et al., 2012). There are challenges associated with using a single CO_2:CO ratio for all on-road vehicles (both gasoline and diesel powered) as well as for all hours of the day (e.g., cold-start emissions from vehicles are different than running emissions).

Therefore, the CO_2 On-road emissions estimated in this study are an approximation of a more complex reality.

2.4.4 Off-road mobile emissions

Off-road emissions include the emissions from any off-road vehicles that do not travel on designated roadways, including aircraft, all off-road engines (such as chainsaws, lawn mowers, snow blowers, and snowmobiles), and locomotives. In the APEI CO inventory, the major emission sources in the Off-road sector include civil aviation (1A3a), railways (1A3c), and agriculture/forestry/fishing: off-road vehicles and other machinery (1A4c). Similar to the Point sector, we found that applying a single CO_2:CO ratio to every grid cell did not produce realistic CO_2 emissions for the two major airports in the GTA, Pearson International Airport (hereafter referred to as Pearson Airport) and Billy Bishop Toronto City Airport (hereafter referred to as Billy Bishop Airport). Therefore, we used air quality assessment reports compiled for each airport (RWDI AIR Inc., 2009; RWDI AIR Inc., 2013) to identify the geocoded location and facility-specific annual average CO_2:CO ratio. Sources of emissions from each airport include aircraft (landing and take-off cycles), auxiliary power units, ground support equipment, roadways, airside vehicles, parking lots, stationary sources and training fires; note that emissions from aircrafts in-transit between airports, which are injected in the free troposphere, have not been included in this inventory (Moran et al., 2015; RWDI AIR Inc., 2009). Based on these two reports, we applied a ratio of 175 kt CO_2/kt CO to the grid cell containing Pearson Airport and a ratio of 20 kt CO_2/kt CO to the grid cell containing Billy Bishop Airport. All other off-road sources belonging to Ontario grid cells were scaled by a sector average CO_2:CO ratio of 7 kt CO_2/kt CO, calculated from NIR-reported Ontario total CO_2 and CO emissions. Similar to On-road emissions, there are challenges associated with using a single CO_2:CO ratio for all vehicles (both gasoline and diesel powered) as well as for all hours of the day. Therefore, the CO_2 Off-road emissions estimated in this study are an approximation for a very complex sector.

2.4.5 Marine emissions

Commercial marine emissions include the emissions from any marine vessels travelling on the Great Lakes (quantified by the Statistics Canada *Shipping in Canada*) (Environment Canada, 2013). In the APEI CO inventory, the major emission source in the Marine sector is national navigation (1A3d). The NIR estimates an Ontario total from this source of 729 CO_2 and 0.86 kt CO, producing a CO_2:CO ratio of 844 kt CO_2/kt CO. This ratio was applied to every marine grid cell in the domain to convert sector CO emissions to CO_2. Note that inclusion of this source sector was desirable because two of the CO_2 measurement stations considered in this study (Turkey Point and Hanlan's Point) are near-shore stations.

2.4.6 Residential and commercial emissions

Residential and commercial CO_2 emissions reflect on-site combustion of natural gas for electricity and heating, a source that we found was not included in the APEI CO inventory because of the high efficiency of the furnaces and resulting low CO emissions. To include the CO_2 emissions from these on-site furnaces, we used the Statistics Canada 2012 Report on Energy Supply and Demand to quantify the amount of natural gas consumed by residential and commercial buildings in Ontario, 7.9×10^3 gigalitres (Gl) and 4.9×10^3 Gl respectively (Statistics Canada, 2012a). The Canadian NIR estimated 1879 g CO_2 m^{-3} natural gas as the CO_2 emission factor specific for the province of Ontario, based on data from a chemical analysis of representative natural gas samples and an assumed fuel combustion efficiency of 99.5 % (Environment Canada, 2012). Using this emission factor, CO_2 emissions from residential and commercial on-site furnaces in Ontario were estimated to be 1.5×10^7 tonnes and 9.2×10^6 tonnes, respectively. These two emission totals were spatially allocated using a "capped-total dwelling" spatial surrogate developed by ECCC and temporally allocated using the SMOKE emissions processing system (Moran et al., 2015).

2.5 Biogenic fluxes

The net ecosystem exchange fluxes used in our simulations were provided by the land surface component of the ECMWF forecasting system, C-TESSEL (Bousetta et al., 2013). Fluxes are extracted at the highest available resolutions, 15 x 15 km and 3 hour for January and February 2016 and 9 x 9 km and 3 hour for March. These data are interpolated in space and time to be consistent with our model resolution. With our main priority being understanding anthropogenic emissions in the GTA, we chose to analyze a period where the biogenic CO_2 flux is minimized and therefore this paper focuses on three winter months in 2016, January to March inclusive.

3.0 Results and Discussion

3.1 The SOCE inventory

Figure 1 displays the PanAm domain total anthropogenic CO_2 emissions estimated by the SOCE inventory for the province of Ontario portion (~0.02° x 0.02°) and by the FFDAS v2 inventory (0.1° x 0.1°) (FFDAS, 2010) for the remainder of the domain. Regions of high emissions typically correspond to population centers, for example the GTA in Ontario, Montreal and Quebec City in Quebec, and Chicago, Boston and New York City (amongst others) in the USA. Emissions from highways and major roadways are only clear in the province of Ontario (at higher spatial resolution) but industrial and large scale area sources are evident across the entire domain.

The total CO_2 emissions can be separated into contributions from the seven sectors in the province of Ontario described in Section 2.4. Figure 2 shows the anthropogenic CO_2 contributions from the Area sector, Residential and Commercial sector, Point sector, Marine sector, On-road sector and Off-road sector, focused on southern Ontario and the GTA. If we consider emissions from a domain including the area solely around the GTA (indicated by the black-box in Figure 2a), the total CO_2 emissions estimated by the SOCE inventory is 94.8 Mt CO_2 per year, Table 2. Figures 2a and b display the CO_2 emissions from the Area sector and from Residential and Commercial natural gas combustion in southern Ontario. These two sectors combined represent the largest source of CO_2 in the black-box area (41.6 Mt CO_2/year, contributing 43.9 % of the total). The majority of these emissions are concentrated in the GTA and surrounding urban areas as a result of a significant portion of the population (64 %) being reliant on natural gas for heat production (Statistics Canada, 2007; Statistics Canada, 2012a). Figure 2c represents emissions from the Point sector, contributing 24.4 Mt CO_2/year, 25.7 % of the total. The largest point source emitters are located on the western shore of Lake Ontario (Hamilton and surrounding areas) as this area is one of the most industrialized regions of the country with intensive metal production activities. Figures 2d, e and f display CO_2 emissions from various transportation sectors, Marine, On-road, and Off-road respectively, which together contribute more than 30 % of total CO_2 emissions in the area within the black box. While emissions from marine activity are minimal, those from On-road and Off-road sources are significant (25.0 % and 5.3 %, respectively), concentrating on the major highways connecting the various population centres of the GTA to the downtown core, as well as at Pearson Airport located within the city.

3.2 Comparison of the SOCE inventory with other inventories

The EDGAR v4.2 inventory estimates CO_2 emissions on an annual basis and by sector based on Selected Nomenclature for Air Pollution (SNAP) sub-sectors while FFDAS v2 provides hourly mean grid cell totals. Table 2 shows a comparison between the sectoral CO_2 estimates of the SOCE and EDGAR v4.2 inventories (SNAP sectors were grouped to correspond to SOCE sectors, Table S2) as well as the domain total estimated by the FFDAS v2 inventory for the area surrounding the GTA (the black-box area outlined in Figure 2a). There is a significant discrepancy between the CO_2 emissions estimated by the SOCE and EDGAR v4.2, inventories both in the relative sectoral contributions as well as domain total (percent difference >35 %). The largest sectoral discrepancies are in the Point and the On-road sectors, where the EDGAR v4.2 inventory estimates a contribution 1.9 and 1.7 times larger than that of the SOCE inventory, respectively. Figure 3 shows a comparison of the spatial distribution of the CO_2 inventory predicted by a) FFDAS v2, b) EDGAR v4.2, and c) SOCE (aggregated to 0.1° x 0.1° to match the resolution of EDGAR v4.2 and FFDAS v2) for the GTA area. Figure 3 reveals that the largest differences between the SOCE inventory and the EDGAR v4.2 inventory is the CO_2 emissions in the GTA; EDGAR v4.2 predicts much higher emissions in the GTA (in some grid cells, differences are an order of magnitude), particularly in the downtown core relative to the SOCE inventory.

Although there is no sectoral breakdown in the FFDAS v2 inventory, the domain total around the GTA can be compared to that of the SOCE inventory, Table 2. Unlike the comparison with the EDGAR v4.2 inventory, there is a closer agreement between the FFDAS v2 inventory and the SOCE inventory (difference of ~10 %). The comparison plots in Figure 3 show a good agreement of the spatial variability of emissions in the GTA between the FFDAS v2 and SOCE inventories; however, the gradient between urban and rural areas is not as sharp in the SOCE inventory as it is in the FFDAS v2 inventory. Furthermore, emissions along the western shore of Lake Ontario (Hamilton and the surrounding areas) are predicted to be larger in the SOCE inventory relative to FFDAS v2. The FFDAS v2 inventory was interpolated to 0.02 ° x 0.02° using a mass conservative interpolation scheme to allow the production of a difference plot of the two inventories, SOCE minus FFDAS v2, shown in Figure S1. The difference plot reveals the largest divergence between the inventories occurs in the GTA and Ottawa, with the FFDAS v2 inventory estimating >1000 g CO_2/second (~30 kt CO_2/year) more than the SOCE inventory in some grid cells. In addition to similar spatial variability, the FFDAS v2 and SOCE inventories also have similar temporal variability. Figure S2 shows the diurnal profile of estimated emissions from January-March for both the FFDAS v2 and SOCE inventories for the black-box area in the PanAm domain. Both inventories allocate the highest emissions between 08:00 and 18:00 and the lowest emission between 00:00 and 5:00, however the amplitude of the diurnal cycle is higher in SOCE, and emissions in the morning are as high as in the afternoon. FFDAS allocates a relatively larger proportion of the emissions to the 15:00 – 19:00 period.

3.3 Preliminary analyses using the SOCE, FFDAS v2 and EDGAR v4.2 inventories with FLEXPART

To investigate the impact of the different inventories on ambient mixing ratios, preliminary analyses were run with footprints generated for every third hour of the day (i.e., 00h, 03h, 06h, 09h, etc.) by the FLEXPART Lagrangian particle dispersion model (Stohl et al., 2005) driven by GEM meteorology for two sites, Downsview and TAO. Footprint areas were multiplied by the inventory estimates to arrive at mixing ratio enhancements and then compared against the measured CO_2 gradient between the Downsview and TAO stations for the year 2014. Gradients were used to capture the CO_2 mixing ratios in the downtown core of the city (since Downsview and TAO are situated just north and south of downtown Toronto, respectively). Observed gradients ranged from +20 to -10 ppm. Figure S3 displays the measured and modelled CO_2 gradients. These results show that when the EDGAR v4.2 inventory was used, simulated CO_2 gradients were consistently overestimated by ~10-60 ppm relative to observations. Conversely, when the SOCE inventory was used, a higher level of agreement was obtained between simulated mixing ratios and measurements; however, none of the model simulations were able to capture times when the gradient was negative ($CO_{2,TAO} > CO_{2,Downsview}$), an effect we believe to be due to the TAO inlet being ~60 m above ground level and surrounded by many high-rise buildings creating canyon flows and turbulence which are not properly accounted for in GEM at this resolution. These factors contributed to the decommissioning of TAO in January 2016. The poor performance of our model system when using the EDGAR v4.2 inventory to simulate CO_2 mixing ratios was also found by a study quantifying on-road CO_2 emissions in Massachusetts, USA (Gately et al., 2013). In this study, EDGAR emission estimates were found to be significantly larger than any other inventory by as much as 9.3 million tons, or >33 %. The difference in estimates between the EDGAR v4.2 and the SOCE inventories is likely explained by their underlying differences in methodology. Being a global product and not specifically designed for mesoscale applications, the EDGAR v4.2 inventory estimates CO_2 emissions based on country-specific activity data and emission factors, however the spatial proxies used to disaggregate the data are not always optimal. A study performed by McDonald et al. (2014) showed that the use of road density as a spatial proxy for vehicle emissions in EDGAR v4.2 causes an overestimation of emissions in population centers (McDonald et al., 2014). Given the much larger emission estimates for On-road CO_2 from EDGAR v4.2 (Table 2), this also seems to be an issue in the GTA. Based on this large discrepancy, the EDGAR v4.2 inventory was not further used in this study and we focussed on the inventories developed for regional scale studies.

When similar preliminary analyses were run with FLEXPART footprints using the FFDAS v2 inventory, Figure S3, good agreement was observed with CO_2 gradients measured between the Downsview and TAO stations. We are confident that the enhanced measurement agreement between the FFDAS v2 and SOCE relative to EDGAR v4.2 is due to improved methodology; spatial allocation of emissions in FFDAS v2 is achieved through the use of satellite observations of nightlights from human settlements from the U.S. Defense Meteorological Satellite Program Operational Linescan System (DMSP-OLS).

Beyond the differences in methodology for estimating and allocating emissions, it is important to note that the emissions reported in Table 2 by the FFDAS v2, SOCE and EDGAR v4.2 inventories also fundamentally differ in time period quantified. The emissions reported for both FFDAS v2 and the SOCE are based on emissions from three winter months (January-March 2010) extrapolated for the entire year. However, emissions from EDGAR v4.2 are annual averages of all twelve months of 2010. Since CO_2 emissions in the GTA are higher in the winter months relative to the summer months because of increased building and home heating, it is likely that the average annual estimates of SOCE and FFDAS v2 are slightly overestimated. This does not affect the relative agreement between SOCE and FFDAS v2 however it does further increase the divergence between the EDGAR v4.2 and SOCE and FFDAS v2 inventories. Following this and the improved agreement with observations, the FFDAS v2 inventory was used with the SOCE inventory for all subsequent modelling analyses.

3.4 Simulation of CO_2 mixing ratios in the Greater Toronto Area

We used the GEM-MACH chemistry-transport model and the SOCE and FFDAS v2 inventories to simulate hourly CO_2 mixing ratios in the PanAm domain. The model framework was evaluated for a continuous three-month period, January-March 2016 using four sampling locations in the GTA, Figure 1 (note that measurements for the Hanlan's Point site were not available until January 14, 2016). Figure 4 displays afternoon (12:00-16:00 EST) measured and simulated CO_2 mixing ratios produced with the SOCE and FFDAS v2 inventories for the two emissions scenarios described in Section 2.3 for the month of February (Figures S4 and S5 show the same figure for other months). We chose to present only afternoon data as this is the time of day when the mixed layer is likely to be the most well-developed; nighttime and morning data showed largest variations in observations as a result of the shallow boundary layer causing surface emissions to accumulate within the lowest atmospheric layers (Breon et al., 2015; Chan et al., 2008; Gerbig et al., 2008). During the night, atmospheric mixing ratios are most sensitive to vertical mixing, an atmospheric process that is difficult to model for stable boundary layers.

The time series comparisons at all four sites demonstrate the model's general ability to capture variability in observations of CO_2, albeit with better skill for the Downsview and Egbert sites (this is particularly clear when we look at model-measurement difference plots, Figure S6). The model is able to capture many extreme events of mixing ratio increases and decreases, such as February 11-14, 2016 at the Downsview site; however, some short time periods are poorly simulated, such as January 21-23, 2016 at Hanlan's Point, when the model significantly overestimated measured CO_2. Generally, mixing ratios simulated by the FFDAS v2 inventory are similar or larger than those produced when the SOCE inventory is used, with differences most noticeable at the Downsview and Hanlan's Point sites. This was expected as the difference plot shown in Figure S1 reveals that the SOCE and FFDAS v2 inventories diverge the most in the GTA (where the Downsview and Hanlan's Point sites are located) and are more similar in rural areas (where the Turkey Point and Egbert sites are located).

Measured CO_2 mixing ratios have a typical diurnal pattern, in which mixing ratios are higher at night and lower during the day, despite higher emissions during the day. This results from the daily cycle of the mixed layer, which is shallow at night due to thermal stratification and deepens during the day due to solar heating of the surface. Figure 5 displays the measured and modelled mean diurnal profile of CO_2 at the four sites in our network using data from January-March, 2016 (note difference in y-axis scale for urban vs. rural sites). At all four sites, the shapes of the modelled and measured mixing ratios throughout the day agree very well, suggesting that the GEM meteorology in our framework is capturing the diurnal variation in emissions and the boundary layer evolution. At the Downsview site, there is a very strong agreement between the modelled and measured diurnal profiles when using the SOCE inventory, whereas the FFDAS v2 simulated profile largely overestimates mixing ratios, particularly at nighttime. This is consistent with the FFDAS inventory having larger emissions than the SOCE inventory during the night (Fig S2). At the Hanlan's Point site, a difference of ~ 5 ppm CO_2 is observed when using the SOCE inventory relative to measurements; however, similar to the Downsview site, the FFDAS v2 simulated profile has a larger difference of ~10 ppm CO_2. At both the Egbert and Turkey Point sites, the use of both inventories similarly overestimates the diurnal pattern of CO_2 mixing ratios by ~3-5 ppm, again likely a result of the similarities of these two inventories at these sites, Figure S1. At all four sites, it is possible that some of the biases that are observed in simulated CO_2 mixing ratios may arise from inaccuracies in the boundary CO_2 provided by MACC; this aspect was not, however, further explored in this study.

3.5 Quantifying model-measurement agreement

Figure 6 shows scatter plots of afternoon (12:00-16:00 EST) modelled versus measured CO_2 mixing ratios from January- March, 2016 at the four sites used in this study. The top row shows the correlation between measured and modelled mixing ratios using the SOCE inventory and the bottom row shows the correlation using the FFDAS v2 inventory. It is immediately clear that there is a stronger model-measurement correlation at the Downsview and Egbert sites ($R > 0.75$) relative to that of Hanlan's Point or Turkey Point ($R < 0.53$). The difficulty with accurately simulating CO_2 mixing ratios at Hanlan's Point and Turkey Point may arise from their proximity to shorelines, Hanlan's Point to Lake Ontario and Turkey Point to Lake Erie (see Figure 1). Differential heating of land versus water near these lakes creates pressure gradients driving unique circulation patterns (Burrows, 1991; Sills et al., 2011). These circulation patterns are difficult for models to capture and therefore may contribute to the relatively poor correlation observed at Hanlan's Point and Turkey Point.

It is also clear from Figure 6 that simulating CO_2 mixing ratios at the Egbert and Turkey Point sites using either the FFDAS v2 or the SOCE inventory results in similar performance, likely because the emissions estimated by the two inventories are similar in the vicinity of these two rural sites (see also Figure 5). However at both the Downsview and Hanlan's Point sites, using the SOCE inventory provided a slightly higher correlation and reduced RMSE and MB relative to using the FFDAS v2 inventory. The improvement by using the SOCE inventory is likely a result of both the improved spatial resolution (2.5 km versus 10 km), and therefore more accurate allocation of emissions to grid cells, and also a better estimation of emission magnitudes, as large differences are shown in Figures 3 and S1.

3.6 Sectoral contributions to simulated CO_2 mixing ratios

One of the major advantages of the SOCE inventory over the FFDAS v2 inventory is the availability of sectoral emission estimates. Figure 7 displays the sectoral percent contributions to diurnal CO_2

mixing ratio enhancements (calculated as local CO_2 mixing ratios above the MACC estimated background) for the Downsview station in February 2016 averaged by the day of week (Figures S7 and S8 displays the same for other months). This figure clearly demonstrates the importance of Area emissions (defined here as the sum of the Area + Residential natural gas combustion + Commercial natural gas combustion) to simulated CO_2 mixing ratios, reaching ~80 % contribution in the early morning and late evening, consistent with times when emissions from home heating are the dominant source of CO_2. Contributions from Area emissions decrease to ~35 % midday, which coincides with when emissions from other sources, such as On-road, gain importance. In the midday, emissions from the On-road sector can contribute ~50 %, which is consistent with transportation patterns of the times when the population is travelling to and from work and other activities. The relative contributions to CO_2 mixing ratios from point source emissions is quite variable during the course of a day and week, but generally seems to increase in the early morning and evening and can contribute a significant portion of total CO_2 emissions (up to ~20 %). Figure 7 indicates that biogenic sources of CO_2 play a negligible role during January-March in the GTA (the Biogenic line is not visible because it is located on the zero line underneath the Marine line). Recent studies, however, have shown the importance of the biospheric contribution (up to ~132-308 g CO_2 km^{-2} s^{-1}) to measured CO_2 in urban environments during the growing season (Decina et al., 2016). Therefore, this finding supports the importance of modelling CO_2 in the wintertime in cities like the GTA to avoid complications associated with biospheric contributions. The new ability to understand the sectoral contributions to CO_2 mixing ratios in the GTA and southern Ontario has implications from a policy perspective; with recent initiatives to curb CO_2 emissions, understanding from which sector the CO_2 is being emitted could be useful to assess how effective applied mitigation efforts have been or where to target future efforts. These efforts could be complemented by running simulations with additional tracers, such as carbon monoxide (CO), nitrogen oxides (NO_x), or stable carbon isotopes (^{12}C and ^{13}C) to gain further insight.

4.0 Conclusions

We presented the SOCE inventory for southern Ontario and the GTA, the first, to our knowledge, high-resolution CO_2 inventory for southern Ontario and for a Canadian metropolitan region. The SOCE inventory provides CO_2 emissions estimates at 2.5 km x 2.5 km spatial and hourly temporal resolution for seven sectors: Area, Residential natural gas combustion, Commercial natural gas combustion, Point, Marine, On-road and Off-road. When compared against two existing CO_2 inventories available for southern Ontario, the EDGAR v4.2 and the FFDAS v2 inventories, using FLEXPART footprints, the SOCE inventory had improved model-measurement agreement; FFDAS v2 agreed well with in situ measurements, but the EDGAR v4.2 inventory systematically overestimated mixing ratios. We developed a model framework using the GEM-MACH chemistry-transport model on a high-resolution 2.5 km x 2.5 km grid coupled to the SOCE and FFDAS v2 inventories for anthropogenic CO_2 emissions and C-TESSEL for biogenic CO_2 fluxes. We compared output simulations to observations made at four stations across southern Ontario and for three winter months, January – March, 2016. Model-measurement agreement was strong in the afternoon using both anthropogenic inventories, particularly at the Downsview and Egbert sites. Difficulty in capturing mixing ratios at the Hanlan's Point and Turkey Point sites was hypothesized to be a result of their close proximity to shorelines (Lake Ontario and Lake Erie, respectively) and the model's inability to capture the unique circulation patterns that occur in those environments. Generally, across all stations and months, simulations using the SOCE inventory resulted in higher model-measurement agreement than those using the FFDAS v2 inventory, quantified using R, RMSE and mean bias. In addition to improved agreement, the primary advantage of the SOCE inventory over the FFDAS v2 inventory is the sectoral breakdown of emissions; using average day of week diurnal mixing ratio enhancements, we were able to demonstrate that emissions from area sources can contribute >80 % of CO_2 mixing ratio enhancements in the early morning and evening with on-road sources contributing >50 % midday. The applications of the SOCE inventory will likely show future utility in understanding the impacts of CO_2 reduction efforts in southern Ontario and identify target areas requiring further improvement.

Author Contributions

The SOCE inventory was prepared by Stephanie C. Pugliese, with critical input from Felix Vogel and Jennifer Murphy. The CO inventory which the SOCE inventory is based upon and the CO_2 emissions fields for residential and commercial natural-gas combustion were provided by Michael D. Moran, Junhua Zhang and Qiong Zheng. The GEM-MACH modelling analyses were performed by Shuzhan Ren and Craig Stroud. The ambient CO_2 data were collected by Douglas Worthy and his team at Environment and Climate Change Canada. The MACC and C-TESSEL products used in our model simulations were provided by Gregoire Broquet. The data was analyzed and interpreted for publication by Stephanie C. Pugliese. This manuscript was written by Stephanie C. Pugliese, with critical input from Jennifer Murphy, Felix Vogel and Mike Moran.

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