

We would like to thank the reviewers for their enthusiasm about our study and for the comments on our work. The review comments have been helpful in reflecting on our work and pointing out parts that required further improvements. Below we address specific issues mentioned by the reviewers point by point. The manuscript has been updated accordingly (changes are highlighted).

Reviewer #1 (J. Turnbull)

This paper describes a combined Eulerian/plume model approach to evaluate CO₂ (and CO) emissions, using Rotterdam, The Netherlands as an example. The authors show clearly that embedding a plume model within the Eulerian model improves the overall model fidelity in areas close to point sources. The results demonstrate that this is due to the Eulerian model resolution being insufficient to capture the details of nearby plumes. Presumably with infinite computing power, the Eulerian model could overcome this limitation, but embedding the plume model is a more computationally efficient solution. Further away from the point sources, the plume model doesn't add much, since the Eulerian resolution becomes sufficient at these spatial scales. They also evaluate the effect of wind direction biases in the Eulerian model (WRF-Chem is used in this case), and show that using observed meteorology makes a big improvement in the model fidelity close to point sources – this is not a surprise, but nonetheless is a nice result. This is a well-written, clear and easy to read paper. It is entirely appropriate for publication in ACP and I recommend it be accepted with minor modifications, detailed below.

General comments:

1. Is there a reason why there are no runs where WRF-Chem is nudged with the local meteorology? Given the results that show using local meteorology in the plume model really helps, this would be an obvious test to do.

We sincerely thank the reviewer for this comment and acknowledge that nudging local meteorological data would be a good step forward. However, we tested the WRF-FDDA system for a short period and found no consistent improvement, as periods of better wind field representation are alternated with periods with decreased performance. Moreover, previous studies have shown that the results from nudging are highly dependent on the type of data that is nudged and the grid resolution^(1,2). Therefore, we believe that more time needs to be dedicated to understanding the effects of wind field nudging to improve the WRF wind field representation. We plan to do so in a next study and thus decided to mention data assimilation as a point for future research.

¹ Deng, A., and N. Seaman, G. Hunter, and D. Stauffer, 2004: Evaluation of interregional transport using the MM5-SCIPUFF system. J. Appl. Meteor., 43, 1864–1886.

² Deng, A., and D. Stauffer, 2006: On improving 4-km mesoscale model simulations. J. Appl. Meteor., 45, 361–381.

2. I would like to see a bit of discussion about the relative difficulty of running the combined Eulerian/plume model simulations. How much more computation time is needed vs running WRF-Chem alone? How much additional effort (not computation time, but people time) is required – is it set up to run easily, or does someone have to sit there and do each plume run individually?

The OPS plume model is a very easy and fast model to run. For the ~100 point source emissions in our domain it needs about 20-25 seconds to calculate hourly mixing ratios at 4 sites for the full three months. In contrast, with the current set-up WRF-Chem needs several weeks to simulate the three months using 8 cores. Since OPS can handle multiple sources and receptor sites at once, it only needs to be run once for each species. The OPS model only needs an emission file and a file with general information about the run (e.g. the period). However, this doesn't allow us to separate between source types; i.e. we do not know which part of the signal is from industrial sources and which part from energy production sites. Nevertheless, this could be done by doing separate simulations per source type with limited additional effort. Thus the combined modelling system doesn't require much extra effort compared to running WRF-Chem alone. This is now shortly mentioned in lines 532-534.

3. The method presented here requires that the point sources are known from a bottom-up inventory and that the bottom-up information has the correct locations. That's going to be difficult in many cities where the information simply isn't available. Some comment on this (in the conclusions or discussion) is needed.

55 We agree with the reviewer that such detailed source characteristics benefit the model results. Except for the location (which could be inferred from Google Maps for example), such details are probably not available everywhere. We added some discussion on this in lines 545-548.

Specific comments:

60 *Line 33 (abstract). “Inevitable” seems a strong word to use – clearly the plume model helps a lot, but one could imagine other ways to address the same problem. Tone down the words used. Same for line 558 in conclusions.*

We thank the reviewer for the suggestion and have revised the text to “adds substantially to” in line 32 and to “is of great added value” in line 581.

65 *Line 65. Consider revising wording from “... that mask the urban signal” to “that mask the overall urban signal”.*

We have revised the text to “that mask the overall urban signal” in line 63.

70 *Lines 175-189 – CO fluxes. I agree that ignoring oxidation of hydrocarbons is probably reasonable for the winter months considered here, but I suspect that biofuel combustion might be important. Biofuel combustion (such as wood fires for home heating) tends to be quite inefficient with high CO:CO₂ ratios, so that even a small contribution to the CO₂ source might mean a significant CO source. The CObiofuel source could be estimated by combining the CO₂biofuel flux estimate with an estimate of the emission ratio. Andreae and Merlet 2001 is a good (even if old) resource to make some guesses about the emission ratio. Andreae, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. Global Biogeochemical Cycles 15, 955-966.*

80 We thank the reviewer for pointing out the importance of biofuel CO emissions. Indeed, biofuel combustion is an important source of CO, also in our study domain. In fact, the biofuel emissions - such as from wood stoves or biomass plants - are already part of the emission data used in our study, although they are part of the total emissions and cannot be quantified separately. The CO and CO₂ biofuel emissions thus do not have to be added in the model, but we do need to mention the term in Eq. 2 and the subsequent descriptions. We apologize for this omission in our manuscript. We have now included the biofuel terms in Eq. 2 and have added biofuel emissions in lines 223-225.

Lines 196-200. I take it the plume model is run forward (not backward as is common when plume models are run as a stand-alone)? Consider stating this explicitly to clarify.

90 We have rewritten line 201 to “The model keeps track of a trajectory forward in time [...]”

Lines 280-291. The choice of background definition from the baseline values is clearly more workable in this particular environment than using an upwind background. Nonetheless, it could be a problem on occasions when the incoming air is unusually polluted – the baseline background will not account for that. Please add a comment on this.

Generally our baseline slightly overestimates the background, meaning that the ΔCO_2 and ΔCO mixing ratios are really local additions. However, the reviewer is correct that for short periods of high pollution our background method underestimates the background mixing ratio. This is now mentioned in lines 293-294.

100 *Lines 333-347. I agree with the interpretation as described here, but I think you also need to discuss other possible explanations for the difference between observed and modeled CO:CO₂ ratios, and why these possibilities are less likely. Is it possible that the point source CO:CO₂ ratio is in fact higher than reported? Perhaps the inventories are wrong, and/or the industries are not scrubbing CO as effectively as they claim to?*

105 *CO from biofuel is not included in the model (see also earlier comments) – how would including this alter the modelled ratios?*

We thank the reviewer for the suggested alternative explanations. There is indeed an uncertainty in the reported stack emissions. Nevertheless, these figures are thoroughly quality-checked by the Netherlands Environmental Assessment Agency according to the IPCC guidelines, as it is part of the National Inventory Report. Therefore, these figures are relatively accurate and it is unlikely that this is the (main) cause for the model-data mismatch. We added this discussion in lines 349-351. As mentioned before, biofuels are included after all. Another potential explanation is that the CO:CO₂ emission ratios are not constant in time, while they are kept constant in the model by applying similar temporal profiles for CO and CO₂. We added this suggestion in lines 351-353.

Line 357. I don't think you ever spell out what RMSE is. Please do so the first time you use it.

RMSE has been spelled out now in line 364.

Lines 365-367. This effect has been seen before. Please add appropriate references.

We have added a sentence saying this, including references, in line 368.

Line 368. I am not sure what you mean by "there is no co-sampling for this comparison". Please revise for clarity.

Here, we compare two data sets. For the first one, we take all data that is above the baseline and satisfies our criteria, separately for the observed and modelled time series. For the second one, we make a similar selection for the observations, but then co-sample the modelled time series. So, whereas the two data sets for the first comparison can have a different size and include different times, for the second comparison they have equal size and contain the same times. We have tried to clarify this in lines 376-378.

Lines 369-370. You remove low wind speed data. Some additional discussion about the overall performance of the model when all data is included is needed. Do you conclude that it is generally difficult to model low wind speed time periods and they should always be discarded? In many environments, low wind speeds are when it is particularly cold and more CO₂ is generated for heating, so removing this data might bias the overall analysis to lower emissions.

Data analysis shows that for the results in Table 4 the addition of low wind speed data slightly increases the median and percentile values in a similar way for the observations and the WRF output. Thus the removal of low wind speed data has limited impact on the results, which is now mentioned in lines 379. However, for the subset in Table 5 the inclusion of low wind speed data (in total 3 data points) significantly deteriorates the results. This indicates that the models have difficulty correctly representing such stagnant conditions, which is now mentioned in lines 414-416.

Indeed, removal of low wind speed data can cause a bias in the estimated emissions, which has now been mentioned in lines 516-517. Similarly, the removal of night time data also causes a bias by not taking into account hours with usually lower emissions. However, including stable stratified and stagnant conditions with a large model bias will result in a large posterior uncertainty and most studies exclude these data ⁽³⁻⁵⁾.

³ Boon, A., Broquet, G., Clifford, D. J., Chevallier, F., Butterfield, D. M., Pison, I., Ramonet, M., Paris, J. D., and Ciais, P.: Analysis of the potential of near-ground measurements of CO₂ and CH₄ in London, UK, for the monitoring of city-scale emissions using an atmospheric transport model, *Atmos. Chem. Phys.*, 16, 6735-6756, 10.5194/acp-16-6735-2016, 2016.

⁴ Bréon, F. M., Broquet, G., Puygrenier, V., Chevallier, F., Xueref-Remy, I., Ramonet, M., Dieudonné, E., Lopez, M., Schmidt, M., Perrussel, O., and Ciais, P.: An attempt at estimating Paris area CO₂ emissions from atmospheric concentration measurements, *Atmos. Chem. Phys.*, 15, 1707-1724, 10.5194/acp-15-1707-2015, 2015.

⁵ Lauvaux, T., Miles, N. L., Deng, A., Richardson, S. J., Cambaliza, M. O., Davis, K. J., Gaudet, B., Gurney, K. R., Huang, J., O’Keefe, D., Song, Y., Karion, A., Oda, T., Patarasuk, R., Razlivanov, I., Sarmiento, D., Shepson, P., Sweeney, C., Turnbull, J., and Wu, K.: High-resolution atmospheric inversion of urban CO₂ emissions during the dormant season of the Indianapolis Flux Experiment (INFLUX), J. Geophys. Res.-Atmos., 121, 5213-5236, 10.1002/2015jd024473, 2016.

Lines 374-376. Sentence beginning “However, if we co-sample...”. I don’t understand how this is different than the previous analysis you discuss. Please clarify.

See our previous comment on the difference between the two analyses. This has been clarified in lines 384-386.

Lines 393 – 395. “At Cabauw ...” This sentence seems out of place.

Previously, the analyses have been done for both Zweth and Cabauw. However, we find that the impact of stack emissions at the Cabauw site is so limited that we don’t apply the plume model to this location. That is what is stated in lines 403-404.

Section 3.3. I would like to see some plots of the comparison in addition to the summary in the table. Perhaps as supplementary material?

We have added the following figure to an appendix. It shows the results related to the ratios (left panel) and to the ΔCO_2 slope (right panel).

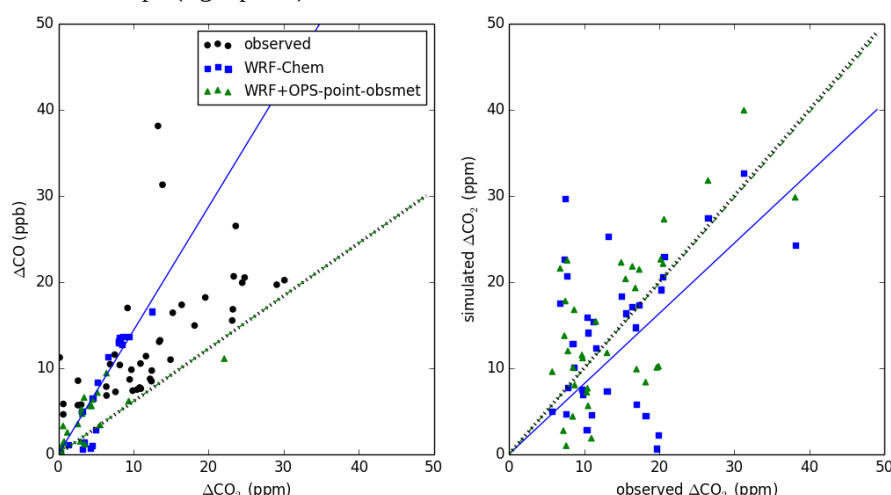


Figure A1: Left: A scatter plot of ΔCO and ΔCO_2 , where the slopes (represented by lines) represent the $\Delta\text{CO}:\Delta\text{CO}_2$ ratio for the observed and modelled values. The slope of WRF+OPS-point-obsmet coincides with the slope of the observations, suggesting a good agreement. Right: A scatter plot of simulated ΔCO_2 to observed ΔCO_2 . The slope of WRF+OPS-point-obsmet coincides with the 1:1 line (dotted line), suggesting a good agreement with the observations.

Lines 415-417. Clarify that you don’t show the data for this particular test.

We have clarified this in line 429.

Line 470. “specifically constrain”, not “constrain specifically”.

We have revised this in line 484.

Reviewer #2

Summary/General comments:

Super et al. combine observations of CO₂ and CO from urban and ex-urban sites in the Netherlands with an Eulerian modeling scheme (WRF-Chem) that explicitly accounts for plumes for large point sources to evaluate the utility of different urban/exurban observations and determine the utility of an Eulerian model in quantifying urban fluxes of CO₂. This is a thorough, well written paper that contributes significantly to the field of urban GHG research and is well placed in ACP. I enthusiastically recommend publication once these minor comments have been addressed.

Major comments:

The largest critique is the breadth of the conclusions implied in the abstract. Most pointedly, line 25, should instead state a plume model can be added to the model framework to account for point sources – the authors have shown that in an Eulerian model of typical regional resolution plumes are incorrectly represented and a plume model can fix this. However, a Lagrangian model, LES model, or very high resolution Eulerian model may not require this and the authors have not demonstrated as such. Similarly, line 33-34 are overstated. Integration of a plume model is not inevitable, as the authors have not shown alternatives are inadequate. The authors have shown that integration of a plume model is a possible solution for using a regional Lagrangian model and surface point observations for CO₂.

We sincerely thank the reviewer for this comment and we agree that other solutions might be possible, such as LES or full Lagrangian models. Our intention was to stress that a Eulerian model alone at the current resolution is not sufficient to represent point source emissions, and that a plume model can overcome some of the limitations. The use of a multi-model framework or a different type of model will depend on the application, and the resolution and scale. As we have shown, the plume model only has an impact up to about 10-15 km from a source. For other models, this might be different. Also, the models differ in how much effort is needed to set it up and do simulations, which might also be an important consideration. In our work we have demonstrated the use of an easy-to-use plume model, but we do not want to rule out other options. Therefore, we have revised the text to “[...], adding a plume model to the model framework is beneficial [...]” in line 25 and “adds substantially to” in line 32.

The authors have shown in compelling fashion the need for accounting for stack CO₂ emissions w/ a plume framework. It is interesting that this is not the case for CO, and it would be nice for that to be highlighted. Further, I wonder then if a plume model representation would be important for methane? Also, the authors are considering surface, point observations. If total column observations are considered, is a plume model essential or is the vertical dilution now irrelevant? This is perhaps a question beyond the current analysis, but it would be an interesting point to comment on.

We thank the reviewer for this interesting comment. Indeed, the plume model has limited added value for CO as most of the CO emissions are coming from area sources (stressed in lines 531-532). For methane the dominant source type in our domain is waste treatment and disposal, especially landfills. Depending on the size of the site relative to the size of the model grid, such sources could usually be considered area sources. Another important source of methane emissions is gas leakages. These are likely point sources, but the location of these leakages is unknown and it can be difficult to add these to a plume model.

Column integrals are of interest in the light of upcoming high-resolution missions. With column observations the vertical distribution would indeed become less relevant. However, the plume model also reduces the horizontal distribution of a point source compared to the grid box averaging done by a Eulerian model. In that sense, a plume model could still be useful. We plan to do more work on column observations in the near future. Whether a plume model is useful in that context would be an excellent question to pose for that work.

Detailed comments:

Line 57: This is dependent on urban typology and emission characteristics. The authors should acknowledge this limitation here.

A note has been added to lines 499-500 to clarify that our conclusions are valid for the Rijnmond area and cannot be generalized to other areas without careful consideration of the urban typology.

Lines 86-90: Other cities have also been studied – most notably Boston and Indianapolis, there are a sequence of INFLUX papers that it would be appropriate to cite here.

We apologize to the reviewer for having missed these references. We have added a reference related to urban scale monitoring of fossil fuel CO₂ emissions ⁽⁶⁾ and another reference related to a high-resolution inversion of urban CO₂ emissions using a Lagrangian Particle Dispersion Model driven by WRF meteorological fields ⁽⁷⁾ (see lines 88-89). We believe that these studies are strongly related to our research and are relevant for our introduction into the topic of urban CO₂ monitoring.

⁶ Turnbull, J. C., Sweeney, C., Karion, A., Newberger, T., Lehman, S. J., Tans, P. P., Davis, K. J., Lauvaux, T., Miles, N. L., Richardson, S. J., Cambaliza, M. O., Shepson, P. B., Gurney, K., Patarasuk, R., and Razlivanov, I.: Toward quantification and source sector identification of fossil fuel CO₂ emissions from an urban area: Results from the INFLUX experiment, *J. Geophys. Res.-Atmos.*, 120, 292-312, 10.1002/2014jd022555, 2015.

⁷ Lauvaux, T., Miles, N. L., Deng, A., Richardson, S. J., Cambaliza, M. O., Davis, K. J., Gaudet, B., Gurney, K. R., Huang, J., O'Keefe, D., Song, Y., Karion, A., Oda, T., Patarasuk, R., Razlivanov, I., Sarmiento, D., Shepson, P., Sweeney, C., Turnbull, J., and Wu, K.: High-resolution atmospheric inversion of urban CO₂ emissions during the dormant season of the Indianapolis Flux Experiment (INFLUX), *J. Geophys. Res.-Atmos.*, 121, 5213-5236, 10.1002/2015jd024473, 2016.

Line 175-183: I worry about this sweeping the VOC CO production under the rug. How much does this really matter? I suspect the authors' analysis is robust to this as the VOC CO production is embedded within the determination of the boundary condition, and thus ignoring it is ok as the amount produced in the near field (within 24 hours) is modest. I'd like a little more discussion of this, and estimates of how much this may matter if the same approach is taken in the summer?

In a study by Griffin et al. (2007), referenced in the manuscript, the contribution of hydrocarbon oxidation to the total CO production rate was investigated for two areas during high-pollution episodes. They found contributions of 5% for an area with significant biogenic hydrocarbon production and of 1% for an area dominated by anthropogenic CO emissions. In contrast, Hudman et al. (2008) (also referenced in the manuscript) come up with an estimate of more than 60% for the eastern United States. The main difference is that the Griffin study uses smaller domains, allowing hydrocarbons to be transported out of the domain before it can be converted into CO. Moreover, the domain of Hudman et al. covers an area with substantial biogenic fluxes and the dominant source of CO is the oxidation of isoprene.

Given the small size of our domain and the dominance of primary CO emissions, we assume the impact of hydrocarbon oxidation will be closer to the estimate of Griffin et al. Additionally, both studies were performed during summer, whereas the conditions during our study are less favourable for photochemistry. We thus believe that neglecting hydrocarbon oxidation in our study will introduce a bias, albeit a small one. This has been discussed in lines 183-184.

The two studies discussed here show that several factors will affect the estimated impact of hydrocarbons. Therefore, it is very difficult to make an estimate of how large this impact will be in our domain for summer months. We therefore believe that giving an estimate, as suggested by the reviewer, might be misleading at this point.

Title: I'd suggest a change as the manuscript is really not monitoring CO emissions, but leveraging CO to better interpret CO₂ emissions, and the current title is a little misleading.

We thank the reviewer for this suggestion. However, we believe that CO emission are fully coupled to the CO₂ emissions in our study through the use of fixed emission factors. So any updated CO₂ emissions automatically also lock the CO emissions. Yet, we do acknowledge that CO emissions were not the main target in this study.

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A multi-model approach to monitor emissions of CO₂ and CO from an urban-industrial complex

Ingrid Super^{1,2}, Hugo A.C. Denier van der Gon², Michiel K. van der Molen¹, Hendrika A.M. Sterk³, Arjan Hensen⁴, Wouter Peters^{1,5}

¹ Meteorology and Air Quality Group, Wageningen University, P.O. Box 47, 6700 AA Wageningen, Netherlands

² Department of Climate, Air and Sustainability, TNO, P.O. Box 80015, 3508 TA Utrecht, Netherlands

³ National Institute for Public Health and the Environment, P.O. Box 1, 3720 BA Bilthoven, Netherlands

⁴ Energy Research Centre of the Netherlands, P.O. Box 1, 1755 ZG Petten, Netherlands

⁵ Centre for Isotope Research, Energy and Sustainability Research Institute Groningen, University of Groningen, Nijenborgh 4, 9747 AG Groningen, Netherlands

Correspondence to: Ingrid Super (ingrid.super@wur.nl)

Abstract. Monitoring urban-industrial emissions is often challenging, because observations are scarce and regional atmospheric transport models are too coarse to represent the high spatiotemporal variability in the resulting concentrations. In this paper we apply a new combination of a Eulerian model (WRF with chemistry) and a Gaussian plume model (OPS). The modelled mixing ratios are compared to observed CO₂ and CO mole fractions at four sites along a transect from an urban-industrial complex (Rotterdam, Netherlands) towards rural conditions for October–December 2014. Urban plumes are well-mixed at our semi-urban location, making this location suited for an integrated emission estimate over the whole study area. The signals at our urban measurement site (with average enhancements of 11 ppm CO₂ and 40 ppb CO over the baseline) are highly variable due to the presence of distinct source areas dominated by road traffic/residential heating emissions or industrial activities. This causes different emission signatures that are translated into a large variability in observed ΔCO:ΔCO₂ ratios, which can be used to identify dominant source types. We find that WRF-Chem is able to represent synoptic variability in CO₂ and CO (e.g. the median CO₂ mixing ratio is 9.7 ppm (observed) against 8.8 ppm (modelled)), but it fails to reproduce the hourly variability of daytime urban plumes at the urban site (R² up to 0.05). For the urban site, adding a plume model to the model framework is beneficial to adequately represent plume transport especially from stack emissions. The explained variance in hourly, daytime CO₂ enhancements from point source emissions increases from 30 % with WRF-Chem to 52 % with WRF-Chem in combination with the most detailed OPS simulation. The simulated variability in ΔCO:ΔCO₂ ratios decreases drastically from 1.5 to 0.6 ppb ppm⁻¹ which agrees better with the observed standard deviation of 0.4 ppb ppm⁻¹. This is partly due to improved wind fields (increase in R² of 0.10), but also due to improved point source representation (increase in R² of 0.05) and dilution (increase in R² of 0.07). Based on our analysis we conclude that a plume model with detailed and accurate dispersion parameters adds substantially to top-down monitoring of greenhouse gas emissions in urban environments with large point source contributions within a ~10 km radius from the observation sites.

1 Introduction

Cities are major contributors to anthropogenic CO₂ and air pollutant emissions (Brioude et al., 2013; Turnbull et al., 2015; Velasco et al., 2014). Both monitoring and modelling of urban/regional concentrations of CO₂ and co-emitted air pollutants, such as CO and NO_x, has therefore received a lot of attention (Brioude et al., 2013; Font et al., 2014; Huszar et al., 2016; Lac et al., 2013; Mays et al., 2009; McKain et al., 2012; Rayner et al., 2014; Ribeiro et al., 2016; Silva et al., 2013; Tolk et al., 2009; Wunch et al., 2009; Zhang et al., 2015). Since current emission inventories at small scales contain substantial uncertainties (Pouliot et al., 2012; Vogel et al., 2013), data assimilation has been applied to urban environments in order to better quantify fossil fuel fluxes. However, modelling urban atmospheric composition remains challenging as the urban environment is complex in both the emission landscape and atmospheric transport. This means that to independently estimate urban emissions from atmospheric observations, urban inversions require a detailed and accurate transport model that allows the mismatch between model and observations to be attributed to errors in the emission inventory, rather than to transport errors (Boon et al., 2016). Previous inversion studies relied heavily on a strict data selection to favour well-mixed conditions with more reliable model output, which results in very small data sets and therefore increased uncertainty on the estimated emissions (Bréon et al., 2015; Brioude et al., 2013). This could be overcome by improving the model representation of urban transport, taking into account that the model requirements are strongly dependent on the type of observation site used in the inversion. In this paper we aim to construct a promising observation and modelling framework to quantify the CO₂ budget of an urban area by addressing two important questions in the context of inverse modelling at the urban scale.

The first question is what type of measurement location (urban vs. rural) can best be used to monitor urban fluxes. Generally, urban sites are most strongly exposed to nearby (<1 km) fluxes and therefore show a large variability (Bréon et al., 2015; Lac et al., 2013). In contrast, rural sites show a much smaller response to urban emissions due to the small range of wind directions at which the site is affected by the urban area. Moreover, the dilution of urban plumes increases with distance (Calabrese, 1990; Finn et al., 2007) and the observed signal at the rural site can be small. Another consideration is that near-ground measurements, as commonly found in cities, are highly influenced by local sources (<100 m) that mask the overall urban signal. Boon et al. (2016) suggested that, even if strict data selection is applied, the usefulness of such sites in inversions with high-resolution Eulerian models (1–10 km) might be limited. Together, these papers suggest that a useful measurement location should be just downwind of an urban area relative to the dominant wind direction at a distance that ensures enough exposure to the urban plume and limits model errors due to large heterogeneity and local emissions. We will examine a transect of measurement sites to see which site best matches this criterion.

The second question we address is what type of modelling framework is best capable of explaining urban transport and the resulting mole fractions at the measurement sites. Since the measurement location determines the level of spatiotemporal variation that can be observed in the concentrations, it also determines the requirements imposed on the modelling framework. In atmospheric composition modelling both Eulerian and Lagrangian (plume, puff or Gaussian) models are used, or a combination of both (Kim et al., 2014; Korsakissok and Mallet, 2010a). Eulerian models use a grid that can be adapted to cover either small or large areas at different resolutions and are therefore widely used. However, Eulerian models assume that trace gasses are instantly mixed within individual grid boxes, which may enhance dispersion in the horizontal and vertical. The resulting errors in transport and mixing are reflected in unrealistic concentrations (Karamchandani et al., 2011;

Tolk et al., 2009). The magnitude of the concentration error depends on the heterogeneity of the emissions and the grid resolution (Tolk et al., 2008). A plume model improves the description of horizontal and vertical mixing and can account for higher spatial heterogeneity of emissions and concentrations. The use of such models has proven useful for both inert and reactive species, and point and line sources at local/urban scales (Briant and Seigneur, 2013; Korsakissok and Mallet, 2010a, b; Rissman et al., 2013; Vinken et al., 2011). However, a plume model is usually only applied to local sources to reduce computational expenses. It therefore does not resolve the impact of remote emissions and synoptic transport. So, when assessing the carbon balance of a whole city or larger areas, a combination of both models might be needed.

Oney et al. (2015) examined an extensive CO₂, CH₄ and CO measurement network in combination with the FLEXPART-COSMO model. However, their framework focused on regional (~100–500 km), terrestrial fluxes. Several other studies focussed on urban scales (Boon et al., 2016; Bréon et al., 2015; Turnbull et al., 2015), but only few incorporated a Lagrangian model. For example, McKain et al. (2012) and Lauvaux et al. (2016) used a Lagrangian model to optimize urban fluxes of CO₂, while Brioude et al. (2013) compared simulated FLEXPART CO₂, CO and NO_x concentrations to small observational datasets from seven flights over Los Angeles. Here, we compare and combine simulations with two different models: the Eulerian WRF-Chem model and the segmented Gaussian plume model OPS. The Gaussian plume model is used here specifically to transport point source emissions. The model output is compared to continuous observations of CO₂ and CO at several measurement sites along an urban-to-rural transect. We included CO, because this species can act as a useful tracer for source attribution. We use the Rijnmond area (The Netherlands) including the city of Rotterdam as our case study, which is surrounded by scattered urban, agricultural, and rural areas. We chose this area because of the availability of a 1x1 km² emission inventory and its complex combination of residential, transport (including shipping), greenhouse and industrial activities. This makes Rijnmond an interesting test case, albeit not a simple one.

This paper starts with a description of the case study (Sect. 2.1), the modelling framework (Sect. 2.2–2.5), and a summary of data selection criteria and methods (Sect. 2.6). Subsequently, we examine the ability of our measurement sites to detect urban signals, and demonstrate the added value of both urban and semi-urban sites (Sect. 3.1). Section 3.2 examines the ability of WRF-Chem to represent the urban signals at the measurement sites. Finally, we discuss the advances made by implementing the Gaussian OPS plume model (Sect. 3.3) and we examine the relative importance of improved meteorological conditions and source representation in Sect. 3.4. Our results lead to recommendations for future monitoring and modelling of urban atmospheric composition in Sect. 4.

2 Methods

2.1 Study area and measurements

We take the Rijnmond area (Fig. 1) in the Netherlands for our case study in which Rotterdam is the major urban area (625.000 inhabitants). The area is situated in flat terrain near the west coast of The Netherlands and includes a large harbour and industrial area. The bottom-up estimated emissions in this area are about 35 Mt CO₂ and 48 kt CO in 2012 (Netherlands PRTR, 2014). In the port area, over three times more CO₂ is emitted than in the city of Rotterdam. In contrast, more than 60 % of all CO is emitted in the city of Rotterdam. The reason for this

455 difference is that emissions within the city are dominated by road traffic, which emits relatively much CO
(CO:CO₂ emission ratio of almost 17 ppb ppm⁻¹). The principal source of CO₂, namely energy production and
industrial processes, is mainly found in the port area and barely emits any CO (CO:CO₂ emission ratio of less
than 1 ppb ppm⁻¹). The CO₂ emissions are therefore dominated by point sources (~80 %).

We have installed two measurement sites to monitor CO₂ and CO mixing ratios 15 km south (Westmaas,
460 51.79° N, 4.45° E) and 7 km northwest (Zweth, 51.96° N, 4.39° E) of the city centre with an inlet at 10 m a.g.l.
We consider Zweth to be an urban site which is highly affected by urban emissions. Westmaas functions as a
background site close to – but not within - the city and it is usually located upwind of the major source areas.
Therefore, Westmaas provides information on the air mass entering the Rijnmond area and we only use this site
to validate the large-scale patterns in WRF-Chem. These measurements have been described in more detail by
465 Super et al. (2017). At Rotterdam-The Hague airport (Fig. 1) meteorological observations are made, which we
also use for transport model validation purposes.

We include two additional, more remote, sites in our framework. The Cabauw site (51.97° N, 4.93° E) is
situated 32 km east of the centre of Rotterdam and is considered a semi-urban site (Van der Laan et al., 2016;
Vermeulen et al., 2011). This means the sampled air masses are influenced by urban emissions, but less often
470 than a truly urban location. CO₂ is measured at several heights (20, 60, 120 and 200 m a.g.l.) along a 200 m tall
tower by the Energy research Centre of the Netherlands (ECN). CO is measured at ground level (2.5–4 m a.g.l.)
by the National Institute for Public Health and the Environment (RIVM). Another observation site is located at
Lutjewad (53.40° N, 6.35° E), close to the coast in the north of the Netherlands. At this rural site, CO and CO₂
mixing ratios are observed at 60 m a.g.l. (Van der Laan et al., 2009a; Van der Laan et al., 2016). These four
475 stations together describe a transect from the city towards rural areas.

For the Cabauw CO₂ measurements we selected the 60 m level. On average the CO₂ mixing ratios are similar
at all levels during well-mixed daytime conditions (Vermeulen et al., 2011), but a large gradient is observed for
stable conditions when the 20 m level is highly affected by surface fluxes surrounding the tower. Similarly,
Turnbull et al. (2015) suggested that measurements closer to the surface are more sensitive to local fluxes and
480 therefore a higher level than 20 m is more suitable to obtain information on more remote fluxes. We choose the
60 m level observations to be able to compare easily to the Lutjewad site. However, a higher level could have
been used without affecting our conclusions.

2.2 Eulerian model

The Eulerian model used in this study is WRF-Chem V3.2.1 (Skamarock et al., 2008). For its initial and
485 boundary conditions we use meteorological fields from the National Centers for Environmental Prediction
(NCEP) Final (FNL) Operational Global Analysis (National Centers for Environmental Prediction/National
Weather Service/NOAA/U.S. Department of Commerce, 2000) at 1x1° horizontal resolution and a temporal
resolution of 6 hours. We define four 2-way nested domains (Fig. 2) which have a horizontal resolution of
48x48, 12x12, 4x4 and 1x1 km respectively, and a vertical resolution of 29 eta levels with the lowest model
490 layer 40 m deep and a total of 8 levels in the lowest 1 km. The outer domain is situated over Europe. Domains 2–
4 zoom in on the Rijnmond area in the southwest of the Netherlands. Based on previous studies over the
Netherlands (Bozhinova et al., 2014; Daniels et al., 2016; Steeneveld et al., 2014), we have used the Yonsei
University (YSU) boundary layer scheme (Hong et al., 2006), the Dudhia scheme for shortwave radiation

(Dudhia, 1989), the Rapid Radiation Transfer Model (RRTM) as longwave radiation scheme (Mlawer et al., 1997), and the Unified Noah Land-Surface Model as the surface physics scheme (Ek et al., 2003). We also used the single-layer urban canopy model (UCM) to account for changes in roughness length and heat fluxes in the urban environment (Chen et al., 2011), although the impact of the UCM model on simulated mixing ratios is very small in our domain.

The CO₂ initial and boundary conditions are taken from the 3D mole fractions from CarbonTracker Europe (Peters et al., 2010). The CarbonTracker 3D fields have a horizontal resolution of 1x1° and 34 vertical levels. Therefore, they are both horizontally and vertically interpolated onto the WRF-Chem grid. The CO initial and boundary conditions are calculated with IFS-MOZART (Flemming et al., 2009) and obtained from the Monitoring Atmospheric Composition and Climate (MACC) project. The boundary conditions are updated every 6 hours (only for the outer domain).

We have implemented a CO₂ budget based on the methodology used by Bozhinova et al. (2014), described in Eq. (1).

$$X_{CO_2,obs} = X_{CO_2,lsbg} + X_{CO_2,ff} + X_{CO_2,bf} + X_{CO_2,p} + X_{CO_2,r} \quad (1)$$

where the indices express the origin of CO₂: obs – total observed concentration at a particular location, lsbg – large-scale background mole fraction, ff – fossil fuels, bf – biofuels, p – photosynthetic uptake, r – ecosystem respiration. Similar to the original study of Bozhinova et al. (2014), we omitted the stratosphere-troposphere exchange and ocean fluxes and assume they are accounted for in the large-scale background. With Eq. (1) we thus only consider regional contributions to the carbon budget in addition to the large-scale background. In the model, any change in the large-scale background CO₂ mole fraction ($X_{CO_2,lsbg}$) is only caused by advection and exchange at the domain boundaries.

In addition, we added the CO budget to WRF-Chem following Eq. (2). The main sources of CO are fossil fuel combustion and oxidation of hydrocarbons (US EPA, 1991). Several scholars have argued that the hydrocarbon oxidation term is important for the large-scale background CO concentration (Gerbig et al., 2003; Griffin et al., 2007; Hudman et al., 2008), contributing a significant percentage to the total CO burden. Yet, these studies were all based on summer time measurements and under conditions favourable for photochemistry. Photochemical oxidation is likely to be less important in the winter months considered here. Moreover, Griffin et al. (2007) found the CO fraction from local anthropogenic emissions to dominate at measurement sites. We assume this is also valid in the urban-industrial environment of our case study. **We nevertheless consider that this introduces an uncertainty in the modelled CO mixing ratios. For summer time studies the oxidation term might be significant.**

The main sink of CO is the reaction with the hydroxyl radical (chemical loss term L), which we account for with a simple first order loss term. We assume steady-state, i.e. the OH concentration is taken as a constant (10^6 molecules cm⁻³). This results in a lifetime for CO of about 2 months at mid-latitudes (Jacob, 1999) during the winter months used in our study:

$$X_{CO,obs} = X_{CO,lsbg} + X_{CO,ff} + X_{CO,bf} + X_{CO,L} \quad (2)$$

The different contributions in Eq. (1) and Eq. (2) are separated as different additive tracers (i.e. labelled) in the WRF-Chem simulations.

2.3 Gaussian plume model

The plume dispersion model OPS (Operational Priority Substances) is a segmented Gaussian plume model that calculates the transport, dispersion, chemical conversion and deposition of pollutants (Sauter et al., 2016; Van Jaarsveld, 2004). It is used to calculate large-scale, yearly averaged concentration and deposition maps for the Netherlands at 1x1 km² resolution. It was initially developed to model dispersion of pollutants like particulate matter and ammonia, but has also been used to study the dispersion of pathogens (Van Leuken et al., 2015).

In this paper we use the so-called "short-term" version of this model (version 10.3.5), which contains mostly the same parameterisations as the "long-term" model described by Sauter et al. (2016). The short-term model provides hourly concentrations at receptors that can be individual sites, or across a gridded domain. The model keeps track of a trajectory **forward in time**, for which plumes consist of so-called segments, taking into account time-varying transport over longer distances (e.g. changes in wind direction and dispersion). If for a time step a specific plume affects the receptor, a Gaussian plume formulation is used to calculate the concentration caused by that source based on the true travel distance along the trajectory.

The OPS model uses primary meteorological variables which are measured by the Royal Dutch Meteorological Institute, and calculates secondary variables such as boundary layer height and friction velocity, but also the turning of the wind with height and a vertical wind profile. Primary meteorological variables are spatially interpolated over the Netherlands to 10x10 km² using 19 observation sites with a weighing factor depending on the distance to the grid point. The variables are subsequently averaged over a pre-defined area (for more information see Sauter et al. (2016)). The use of observed meteorology in OPS versus model-calculated meteorology in WRF-Chem could result in an unfair comparison of the models, and we therefore replaced the primary parameters (temperature, humidity, wind speed, and wind direction) and the boundary layer height with those calculated by WRF-Chem. The secondary (dispersion) parameters are automatically also updated, since they are calculated from the primary parameters. Note that the meteorological conditions in OPS remain constant during each simulated hour and over a large region.

Although potentially the OPS model can be used for both area and point source emissions, we believe that point sources will benefit most from a more detailed description of dispersion as they are affected most by the instant dilution in a Eulerian model. When using OPS, we assume wet deposition plays no role due to the relative insolubility of CO₂, while dry deposition of CO₂, i.e. photosynthetic uptake, is accounted for by WRF-Chem (Eq. (1)). We do not simulate CO with the OPS model. The point source contribution to the total CO concentrations is very small and therefore the impact of OPS is limited.

2.4 Emissions

The fossil fuel and **biofuel** emissions for domains 1–3 in the WRF-Chem simulation are taken from the TNO-MACC III inventory for 2011 (Kuenen et al., 2014) and have a horizontal resolution of 0.125x0.0625°. Fossil fuel and **biofuel** emissions for domain 4 in WRF-Chem are collected from the Dutch Emission Registration (Netherlands PRTR, 2014) and compiled by TNO (Netherlands Organization for Applied Scientific Research) to a 1x1 km² emission map for the year 2012. In the OPS simulations we only include the point source emissions from domain 4 in WRF-Chem (hereafter referred to simply as the Rijnmond area).

The emissions are divided over ten SNAP emission categories, summarised in Table 1, which may include both area and point sources. We apply a temporal profile to the emissions by assigning hourly, daily and monthly fractions to the emissions per emission category (Denier van der Gon et al., 2011). In WRF-Chem, area source

emissions are added to the lowest surface model level every hour. Point source emissions (only SNAP 1, 3, 4, 8 and 9) are given a simplified, fixed vertical distribution based on previous research with plume rise calculations (Bieser et al., 2011). These emissions are emitted at the heights shown in Table 1. OPS allows for more detailed point source characteristics and accounts for stack height and plume rise (based on heat content) per individual point source.

The biogenic (non-biofuel) CO₂ fluxes in WRF-Chem are generated as described by Bozhinova et al. (2014). The SiBCASA model (Schaefer et al., 2008) calculates monthly averaged 1x1° photosynthetic uptake (A_n) and ecosystem respiration (R) for nine different land use types. Combining the high-resolution land-use map of WRF-Chem with the SiBCASA fluxes gives us biogenic fluxes on the resolution of the WRF-Chem grid. The temporal resolution is enhanced by scaling the A_n and R at each WRF-Chem time step with modelled shortwave solar radiation (SW_{in} in W m⁻²) and 2m temperature (T_{2m} in K):

$$A_n = A_{n,f} \cdot SW_{in} \quad (3)$$

$$R = R_f \cdot 1.5^{(T_{2m}-273.15)/10} \quad (4)$$

where $A_{n,f}$ is the monthly average photosynthetic flux divided by the monthly total incoming shortwave radiation (mole CO₂ km⁻² h⁻¹ (W m⁻²)⁻¹), and R_f the monthly average respiration flux (mole CO₂ km⁻² h⁻¹) divided by the monthly total of the empirical function $1.5^{(T_{2m}-273.15)/10}$ (unitless). This procedure was first described in Olsen and Randerson (2004). It neglects the impact of water stress, temperature and CO₂ concentration on the photosynthetic uptake. Given that we consider only winter months in which photosynthesis is limited, we assume the error resulting from this simplification to be small.

2.5 Overview of simulations

We simulated a period of 3 months, October–December 2014. We choose this period because of the high data coverage at all measurement sites and to limit the impact of biogenic fluxes and hydrocarbon oxidation. We considered four simulations for CO₂, using two different model systems as described in Table 2. All simulations include the WRF-Chem contributions of $X_{CO_2,lsbg}$, $X_{CO_2,p}$, $X_{CO_2,r}$, and $X_{CO_2,bf}$ and $X_{CO_2,ff}$ from area sources. Also, the first three simulations make use of meteorological conditions as simulated by WRF-Chem. Therefore, the simulations only differ in the representation of point source emissions in the Rijnmond area. To identify the importance of a correct representation of meteorological conditions we do an additional OPS simulation with interpolated meteorological observations (see Sect. 2.3). The simulations are designed to gradually increase the complexity of the point source representation towards more realistic point source contributions:

- In simulation 1 (WRF-Chem) the point sources are represented as area sources in WRF-Chem;
- In simulation 2 (WRF+OPS-area) the point sources are treated as area sources in OPS;
- In simulation 3 (WRF+OPS-point) the point sources are represented as true point sources with detailed source characteristics in OPS;
- In simulation 4 (WRF+OPS-point-obsmet) the point sources are represented as true point sources with detailed source characteristics in OPS and the meteorology in OPS is replaced by interpolated observations and OPS calculated boundary layer height.

In the WRF-Chem run we labelled the point source emissions from the Rijnmond area separately, so we can replace them by the OPS counterparts. The OPS model simulates concentrations directly at the measurement

sites, whereas from WRF-Chem we extract the grid box average mixing ratio of the boxes in which the measurement sites are located.

2.6 Baseline determination and data selection criteria

In this study we are especially interested in the contribution of urban emissions and the ability of the models to represent the transport of those emissions to the observation sites. However, the observed CO₂ and CO mixing ratios are also affected by background signals and other fluxes. Therefore, in order to purely compare the transport of urban emissions, we need to separate the fossil fuel contribution from all other contributions. In the models we can separate the fossil fuel contribution $X_{CO_2,ff}$ coming from the Rijnmond area (hereafter referred to as “urban plume”) from all other contributions (i.e. $X_{CO_2,ff}$ from outside the Rijnmond area, $X_{CO_2,lsbg}$, $X_{CO_2,p}$, $X_{CO_2,r}$, and $X_{CO_2,bf}$, hereafter referred to as “baseline”) by using labelled tracers. To quantify the urban plume contribution to the total observed mixing ratio, we also need to subtract a baseline.

Previous studies have suggested various methods to calculate the baseline from observations, for example using a remote/upwind measurement site or statistical methods (e.g. (Djuricin et al., 2010; Lopez et al., 2013; Turnbull et al., 2015; Van der Laan et al., 2010). An in-model comparison with WRF-Chem shows that Westmaas is a suitable background site for Zweth (Super et al., 2017), but Westmaas gives a biased baseline estimate for the more remote sites (Cabauw and Lutfjewad) because of the interference of other sources and sinks along the transect from Rijnmond to the measurement site. Another suggested method is to subtract a smoothed representation of the original time series (Press et al., 1992; Super et al., 2017; Thoning and Tans, 1989) which filters out variations below a certain cut-off time scale. For seasonal cycle smoothing for example, a typical cut-off value is 80 days. In our study however, the baseline needs to filter out synoptic variations across the domain and we therefore chose a cut-off time of 5 days. We tested this baseline definition by applying it to the WRF-Chem time series and comparing the resulting concentrations to the true WRF-Chem baseline based on the labelled tracers. We found satisfactory agreement (R^2 is between 0.65 and 0.81 for both species at all 3 locations). Note that this method does not account for short pollution events bringing polluted air into the domain as only synoptic variations are captured.

To prevent any differences between model and observations resulting from the baseline selection, we choose to apply this subtraction of a smooth cycle method with a 5-day cut-off to both observations and our model time series at all measurement sites (see Fig. 3 for an example). The concentrations above the baseline are considered to be the urban plume concentrations and are denoted ΔCO_2 and ΔCO . Note that data points can also be below the baseline if clean air is advected and only a small fossil fuel contribution is calculated. We discard these data points, because we cannot accurately estimate the fossil fuel concentrations in those urban plumes.

In all the analyses, we applied a wind sector selection to ensure that the observations are affected by emissions in the Rijnmond area rather than from other urban areas nearby. For Zweth we selected wind directions of 90–220 degrees, for Cabauw 230–270 degrees, and for Lutfjewad 210–230 degrees. For Zweth we can also separate between signals from the residential area (90–150 degrees, Zweth-city) and industrial area (160–220 degrees, Zweth- port). Wind direction observations at Rotterdam airport are used for this purpose. Additionally, a daytime selection criterion (8:00–17:00 LT) is applied to favour well-mixed conditions.

3 Results

3.1 Comparison of measurement sites

The urban-to-rural transect of observation sites provides an opportunity to evaluate the ability of different types of sites to detect urban plumes. We find that a semi-urban site can provide a constraint on the total emissions in the Rijnmond area, whereas an urban site is able to separate between different source areas. This is illustrated in Fig. 4 (left panel), where we display the probability density functions of the urban plume CO:CO₂ concentration ratio (i.e. $\Delta\text{CO}:\Delta\text{CO}_2$) at the three sites. A probability density function illustrates the likelihood that an observed urban plume concentration ratio takes a certain value. The narrower the distribution, the less variable the ratios are and the more likely a ratio is to take the mean value (largest probability). Figure 4 also displays the mean bottom-up derived emission ratio of the Rijnmond area (vertical solid line, 2.5 ppb ppm⁻¹) and its range, which is taken from the emission inventory taking into account the temporal profiles of the separate emission categories.

We see that the $\Delta\text{CO}:\Delta\text{CO}_2$ distribution at Cabauw is relatively narrow. Also, the mean $\Delta\text{CO}:\Delta\text{CO}_2$ at Cabauw (2.2 ppb ppm⁻¹) is very close to the bottom-up Rijnmond emission ratio. This indicates that Cabauw observes an integrated, well-mixed signal from the Rijnmond area and therefore contains information on the entire urban area. Interestingly, Lutjewad shows a much wider distribution with a mean of 3.9 ppb ppm⁻¹. The urban plume from Rijnmond is mixed with signals from other industrial and urban areas (such as Amsterdam) before it reaches Lutjewad, causing more variability. This suggests that a site too far away from the urban sources is unable to uniquely identify the urban plume coming from a specific region. Also, the wind direction is heterogeneous between Rijnmond and Lutjewad. So, despite that the wind in Rijnmond is blowing towards Lutjewad according to our wind sector selection, the urban plume might never reach the site if the wind direction is changing during transport. This makes it difficult to filter out the Rijnmond urban plume and Lutjewad will be disregarded for the remainder of this study. The Zweth site has an even wider distribution than Lutjewad and a mean ratio of 4.5 ppb ppm⁻¹. This site is affected by different source areas with distinct emission ratios depending on the wind direction, resulting in a large variability in observed concentration ratios. This variability contains a lot of information about the Rotterdam emissions and their spatiotemporal variations. Therefore, we examine the Zweth distribution in more detail by selecting wind sectors that sample different source areas with distinct emission characteristics (Fig. 4, right panel). Zweth-city is illustrative for the signal from the urban residential area dominated by road traffic and the Zweth-port signal contains mostly industrial and power plant emissions.

We find a large difference in bottom-up emission ratios for the residential (6.6 ppb ppm⁻¹, vertical dash-dotted line) and port area (1.2 ppb ppm⁻¹, vertical dashed line), which is not fully reproduced by the observed $\Delta\text{CO}:\Delta\text{CO}_2$ ratios. Whereas the observed $\Delta\text{CO}:\Delta\text{CO}_2$ ratio for Zweth-city (5.0 ppb ppm⁻¹) is in reasonable agreement with the emission ratio, Zweth-port has a mean observed ratio that is much higher than expected (4.1 ppb ppm⁻¹). This discrepancy is related to the presence of high stack emissions in this area, which make up almost 75 % of the total Rijnmond CO₂ emissions. The stack emissions from industrial processes and energy production have a small emission ratio of ~1 ppb ppm⁻¹ and dominate the total emission ratio. However, stack emissions have small plume dimensions that can easily be missed at the Zweth site and not be visible in the observations, especially for stacks in the vicinity of Zweth. Therefore, the observed concentration ratio can turn out much higher than what is expected based on the emission inventory including stack emissions. Indeed, the emission ratio of the Zweth-port area without point sources would be 3.9 ppb ppm⁻¹, which is very close to the observed 4.1 ppb ppm⁻¹. This finding indicates that stack emissions only occasionally affect the Zweth

observations and it is very important to represent those events well with a model in order to constrain this large fraction of CO₂ emissions. Although there might be an uncertainty in the emission inventory, reported emissions from industrial stacks are relatively accurate. Thus, it is unlikely that this explains the full discrepancy found for Zweth-port. Another potential cause of the discrepancy could be that the emission ratio is variable in time – for example due to a change in fuels used for energy production, while this is not accounted for in the inventory. However, this would likely have a smaller impact than the discrepancy found here. The impact of stack emissions on the Zweth observations is discussed in more detail in Sect. 3.3.

3.2 WRF-Chem urban plume transport

We have now seen that the observations at Zweth and Cabauw contain valuable information about the emissions in the Rijnmond area. In order to use that information to estimate the emissions, we explore the ability of WRF-Chem to represent observed time series, and especially their urban plume components.

First, we analyse the model performance on a day-to-day basis by looking at daytime averages and find that WRF-Chem is able to resolve day-to-day variations reasonably well. Table 3 shows that, respectively, 65 % and 53 % of the variability in the CO₂ and CO mixing ratios is captured at the Westmaas background site. Although the explained variances are slightly smaller at the urban (Zweth) and semi-urban (Cabauw) site, the performance at Cabauw for CO₂ is comparable to previous modelling studies (Bozhinova et al., 2014; Tolk et al., 2009). Yet, the RMSE (Root Mean Square Error) is relatively large for CO and CO₂ at all sites. Since Westmaas is nearly unaffected by urban emissions, the cause of the large RMSE is related to larger scale transport. Looking at meteorological variables, there is a good agreement for temperature, humidity and wind speed. However, the model has difficulties simulating the correct wind direction, which is especially expressed in the large RMSE. Similar errors have been observed before (Deng et al., 2017; Srinivas et al., 2016). The largest error is found in the second half of November, causing a large model-data discrepancy (also visible in Fig. 3). Table 3 also shows that the RMSE in the mixing ratios further increases for sites that are more influenced by the urban area. This finding indicates that WRF-Chem has difficulties representing the full variability caused by urban-industrial emissions.

Second, looking closer at the urban plumes we find that WRF-Chem represents the typical characteristics of urban plumes reasonably well, but it simulates the peaks at the wrong time at the wrong location compared to the measurements (Table 4). We tried to isolate the impact of errors in urban transport by looking statistically at the urban plume concentrations (ΔCO_2 and ΔCO) at Zweth and Cabauw. We select all data points that satisfy our criteria, separately for the observed and modelled time series such that both data sets can have a different size. We disregard data points associated with wind speeds of less than 3 m s⁻¹ to favour well-mixed conditions that are easier to interpret. However, we find that the inclusion of low wind speed data has limited impact on the average statistics. Table 4 shows that, on average, there is a good agreement between WRF-Chem and the observations in the median and the 80th percentile. The median values of CO₂ are somewhat lower in WRF-Chem, indicating there are more small values and less high peak values in the model. Because the frequency distribution of the wind direction is similar between the observations and WRF-Chem, we expect no bias is introduced by the wind direction error. However, if we now co-sample WRF-Chem and the observations in time (i.e. we select observations that match our criteria and then take the same time from the WRF-Chem time series, which creates two data sets of equal size) we find a very small explained variance (R^2) for both species at both

sites based on hourly data. An inversion using these hourly data would thus be subject to a large model-data mismatch that increases the uncertainty in the optimized fluxes. Therefore, we next look more specifically at the data points responsible for the highest mismatch in observed and simulated ΔCO_2 .

We find that the largest differences between WRF-Chem and the observations at Zweth when co-sampling urban plumes results from errors in simulated wind direction, as well as from an inability of WRF-Chem to simulate the impact of point source emissions. This is illustrated in Fig. 5, where we binned the absolute errors in hourly ΔCO_2 into four magnitude classes of 10 ppm each and correlate them with the error in simulated wind direction (as binned into three classes of 20 degrees, scatter plots) and with the observed $\Delta\text{CO}:\Delta\text{CO}_2$ ratio (whisker plots). We find that the smallest ΔCO_2 model error class (0–10 ppm) is dominated by the smallest wind direction error (0–20 degrees, 68 %), while in the largest ΔCO_2 model error class (30–40 ppm) 70 % of the data points have a wind direction error of more than 20 degrees. With such large wind direction errors, the trajectory of urban plumes is misrepresented and the modelled mixing ratios are affected by the wrong source area, or plumes may even entirely miss the sites in the model. In addition, we find that in the largest ΔCO_2 model error class (30–40 ppm) the observed $\Delta\text{CO}:\Delta\text{CO}_2$ is lower (2.5 ppb ppm⁻¹) and less variable than in the other classes, suggesting a larger influence of industrial (stack) emissions. Although the number of data points in the largest ΔCO_2 model error class is small (N=14), these tendencies give a good indication of what might cause these errors. At Cabauw, the impact of stack emissions is not visible, because the point source emissions are already well-mixed when the air mass arrives at Cabauw. Hence, we will next examine the added value of the OPS plume model **only** at Zweth to better represent the dispersion of CO₂ emitted from stacks and the impact of wind direction in OPS.

3.3 WRF-Chem and OPS point source representation

When we focus exclusively on point source emissions, we find that all simulations that include the OPS plume model are in better agreement with the observations than the WRF-Chem simulation (based on the R^2 and regression slope). This is illustrated in Table 5, where we compare co-sampled simulated and observed events with a high point source contribution (see also Appendix A for more details). These events are selected based on a low observed $\Delta\text{CO}:\Delta\text{CO}_2$ ratio (the threshold is 1.5 ppb ppm⁻¹, events illustrated as grey bars in Fig 4). In the models, these events are highly correlated with a high point source contribution (of at least 90 %) in the simulated ΔCO_2 mixing ratio (r is -0.76 (WRF+OPS-point-obsmet) and -0.61 (WRF-Chem)). Including low wind speed data deteriorates most of the statistics for all simulations (not shown), meaning that the models have difficulties representing stagnant conditions.

For WRF-Chem the explained variance in the co-sampled observations is limited ($R^2=0.30$) and the regression slope of ΔCO_2 is significantly lower than one (i.e. the 1:1 line of modelled vs. observed ΔCO_2). Both the mean $\Delta\text{CO}:\Delta\text{CO}_2$ and the standard deviation are larger than the observed mean and standard deviation. This suggests that the lack of agreement is partly caused by an error in the WRF-Chem wind direction, causing the model to sample air from a wrong source area.

In contrast to WRF-Chem, WRF+OPS-point-obsmet shows a larger explained variance ($R^2=0.52$), a regression slope that is nearly one, and a $\Delta\text{CO}:\Delta\text{CO}_2$ ratio that agrees with observations both in mean and in standard deviation. Since only about 10 % of the Zweth-port observations are affected by stack emissions due to the small dimension of the plumes (N=42), a better representation of atmospheric conditions has a large impact. An

advantage of the OPS model is the ability to estimate the model uncertainty by providing a plume cross-section. Receptor points can be positioned anywhere and by adding several receptor points around the true measurement location we can account for transport errors (e.g. in the wind direction). If we allow for a maximum wind direction error of 5 degrees, this has no significant impact on the R^2 or slope (results not shown), suggesting that the results from the WRF+OPS-point-obsmet simulation are robust against small random errors in wind direction. However, systematic errors in the wind direction or the treatment of point source emissions such as present in WRF-Chem will have an impact on its performance, as we will explore next.

3.3.1 Dispersion

When comparing WRF-Chem and WRF+OPS-area we find that the OPS model reduces the dispersion of point source emissions, which causes emissions from high stacks to barely reach ground level. Vertical profiles of ΔCO_2 near an energy production stack for both model simulations are shown in Fig. 6. Energy production sources often have the highest stacks and the lowest $\Delta\text{CO}:\Delta\text{CO}_2$ ratios. Near an energy production stack the vertical dimension of the plume in WRF+OPS-area is smaller than in WRF-Chem. The plume remains more concentrated in WRF+OPS-area, leading on average to lower mixing ratios at ground level (left panel) and to higher maximum values at around 200 m (right panel). This effect is also clearly visible at Zweth (not shown) and results in a higher mean $\Delta\text{CO}:\Delta\text{CO}_2$ ratio in Table 5 for WRF+OPS-area (i.e. less influence of the low-ratio stack emissions) and a higher explained variance (37 %).

3.3.2 Point source representation

From a comparison of WRF-Chem, WRF+OPS-point and WRF+OPS-point-obsmet it follows that having a plume model with full point source characteristics can improve the agreement with the observed mixing ratios, even if the meteorological conditions are biased. Implementing detailed source characteristics (WRF+OPS-point) not only increases the explained variance to 42 %, it also increases the $\Delta\text{CO}:\Delta\text{CO}_2$ standard deviation. This is the result of larger spatial (both horizontal and vertical) variability in the emission landscape. These effects are also visible in Fig. 7, which shows a time series of six days of observations and model output. When differences between the simulations are small, this indicates the absence of point source signals. On October 23 (event A) an improvement is made by using observed meteorological conditions due to the large wind direction error, while the difference between WRF-Chem and WRF+OPS-point is small. However, on other occasions the use of the OPS model, irrespective of the meteorology used, already improves the simulated urban plume mixing ratio. For example, on October 24 (event B) both OPS runs reduce the urban plume mixing ratios and are in better agreement with the observations. On October 26 (event C) the opposite is happening. Whereas WRF-Chem is only above the background for four hours, the observations show a longer and more severe pollution event, despite a relatively small wind direction error. Although an additional improvement can be made using the observed wind fields, using WRF+OPS-point already improves the length and strength of the pollution event. Note that, although WRF-Chem sometimes performs better than the simulations including OPS, the overall statistics suggest that it is recommended to use WRF+OPS-point-obsmet.

4 Discussion

In this study we focused on two major questions in urban greenhouse gas modelling studies: what type of measurement locations can provide the best information on urban fluxes of CO₂ and CO, and what type of modelling framework can best represent urban plume mixing ratios at these measurement sites. In a previous study, Lauvaux et al. (2016) have used nine observation towers to estimate CO₂ fluxes from Indianapolis. They have argued that the optimum number of towers is dependent on the spatial heterogeneity of the emissions within the city. They also state that it is impossible to attribute changes in the total CO₂ concentration to specific source sectors when only CO₂ observations are available. Based on our current findings, we believe that with the use of other co-emitted species, like CO, information can be gained about source sector contributions, as was also shown by Turnbull et al. (2015). Additionally, Brioude et al. (2013) have shown that with only a few flights a reasonably robust flux estimate can be made for CO and NO_y. These studies thus show that with additional species and strategically placed measurements the need for a large observation network can be reduced. However, an important pre-condition is that atmospheric transport is correctly represented. Lauvaux et al. (2016) discussed that the atmospheric transport in high-resolution Eulerian models might suffer from errors due to assumptions about turbulence and other fine-scale processes, which causes urban plumes to violate the well-mixed assumptions of the model. This is especially relevant for emission sources with dimensions that are significantly smaller than the model resolution, i.e. point sources. Indeed, in this study we find that a plume model is a useful addition to the Eulerian model to correctly represent the transport of emissions from large point sources.

4.1 Comparison of observation sites

We first examined the use of the measurement sites to detect urban plumes, since the measurement sites in an inversion determine the demand put on the model performance. At the rural site (Lutjewad), the urban plume has become mixed with other signals and the urban plume is difficult to distinguish. This site (at ~200 km from the Rijnmond area) is therefore too far removed to specifically constrain the Rijnmond emissions, although it was shown to constrain emissions from the larger urban conglomerate of the Randstad quite well (Van der Laan et al., 2009b; Van der Laan et al., 2010). The semi-urban site (Cabauw) detects urban plumes from Rijnmond which have already become well-mixed during transport. Moreover, the mean concentration ratio matches well with the emission ratio for the Rijnmond area. We therefore argue that the Cabauw site could constrain the overall emissions of the Rijnmond area due to its integrating power without the need for a multi-model approach. In contrast, the urban location (Zweth) is highly exposed to the urban fluxes and is able to detect spatial variations in emissions inside the urban area. We find distinct concentration ratios for different source areas that can provide valuable information about dominant source types and areas. These findings are similar to a previous study concluding that a network of in-city sites provides good constraints due to their high exposure and ability to separate between different parts of the source area (Kort et al., 2013). However, the difference between the emission ratio and observed concentration ratio for the Zweth-port area indicates that stack emissions might frequently be missed at the Zweth measurement site due to the limited plume dimensions. Therefore, a correct representation of the transport becomes increasingly important. Thus, we conclude that the Cabauw and Zweth site have their own particular (dis)advantages and a combination of an urban and semi-urban site could be most beneficial to constrain urban fluxes in detail. Note that this conclusion is specifically valid for the Rijnmond area with the presence of major point sources and the requirements might be different for other urban topologies.

4.2 Model skill

Next, we evaluated the skill of the Eulerian WRF-Chem set-up. The ability of our WRF-Chem framework to represent daytime average mixing ratios is comparable with other model frameworks in the urban environment (Bozhinova et al., 2014; Bréon et al., 2015; Lac et al., 2013; Tolk et al., 2009). However, WRF-Chem has a large wind direction bias that makes it difficult to compare modelled and observed mole fractions. The monthly average WRF-Chem wind direction shows an absolute bias of 1 (October), 51 (November) and 10 (December) degrees compared to the observed wind direction at Rotterdam airport. The error in November is large compared to previous findings (Jiménez et al., 2016) and this results in a large model-observation mismatch in tracer mixing ratios (Fig. 3). Also at the Cabauw site, which is less influenced by build-up areas, the model-data agreement for the 10 m wind direction in November is limited. Previous research has also shown an uncertainty of 30–40 % in the tracer mixing ratio due to the uncertainty in meteorological conditions (Angevine et al., 2014; Srinivas et al., 2016). Additionally, Angevine et al. (2014) have shown that using an ensemble mean of model simulations with different meteorology does not necessarily lead to a better representation of plume transport and dispersion in a Lagrangian model for area sources. We therefore speculate that assimilating observed wind fields in WRF-Chem, as was done by Lauvaux et al. (2013), could be more beneficial to improve the modelled wind fields and as such improve the plume transport. Furthermore, the model performance under stratified and low wind speed conditions need to be addressed, since removing these data can lead to biased emission estimates.

Some studies argued that the main limitations of a Eulerian model are the enhanced dispersion due to instant mixing of species throughout the grid box and, related to that, the absence of a good point source representation (Karamchandani et al., 2011; Tolk et al., 2009). Our results show evidence for both limitations in the WRF-Chem set-up. First, WRF-Chem underestimates the median urban plume mixing ratios of both CO₂ and CO which should mainly be attributed to errors in transport and mixing. Whereas CO mixing ratios at the Zweth site are dominated by area sources, CO₂ mixing ratios are also highly affected by point source emissions. Therefore, their consistent underestimation cannot be caused solely by errors in point source emissions. Second, looking more specifically at the point source contribution, WRF-Chem can only explain 30 % of the variance and the spread in the $\Delta\text{CO}:\Delta\text{CO}_2$ ratio is too large compared to the observations. Thus the resolution appears to be too low to fully represent the transport of the urban plumes from point sources, similar to previous findings related to power plant plumes (Lindenmaier et al., 2014) and megacities (Boon et al., 2016).

In order to overcome the limitations of WRF-Chem related to point source representation and wind field errors, we evaluated the use of the OPS plume model with full point source characteristics and observed meteorological conditions. As discussed before, the OPS plume has limited impact on the CO mixing ratios as point sources only contribute a small fraction to the total CO emissions. Therefore, the focus in the remainder is on CO₂. The OPS plume model requires limited effort to be run in addition to WRF-Chem (it requires 2 input files and takes only a few seconds to run) and is therefore a relatively easy solution to improve the point source representation.

Several previous plume modelling studies with different species showed improvements compared to the gridded approach (Briant and Seigneur, 2013; Ganshin et al., 2012; Karamchandani et al., 2006; Karamchandani et al., 2012; Korsakissok and Mallet, 2010a; Rissman et al., 2013). In this study we find a significant improvement with WRF+OPS-point-obsmet at Zweth, both in the explained variance and the $\Delta\text{CO}:\Delta\text{CO}_2$ ratio. Also the observed-vs-simulated regression slope of the point source ΔCO_2 mixing ratio becomes nearly one. In this analysis the number of selected data points is relatively small, because stack emissions can easily be missed

by an observation site due to the small plume dimensions. Therefore, only a few events can be used to constrain point source emissions and a good representation of the plume transport is essential. Although there are only ~100 individual point sources in the Rijnmond area, they make up about 75 % of the total CO₂ emissions. Thus we argue that in an urban-industrial area with a significant point source contribution the use of a plume model is critical to get a reliable emission estimate. If detailed point source characteristics are unknown, these would have to be estimated and this adds an uncertainty to the modelled mixing ratios. Nevertheless, we have shown that even with the WRF-Chem point source representation (i.e. 1x1km² in size and fixed vertical distribution) the plume model can already improve the agreement with the observations. Further improvements can possibly be made by representing traffic emissions as line source emissions in a plume model (Briant and Seigneur, 2013) rather than considering them as gridded area sources in the Eulerian model.

Although part of the OPS-driven improvement can be attributed to the use of observed meteorological conditions, we have shown with the WRF+OPS-point simulation that there is also an improvement in point source representation. We found that a higher spatial variability in the emissions causes more variability in the concentration ratios. Representing point sources as area sources, as is done in WRF-Chem, results in lower correlations and less variability in concentration ratios, which is consistent with previous studies that demonstrated the importance of a good source representation (Kim et al., 2014; Korsakissok and Mallet, 2010b; Touma et al., 2006). Besides the ability to include detailed source characteristics and to use observed meteorology, the OPS model has some additional advantages. We have shown that looking at individual stacks can provide valuable information about the underlying transport and dispersion processes and how they are affected by source characteristics. Additionally, receptor sites can be positioned anywhere, which allows us to study the spatial variations at much higher resolution than currently possible with WRF-Chem.

At Cabauw, the difference between WRF-Chem and the WRF+OPS-point simulation is small, although the model-data mismatch at Cabauw is further reduced when observed meteorology is used. This leads to the question for which spatial extent a plume model is beneficial. In previous plume-in-grid models at high resolution (<25 km) plumes or puffs are often injected in the Eulerian parent model when the width of the plume is similar to the grid size (Karamchandani et al., 2006; Kim et al., 2014; Korsakissok and Mallet, 2010b). According to the definition of the lateral dispersion factor in OPS this would mean that a plume will have reached a horizontal width of 4 km (the resolution of the domain in which Cabauw is located) after about 8 km travel distance under well-mixed conditions. To test this, we compared a monthly average WRF-Chem CO₂ mixing ratio field in and around Rijnmond with a monthly averaged gridded OPS mixing ratio field. The OPS model was only applied for emissions within the Rijnmond area and therefore the distance outside the WRF-Chem domain at which the mixing ratio fields become similar gives an indication of the spatial extent for which the OPS model is still beneficial. We find that the difference between the mixing ratio fields disappears quickly outside the Rijnmond area and WRF-Chem and OPS become similar at about 10–14 km outside the boundary of domain 4.

5 Conclusions

Our ultimate ambition is to quantify the total urban CO₂ budget using multiple observation sites and an inverse modelling system. Such information could be used to monitor the impact of implemented policies and progress towards objectives. Based on the work reported here, we state that the modelling framework should ideally

consist of a Eulerian model in combination with a plume model for point source emissions within the city, preferably driven by locally observed meteorology. The use of a plume model **is of great added value to** correctly represent the transport of point source emissions in a diameter closer than ~10 km to the site. Although the additional computational demand with the OPS plume model is limited, detailed model input is required given that the results are very sensitive to source characteristics and wind fields. Given the importance of observed local meteorology for the model performance, we strongly recommend inclusion of a (simple) meteorological station in any similar monitoring set-up. Also, Lagrangian particle dispersion models driven by WRF meteorological fields have proven useful in describing the transport of point source emissions and in inverse modelling (Brioude et al., 2013; Pan et al., 2014; Srinivas et al., 2016), but such set-up would suffer from wind field errors. The optimal set-up for an urban monitoring network requires a semi-urban measurement site (here ~30 km from the urban area with no other urban areas in between) and at least one additional urban measurement site (here at the edge of the urban area, at ~7 km from the city centre). The semi-urban site provides a robust and integral constraint on the urban fluxes and can be used in combination with a high-resolution Eulerian model framework. The urban measurement site can provide useful information about local differences, such as the dominance of road traffic in a certain source area or local changes due to implemented measures. Observing additional species besides CO, like $^{14}\text{CO}_2$, $^{13}\text{CO}_2$, O_2/N_2 , NO_2 , SO_2 or black carbon, could be a useful extension of our framework for identifying source sector contributions. Such a set-up is a promising step towards independent verification of urban CO_2 budgets.

Data availability

Observations from Zweth and Westmaas and the TNO-MACC III emission inventory are available via TNO (hugo.deniervandergon@tno.nl). Lutjewad and Cabauw observations can be downloaded from the GLOBALVIEWplus product (Cooperative Global Atmospheric Data Integration Project, 2015). The Dutch Emission Registration emission inventory can be accessed online (<http://www.emissieregistratie.nl/>).

Acknowledgements

This research was partly funded by EIT Climate-KIC project Carbocount-CITY (APIN0029_2015-3.1-029_P040-04) and the EIT Climate KIC Fellows programme (ARED0004_2013-1.1-008_P017-0x). We sincerely thank the RIVM LML (Westmaas) and Hoogheemraadschap Delfland (De Zweth) for allowing us access to and the use of facilities on their sites. We thank Ferd Sauter (RIVM) for helping us with setting up the OPS model for this study and for correcting the manuscript. Finally, we acknowledge Huilin Chen for giving us access to the Lutjewad observations, and the Dutch Emission Registration for providing the point source characteristics needed for OPS.

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Table 1: Overview of SNAP categories and the vertical distribution of point source emissions in WRF-Chem.						
SNAP	Description	% of point source emissions per model layer [m above surface]				
		0–55 m	55–130 m	130–235 m	235–360 m	>360 m
1	Combustion in energy and transformation industries			18.5 %	42 %	39.5 %
2	Non-industrial combustion plants					
3	Combustion in manufacturing industry	12.2 %	37.3 %	46.2 %	4.3 %	
4	Production processes	12.2 %	37.3 %	46.2 %	4.3 %	
5	Extraction and distribution of fossil fuels					
6	Solvents and other product use					
7	Road transport					
8	Other mobile sources and machinery	100 %				
9	Waste treatment and disposal		16.5 %	44.5 %	39 %	
10	Agriculture					

Table 2: Overview of the simulations, which model is used to calculate the urban plume mixing ratio from point sources in the Rijnmond area, how point sources are represented and the source of meteorological conditions.

Simulation name	Point source contribution	Point source representation	Meteorological input
WRF-Chem	WRF-Chem	area	WRF-Chem
WRF+OPS-area	OPS	area	WRF-Chem
WRF+OPS-point	OPS	point	WRF-Chem
WRF+OPS-point-obsmet	OPS	point	observations

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Table 3: Statistics for WRF-Chem daytime (8:00–17:00 LT) average meteorological variables and total CO₂ and CO mixing ratios as compared to observed daytime averages (full simulation period). $\overline{X_{obs}}$ is the average observed mixing ratio and N gives the number of days included. This table shows that WRF-Chem is able to represent day-to-day variations in meteorological conditions and mixing ratios, except for the wind direction.

Variable	Site	R ²	RMSE	bias	$\overline{X_{obs}}$	N
Temperature	Rotterdam airport	0.77	2.5 °C	+ 0.9 °C		90
Specific humidity	Rotterdam airport	0.81	1.0 g kg ⁻¹	+ 0.5 g kg ⁻¹		90
Wind speed	Rotterdam airport	0.72	1.2 m s ⁻¹	<0.1 m s ⁻¹		90
Wind direction	Rotterdam airport	0.20	53 degrees	- 13 degrees		90
CO ₂ mixing ratio	Westmaas	0.65	8.8 ppm	+ 1.1 ppm	418 ppm	83
	Zweth	0.45	13.0 ppm	+ 2.5 ppm	423 ppm	85
	Cabauw (60 m)	0.48	10.6 ppm	+ 3.6 ppm	417 ppm	86
CO mixing ratio	Westmaas	0.53	55 ppb	- 23 ppb	187 ppb	83
	Zweth	0.41	69 ppb	- 1 ppb	198 ppb	85
	Cabauw (60 m)	0.35	53 ppb	+ 18 ppb	156 ppb	89

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Table 4: Statistics for the distribution of the observed and modelled (WRF-Chem) urban plume mixing ratios (ΔCO_2 and ΔCO) at the Zweth and Cabauw site. N is number of hours included for either the observed or simulated time series. The R^2 in the final column is based on co-sampling of WRF-Chem with the observations. The agreement between WRF-Chem and the observations is satisfactory when considering the distribution of the plume mixing ratios, but the low explained variance when co-sampling suggests a large impact of transport errors on individual plumes.

Species	Site	Obs/model	Median	80 th percentile	N	R^2
CO₂	Zweth	Observed	9.7 ppm	17.3 ppm	284	0.05
		WRF-Chem	8.8 ppm	16.9 ppm	249	
	Cabauw (60 m)	Observed	6.0 ppm	9.1 ppm	32	<0.01
		WRF-Chem	5.6 ppm	6.4 ppm	37	
CO	Zweth	Observed	29 ppb	57 ppb	274	0.01
		WRF-Chem	33 ppb	50 ppb	207	
	Cabauw (60 m)	Observed	13 ppb	28 ppb	58	<0.01
		WRF-Chem	18 ppb	31 ppb	51	

Table 5: Statistics for CO₂ point source peaks at Zweth in four different model simulations as compared to observations. N is number of hours included and the slope is based on a linear regression. $\Delta\text{CO}:\Delta\text{CO}_2$ denotes the mean ($\pm 1\sigma$ standard deviation) of the urban plume concentration ratio in ppb ppm⁻¹.

Model run	R^2	$\Delta\text{CO}:\Delta\text{CO}_2$	ΔCO_2 slope	N
WRF-Chem	0.30	0.9 (± 1.5)	0.82	42
WRF+OPS-area	0.37	1.2 (± 1.1)	0.87	42
WRF+OPS-point	0.42	1.2 (± 1.6)	0.86	42
WRF+OPS-point-obsmet	0.52	0.7 (± 0.6)	0.99	40
<i>Observed</i>		0.7 (± 0.4)		

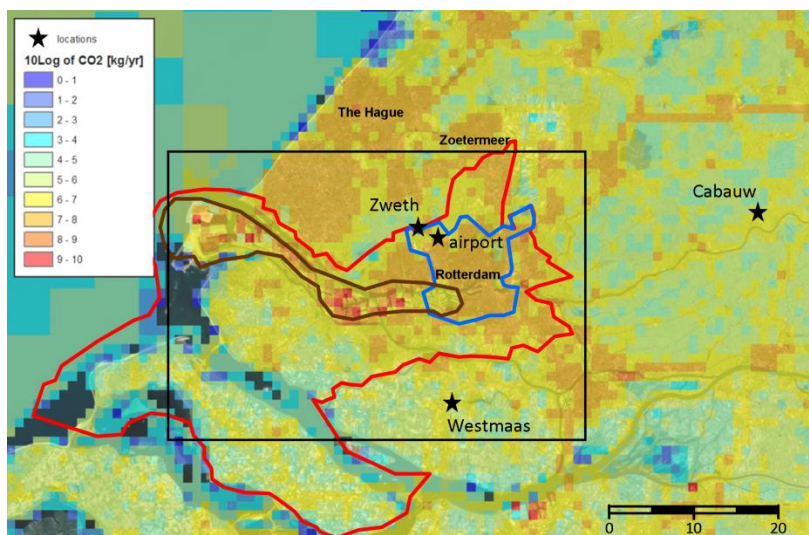


Figure 1: CO₂ emission map of the Rijnmond area (red outline), including the city of Rotterdam (blue outline) and the port area (brown outline); the observation sites are indicated with black stars (Lutjewad is shown in Fig. 2). The boundaries of domain 4 in WRF-Chem are indicated by the black square. Source: Netherlands PRTR (2014).

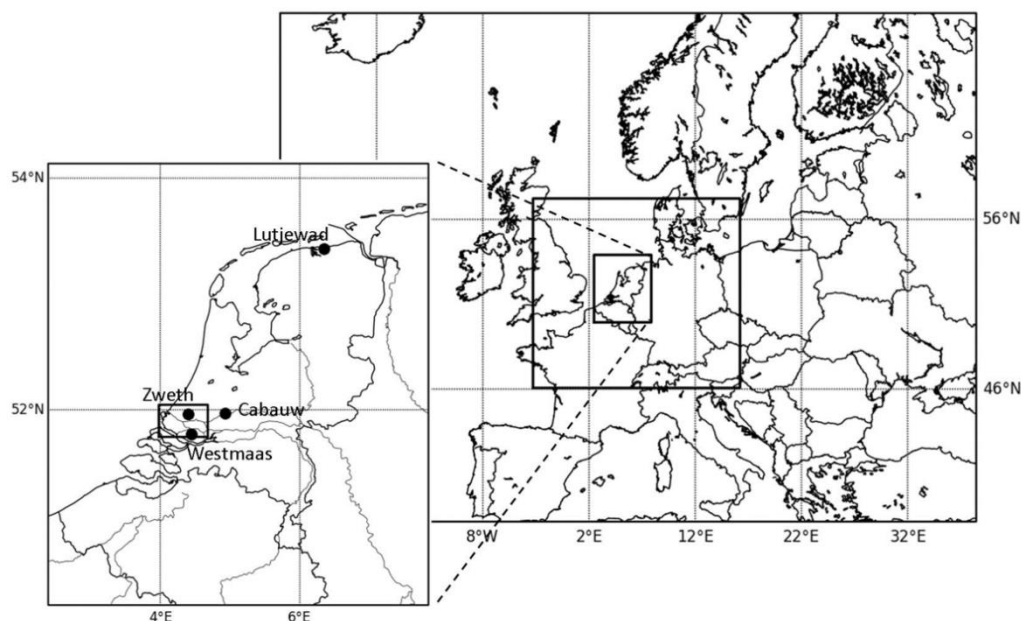


Figure 2: Location of the domains is indicated with squares. The horizontal resolutions of the domains are (from outer to inner domain): 48x48 km, 12x12 km, 4x4 km and 1x1 km. Black circles represent the observation sites.

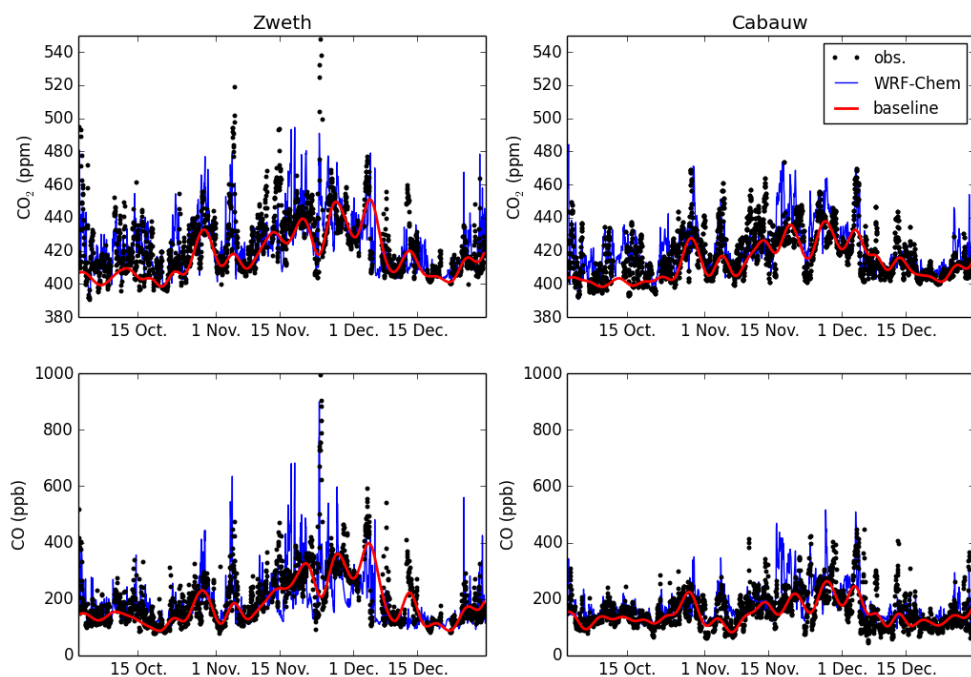


Figure 3: Time series of modelled (WRF-Chem) and observed CO₂ and CO mixing ratios at Zweth (left) and Cabauw (right). The observation-based baseline used in this study is also shown.

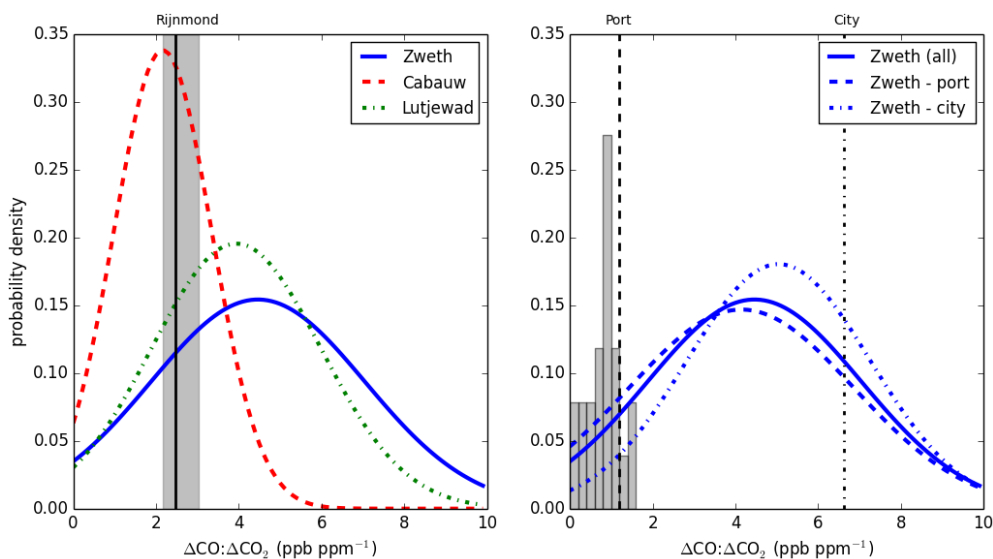


Figure 4: Left: Smooth Gaussian fit of probability density functions of observed $\Delta\text{CO}:\Delta\text{CO}_2$ at the Zweth, Cabauw and Lutfjewad measurement sites. The solid vertical line (shaded area) shows the mean emission ratio (Q1–Q3 range) for all emissions integrated over the Rijnsmond area (see Fig. 1). Right: The Zweth observations separated into two distinct source areas based on the observed wind direction. The dash-dotted and dashed vertical lines represent the mean emission ratios from the residential area and the port, respectively. Generally, there is a reasonable match between the bottom-up emission ratio and the concentration-derived ratio, but observed ratios from the Zweth-port wind sector are much higher than expected because of the intermittency of plume transport from the many stacks in this area. The grey bars in the right panel show the point source events selected in Sect. 3.3.

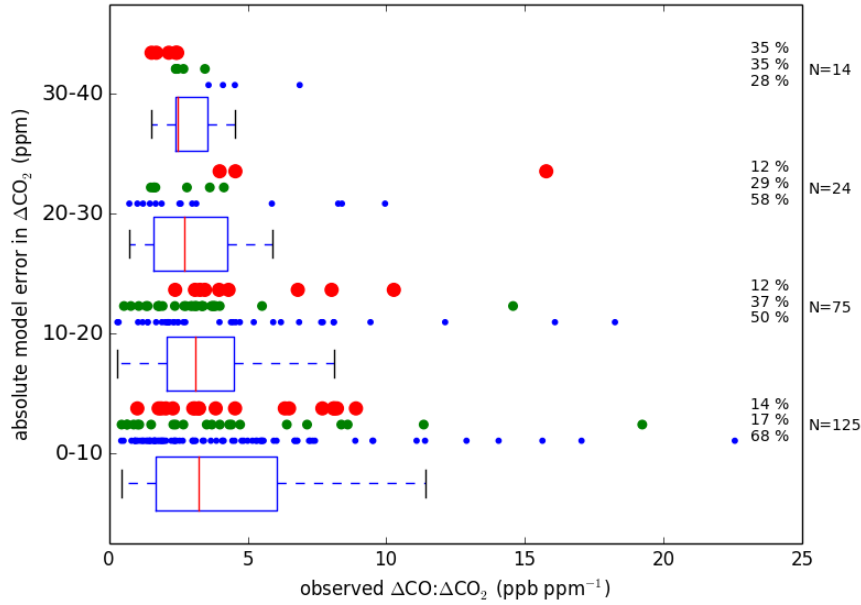


Figure 5: This figure shows four classes of the absolute model error in ΔCO_2 compared with the Zweth measurement site. For each class two quantities are displayed. 1) A whisker plot of observed $\Delta\text{CO}:\Delta\text{CO}_2$, which shows that the largest absolute ΔCO_2 model error (y-axis) is related to small observed concentration ratios (x-axis). This indicates an important role for low-ratio stack emissions (industrial and power plant sources) in the large model error class. 2) A coloured scatter plot for which data points are divided into three classes based on the absolute error in simulated wind direction (<20 degrees in small blue dots on bottom row, 20–40 degrees in larger green dots on middle row, and >40 degrees in large red dots on top row). Each dot represents one hour. The percentage contribution of each wind direction error class to the total number of data points (N) is shown on the right. These numbers show that the model error in wind direction also plays an important role in the ΔCO_2 model error.

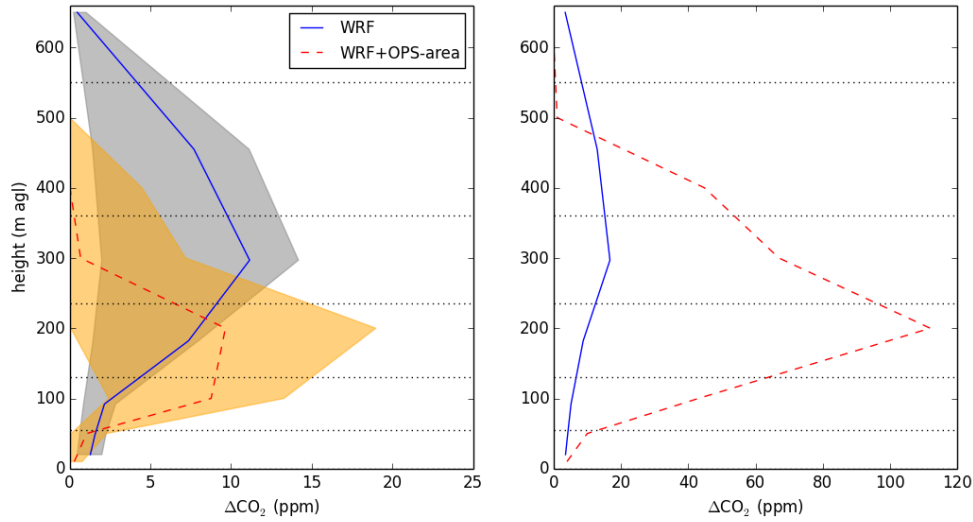


Figure 6: Vertical profiles of the median (Q1–Q3) (left panel) and maximum (right panel) ΔCO_2 mixing ratio at 14 h UTC at about 500 m from an energy production point source in WRF-Chem and WRF+OPS-area. The horizontal lines represent the boundaries of the vertical levels in WRF-Chem. Emissions are taking place in levels 3, 4 and 5 in WRF-Chem or at 130, 235 and 360 m in WRF+OPS-area. The figure shows on average lower mixing ratios at ground level in WRF+OPS-area than in WRF-Chem, despite an identical treatment of the vertical emission structure. WRF+OPS-area also shows higher maximum values, reflecting a reduction in vertical dispersion compared to the Eulerian box representation in WRF-Chem.

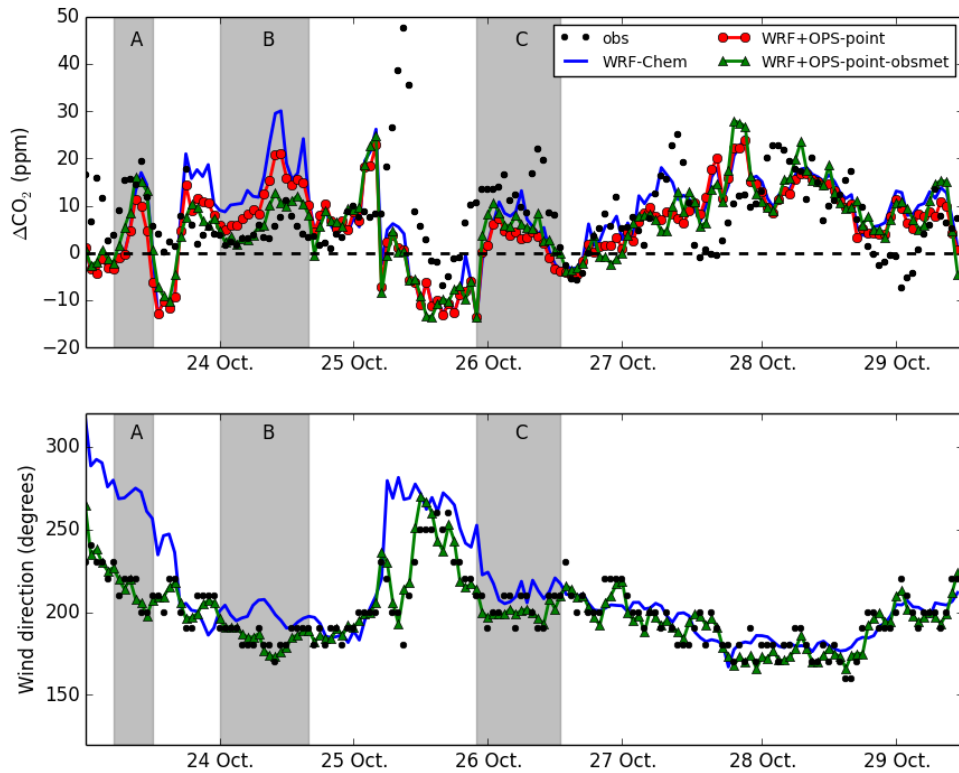


Figure 7: Time series of ΔCO_2 at Zweth from observations and three model simulations (top panel) and of the wind direction at Rotterdam airport from WRF-Chem, WRF+OPS-point-obsmet, and observations (bottom panel). Shaded areas indicate specific events discussed in more detail in the text.

Appendix A

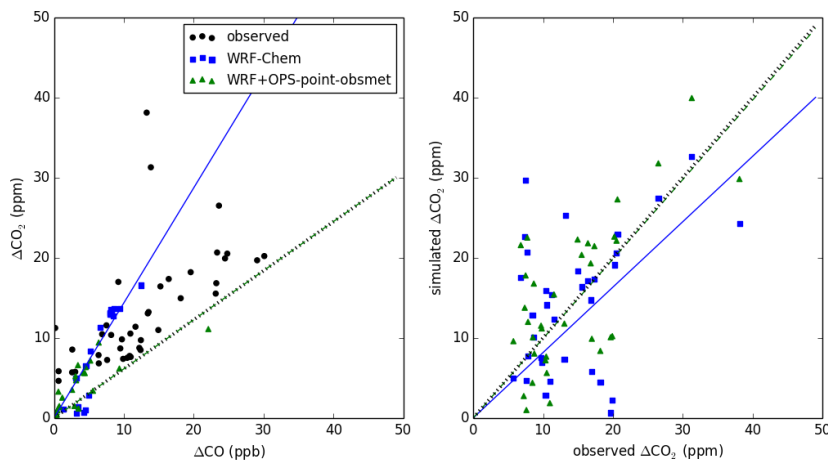


Figure A1: Left: A scatter plot of ΔCO and ΔCO_2 , where the slopes (represented by lines) represent the $\Delta\text{CO}:\Delta\text{CO}_2$ ratio for the observed and modelled values. The slope of WRF+OPS-point-obsmet coincides with the slope of the observations, suggesting a good agreement. Right: A scatter plot of simulated ΔCO_2 to observed ΔCO_2 . The slope of WRF+OPS-point-obsmet coincides with the 1:1 line (dotted line), suggesting a good agreement with the observations.