Estimation of OH in urban plumes using TROPOMI inferred NO$_2$/CO

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Abstract.

A new method is presented for estimating urban hydroxyl radical (OH) concentrations using the downwind decay of the ratio of nitrogen dioxide over carbon monoxide column mixing ratios (XNO$_2$/XCO) retrieved from the Tropospheric Monitoring Instrument (TROPOMI). The method makes use of plumes simulated by the Weather Research and Forecast model (WRF-CHEM) using passive tracer transport, instead of the encoded chemistry, in combination with auxiliary input variables such as Copernicus Atmospheric Monitoring Service (CAMS) OH, Emission Database for Global Atmospheric Research v4.3.2 (EDGAR) NOx and CO emissions, and National Center for Environmental Protection (NCEP) based meteorological data. NO$_2$ and CO mixing ratios from the CAMS reanalysis are used as initial and lateral boundary conditions. WRF overestimates NO$_2$ plumes close to the center of the city by 15% to 30% in summer and 40% to 50% in winter compared to TROPOMI observations over Riyadh. WRF simulated CO plumes differ by 10% with TROPOMI in both seasons. The differences between WRF and TROPOMI are used to optimize the OH concentration, NOx, CO emissions and their backgrounds using an iterative least square method. To estimate OH, WRF is optimized using a) TROPOMI XNO$_2$/XCO, b) TROPOMI derived XNO$_2$ only.

For summer, both the NO$_2$/CO ratio optimization and the XNO$_2$ optimization increase the OH prior from CAMS by 32 ± 5.3% and 28.3 ± 3.9%, respectively. EDGAR NOx and CO emissions over Riyadh are increased by 42.1 ± 8.4% and 101 ± 21%, respectively, in summer. In winter, the optimization method doubles the CO emissions, while increasing OH by ~52 ± 14% and reducing NOx emissions by 15.5 ± 4.1%. TROPOMI derived OH concentrations and pre-existing Exponentially
Modified Gaussian function fit (EMG) method differ by 10 % in summer and winter, confirming that urban OH concentrations can be reliably estimated using the TROPOMI-observed NO2/CO ratio. Additionally, our method can be applied to single TROPOMI overpass, allowing to analyze day to day variability in OH, NOx and CO emission.

1. Introduction

The rapidly growing urbanization has led to an increase in the number of big cities globally. More than 55 % of the global population resides in cities and this fraction is projected to increase to 68 % in 2050 (United Nations, 2018). The associated rise in consumption of energy and materials leads to severe air pollution that is estimated to have caused premature death of 4 to 9 million people globally in 2015 (Sicard et al., 2021; Pascal et al., 2013; Burnett et al., 2018). Air pollution control measures and the application of cleaner technology have reduced the NO2 concentrations in developed cities such as Los Angeles and Paris by 1.5 % to 3.0 % yr\(^{-1}\) between 1996 to 2017 (Georgoulias et al., 2019). The CO emission is reduced by 28.8 % to 60.7 % in these cities in the period 2000 to 2008 (Dekker et al., 2017). In developing cities such as Tehran and Baghdad, however, NO2 concentrations have increased by 8.6 % yr\(^{-1}\) and 16.9 % yr\(^{-1}\) between 1996 to 2017 (Georgoulias et al., 2019). The CO emission increased by 15 % in New Delhi in the period 2000 to 2008 (Dekker et al., 2017). As a consequence, air pollution monitoring and mitigation in developing cities is becoming an increasingly important priority.

Nowadays, urban air pollution can be studied using a combination of ground-based measurement networks and satellite observations (Sannigrahi et al., 2021; Ialongo et al., 2020). Satellite observations have helped to investigate urban air pollution, particularly in cities without a ground-based monitoring network (Beirle et al., 2019; Borsdorff et al., 2019). In past decades, improvements in the quality and spatial resolution of satellite measurements have allowed the detection of trends in air pollutants and the quantification of urban emissions (Lorente et al., 2019; Verstraeten et al., 2018; Wennberg et al., 2018). Several studies have focused on NOx, using NO2 observations from the SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY (SCIAMACHY), the Ozone Monitoring Instrument (OMI) and TROPOMI (Ding et al., 2017; Lorente et al., 2019). At the resolution and sensitivity of TROPOMI, urban NO2 enhancements can be detected readily, even in single satellite overpass. OMI derived NO2 data have been used to quantify NOx emissions, as well as the urban lifetime of NO2, as demonstrated by Beirle et al. (2011) using the Exponentially Modified Gaussian function fit (EMG) method.

In the EMG method, the satellite observed exponential decay of NO2 downwind of the city centre is used to quantify the first order loss of NO2, which is used to quantify the hydroxyl radical (OH) neglecting other NOx removal pathways. Liu et al. (2016) modified the EMG method for application to complex emission patterns. The quantification of CO emissions from cities is more complicated compared with NO2 because of its longer lifetime, and the related importance of CO sources from the surroundings of cities. Nevertheless, a few studies have demonstrated the feasibility of quantifying relative changes in urban CO emission, using Measurement of Pollution in the Troposphere (MOPITT), Infrared Atmospheric Sounding Interferometer (IASI), Atmospheric Infrared Sounder (AIRS), and TROPOMI observations (Borsdorff et al., 2019; Dekker et al., 2017; Pommier et al., 2013).
In recent years, methods have been developed that combine satellite measurements of different trace gases, for example the combined use of \( \text{NO}_2 \) and CO, to obtain specific information about pollutant sources (Lama et al., 2020; Hakkarainen et al., 2015; Miyazaki et al., 2017; Reuter et al., 2019; S. Silva & Arellano, 2017). The emission factors of CO and NO\(_x\) from fuel combustion are uncertain and vary strongly with the combustion efficiency (Flagan and Seinfeld, 1988). The satellite observed \( \Delta \text{NO}_2/\Delta \text{CO} \) ratio is particularly sensitive to this fuel burning efficiency, as demonstrated by Lama et al., (2020) and can be used to evaluate emission inventories. However, another important uncertainty arises from the removal of NO\(_2\) by OH. OH is an important oxidant in the atmosphere, which determines the lifetime of trace gases such as CO, NO\(_x\), sulphur dioxide (SO\(_2\)) and volatile organic compound (VOCs) (Monks et al., 2009). OH plays the important role in atmospheric chemistry on scales ranging from urban air pollution to the global residence times of greenhouse gases. The direct measurement of OH is possible using spectroscopic methods, but the spatial representativeness of the data is limited due to its short lifetime (de Gouw et al., 2019). OH estimates from global Chemical Transport Models (CTM’s) has an uncertainty of > 50% (Huijnen et al., 2019). Urban measurement campaigns point to large discrepancies between modelled and observed OH abundances, for example in Lu et al., (Lu et al., 2013) who found a factor 2.6 difference in a campaign in the suburbs of Beijing.

The aim of this study is therefore to estimate the average OH concentration in the urban plume of large cities (hereafter referred to as urban OH) from the downwind decay of the TROPOMI observed NO\(_2/\text{CO}\) ratio. The proposed method makes use of the WRF model (Grell et al., 2005) to simulate the meteorological fields and atmospheric transport. The TROPOMI instrument (Veefkind et al., 2012), launched on 13 October 2017 on board the Sentinel-5 Precursor satellite, is particularly well suited for this task, as it measures both compounds with high sensitivity and spatial resolution. Our method uses CO, because it has a longer lifetime than NO\(_2\) (weeks-months compared to a few hours). Therefore, CO can be considered as an inert tracer at the time-scale of urban plumes. The difference in the rate of decay between NO\(_2\) and CO provides therefore information about the photochemical oxidation of NO\(_2\), because atmospheric dispersion is expected to have a very similar impact on both tracers and therefore cancels out in their ratio. The use of the NO\(_2/\text{CO}\) ratio for estimating urban scale OH is further compared to the Exponentially Modified Gaussian function fit (EMG) method, using only satellite retrieved NO\(_2\) (Beirle et al., 2011).

The city of Riyadh (24.63° N, 46.71° E) is chosen as a test case. Riyadh is an isolated city and a strong source of CO and NO\(_2\) pollution (Beirle et al., 2019; Lama et al., 2020). The frequent clear sky conditions over Riyadh yield a large number of valid TROPOMI CO and NO\(_2\) data. The signal to noise in TROPOMI is high enough to detect the enhancement of CO and NO\(_2\) over Riyadh in a single overpass (Lama et al., 2020). Model results from the Copernicus Atmospheric Monitoring Service (CAMS) for Riyadh show a distinct seasonality in OH (see Fig S1), which we attempt to evaluate using TROPOMI data for summer and winter.

This paper is organized as follows: Section 2 describes the TROPOMI NO\(_2\) and CO data, the WRF model setup that was used, and the optimization method that is used for estimating OH. Optimization results and comparisons between TROPOMI and WRF are presented in section 3, followed by a summary and conclusion of the main finding in section 4. Additional figures and information about the optimization method are provided in the Supplement.
2. Data and Method

2.1 TROPOMI NO2 tropospheric column

We used the offline TROPOMI level 2 tropospheric column NO2 [mole m\(^{-2}\)] data from retrieval versions 1.2.x for 2018 and 1.3.x for 2019 available at https://s5phub.copernicus.eu; http://www.tropomi.eu (last access: 21 September, 2020). NO2 data of versions 1.2.x and 1.3.x have minor processing differences such as removal of negative cloud fraction, better flagging and uncertainty estimation. However, they use the same retrieval algorithm applied to level-1b version 1.0.0 spectra (Babic et al., 2019) recorded by the TROPOMI UV-Vis module in the 405-465nm spectral range. The TROPOMI NO2 DOAS software, developed at KNMI, is used for the processing of NO2 slant column densities (van Geffen et al., 2019). The improved NO2 DOMINO algorithm of Boersma et al. (2018) has been used to translate slant columns into tropospheric column densities. In this algorithm, stratospheric contributions are subtracted from the slant column densities and the residual tropospheric slant column density is converted to tropospheric vertical column density using the air mass factor (AMF). The AMF depends on the surface albedo, terrain height, cloud height, cloud fraction and a priori NO2 profiles from TM5-MP at 1° × 1° (Eskes et al., 2018; Lorente et al., 2017). The comparison of MAX-DOAS ground based measurements in European cities shows that TROPOMI underestimates of NO2 columns by 7% to 29.7% (Lambert et al., 2019). To reduce the differences between satellite and model, we re-calculated the AMF by replacing the tropospheric AMF based on TM5 simulated vertical NO2 columns, with the WRF-chem equivalent (Lamsal et al., 2010; Boersma et al., 2016; Visser et al., 2019; Huijnen et al., 2010), using the equation provided in the Appendix A. After the AMF recalculation, the NO2 vertical profiles are consistent between satellite and model. Furthermore, the use of WRF-Chem has the advantage that it resolves NO2 gradients between urban and downwind regions better than the coarser resolution TM5-MP model (Russell et al., 2011; McLinden et al., 2014; Kuhlmann et al., 2015). During summer, the AMF recalculation increases TROPOMI NO2 by 5% to 10% and in winter by 25% to 30% in the urban plume over Riyadh, whereas background areas are less affected (see Fig S2). The S5P-PAL reprocessed NO2 data available at https://data-portal.s5p-pal.com/products/no2.html differs by 7.5% to 10% in summer (June to October, 2018) and 13.5% to 16% in winter (November, 2018 to March, 2019) compared to the AMF recalculated TROPOMI NO2 data used in this study. These differences have been used to quantify the systematic uncertainty of the NO2 data and its contribution to the uncertainty in the NOx emission and lifetime derived using our method (see Table S1, S2 and S3).

2.2 TROPOMI CO

For CO, the offline level 2 CO data product version 1.2.2 has been used, available at https://s5phub.copernicus.eu (last access: 20 September, 2020). The SICOR algorithm is applied to TROPOMI 2.3 μm spectra to retrieve CO total column density [molec cm\(^{-2}\)] (Landgraf et al., 2016). The retrieval method is based on a profile scaling approach, in which TROPOMI-observed spectra are fitted by scaling a reference vertical profile of CO using the Tikhonov regularization technique (Borsdorff et al., 2014). The reference CO profile is obtained from the TM5 transport model (Krol et al., 2005). The averaging kernel (A)
quantifies the sensitivity of the retrieved total CO column to variations in the true vertical profile ($\rho_{\text{true}}$), as follows (Borsdorff et al., 2018a):

$$C_{\text{retrieval}} = A \cdot \rho_{\text{true}} + \varepsilon_{\text{CO}}$$  \hspace{1cm} (1)

where, $C_{\text{retrieval}}$ is the retrieved column average CO mixing ratio, $\varepsilon_{\text{CO}}$ is the retrieval error, statistically represented by the retrieval uncertainty that is provided for each CO retrieval.

The comparison of TROPOMI derived XCO to the 28 different TCCON ground based station suggest that difference between TCCON and TROPOMI is in the range of $9.1 \pm 3.3\%$ (Shah et al., 2020). Such difference is used to estimate the uncertainty in the emission and life time (see Table S1, S2, S3 and Text S6).

2.3 Satellite Data Selection and Filtering Criteria

As NO$_2$ and CO are retrieved from different channels of TROPOMI using different retrieval algorithms, the filtering criteria and spatial resolutions of CO and NO$_2$ are different. The data filtering makes use of the quality assurance value (qa) and is provided with the CO and NO$_2$ retrievals, ranging from 0 (no data) to 1 (high quality data). We selected NO$_2$ retrievals with qa $\geq 0.75$ (clear sky condition) and CO retrievals with qa $\geq 0.7$ (clear sky or low level cloud) as in Lama et al., (2020). The SICOR algorithm was originally developed for SCIAMACHY to account for the presence of low elevation clouds, increasing the number of valid measurements (Borsdorff et al., 2018a). In addition, the CO stripe filtering technique is applied as described by Borsdorff et al. (2018). Using dry air column density derived from the surface pressure data in CO and NO$_2$ TROPOMI files, the total CO column and tropospheric NO$_2$ column densities are converted to dry column mixing ratios XCO (ppb) and XNO$_2$ (ppb). The spatial resolution of the NO$_2$ data is finer compared to the CO data (3.5x7 km$^2$ versus 5.5x7 km$^2$). After the CO and NO$_2$ retrievals pass the filtering criteria, their co-location is approximated by assigning the centre coordinates of an NO$_2$ retrieval to the CO footprint in which it is located (Lama et al., 2020).

2.4 Weather Research Forecast model (WRF)

We have used WRF- chemistry model (http://www.wrf-model.org/), version 3.9.1.1 to simulate NO$_2$ and CO mixing ratios over Riyadh. WRF is a non-hydrostatic model designed by the National Center for Environmental Protection (NCEP) for both atmospheric research and operational forecasting applications. For this study, we have setup three nested domains in the model at resolutions of 27 km, 9 km and 3 km, centred at 24.63°N, 46.71°E. The first and second domain cover Saudi Arabia and provide the boundary conditions for the nested third domain (see Fig. S3). The analysis in this paper uses the 500 x 500 km$^2$ sub region around Riyadh in the third domain, containing 161 by 161 grid cells. All domains are extended vertically from the Earth’s surface to 50 hPa, using 31 vertical layers, with 17 layers in the lowermost 1500 m. WRF simulations are performed using a time step of 90 seconds for the period June 2018 to March 2019, using a spin-up time of 10 days.

We have used the Unified Noah land surface model for surface physics (Ek et al., 2003; Tewari et al., 2004), an updated version of the Yonsei University (YSU) boundary layer scheme (Hu et al., 2013) for the boundary layer processes, and the
Rapid Radiative Transfer Method (RRTM) for short-wave and long-wave radiation (Mlawer et al., 1997). Cloud physics is solved with the new Tiedtke cumulus parameterization scheme (Zhang and Wang, 2017). The WRF Single Moment 6-class scheme is used for microphysics (Hong and Lim, 2006). The WRF coupling with chemistry (WRF-chem) allows the simulation of tracer transport and the chemical transformation of trace gases and aerosols. Here, we used the passive tracer transport function instead of the encoded chemistry in WRF to speed up the model simulation and reduce the computational cost. In addition, the passive tracer option helps in separating the influences of wind, OH and the rate constant of the NO$_2$+OH reaction ($K_{\text{NO}_2\cdot\text{OH}}$) on the NO$_2$/CO ratio in the downwind city plume. Compared to previously used methods (Beirle et al., 2011b; Valin et al., 2013) which did not use a transport model at all, we consider this an important improvement. The function of different tracers, their acronym and explanation of different WRF simulations is provided in Table 1.

The meteorological initial and boundary conditions are based on NCEP data at 1°x1° spatial and 6-hr temporal resolution available at [https://rda.ucar.edu/datasets/ds083.2/](https://rda.ucar.edu/datasets/ds083.2/). Nitrogen Oxides (NOx = NO$_2$ + NO) and CO anthropogenic emissions have been taken from the Emission Database for Global Atmospheric Research v4.3.2 (EDGAR) 2012 at 0.1°x0.1° spatial resolution (Crippa et al., 2016). The EDGAR 2012 data have been re-gridded to the resolution of the WRF domains and hourly, weekly and monthly emission variations are taken into account using the temporal emission factors provided by van der Gon et al. (2011). The chemical boundary conditions for CO and NOx are based on the CAMS chemical reanalysis product at 0.75°x0.75° spatial, and 3-hourly temporal resolution (Inness et al., 2019), retrieved from [https://ads.atmosphere.copernicus.eu/cdsapp#!/dataset/cams-global-reanalysis-eac4?tab=form](https://ads.atmosphere.copernicus.eu/cdsapp#!/dataset/cams-global-reanalysis-eac4?tab=form), last access: 1st November, 2020). XCO and XNO$_2$ boundary condition based on CAMS is assumed to be representative as background value within the domain. Since we do not explicitly compute the sources and sinks of background NO$_2$ inside the domain, we decide to transport the boundary conditions as background passive tracers.

### Table 1. Summary of WRF simulations and the definition of tracers and acronym used.

<table>
<thead>
<tr>
<th>WRF Simulation / Tracer</th>
<th>WRF input / Tracer definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prior</td>
<td>WRF run using NCEP meteorological data, EDGAR CO and NOx emissions, CAMS OH, and CAMS CO and NOx as initial and lateral boundary conditions.</td>
</tr>
<tr>
<td>WRF$_{OH*1.1}$</td>
<td>Prior run with CAMS OH increased by 10%</td>
</tr>
<tr>
<td>Optimized run$_{1st \text{ iter}}$</td>
<td>Optimized state (background, emission, OH) after iteration 1</td>
</tr>
<tr>
<td>Optimized run$_{2nd \text{ iter}}$</td>
<td>Optimized state (background, emission, OH) after iteration 2</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>CO</th>
</tr>
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<tbody>
<tr>
<td>XCO$_{\text{emis}}$</td>
</tr>
<tr>
<td>XCO$_{\text{Bg}}$</td>
</tr>
<tr>
<td>XCO$_{\text{WRF}}$</td>
</tr>
<tr>
<td>XCO$_{\text{WRF,1st \text{ iter}}}$</td>
</tr>
</tbody>
</table>
The atmospheric transport in WRF causes the influence of NOx and CO emissions from Riyadh on their column average mixing ratios to be linear. Instead of a simplified photochemistry solver, we make use of a WRF-chem module for passive tracer transport for transporting NOx. This WRF module has been modified to account for the first order loss of NOx in reaction of NO2 with OH, using NOx/NO2 ratios from CAMS to translate NOx into NO2 and CAMS OH fields to compute the chemical transformation of NO2 to HNO3 (see Text S1 for detail).

In addition, we account for the chemical transformation of NOx to HNO3 in the reaction of NO2 with OH. This is a simplified treatment of the lifetime of NOx as other photochemical pathways play a role, such as:

- The oxidation of NO2 in reaction with organic radicals (RO2) to form the alkyl and multifunctional nitrates (RONO2) (Romer Present et al., 2019)
- NOx loss due to the formation dinitrogen pentoxide (N2O5) followed by heterogeneous transformation to HNO3 (Shah et al., 2020).
- Peroxyacetyl nitrate (PAN) formation in equilibrium between NO2 and the peroxyacetyl radical (Moxim, 1996).
- The dry deposition of NO2 on the surface and plant stomata (Delaria et al., 2020).
The loss of NO\textsubscript{2} by OH to HNO\textsubscript{3} accounts for 60 \% of the global NOx emission (Stavrakou et al., 2013). Macintyre and Evans., (2010) showed that the N\textsubscript{2}O\textsubscript{5} pathway reduces NOx concentrations by 10 \% in the tropics (30° N to 30° S) and 40 \% at northern latitudes. The NOx loss through N\textsubscript{2}O\textsubscript{5} hydrolysis is largest at northern latitudes during winter (50 \% to 150 \%), unlike the tropics where its seasonality is small. Moreover, the removal of N\textsubscript{2}O\textsubscript{5} is primarily important during night time because of its photolysis during daytime, whereas our analysis focuses on the midday overpass time (13:30) of TROPOMI when OH abundances are highest. For these reasons, we consider it safe to neglect the loss of NO\textsubscript{x} through N\textsubscript{2}O\textsubscript{5} in our analysis for Riyadh. The dry deposition flux is also expected to be low as it is controlled largely by stomatal uptake, which is assumed to be insignificant for the low vegetation cover of Riyadh. The same is expected to be true for PAN formation because of its thermal decomposition at increasing temperatures. We acknowledge that our OH estimates should be regarded as upper limits due to the neglect of other NO\textsubscript{x} transformation pathways. A quantification of the combined effect would require full chemistry simulations, which we consider outside of the scope of this paper.

Note that in this study, OH is only applied to the urban NO\textsubscript{x} emission tracer (XNO\textsubscript{x\text{emis}}). The CAMS NO\textsubscript{x} background tracer (XNO\textsubscript{x\text{Bg}}) is transported in WRF without OH decay, since it already represents the balance between regional sources and sinks. CAMS hydroxyl radical (OH) data at a resolution of 0.75° x 0.75° spatial and 3 hourly temporal resolution (Inness et al., 2019) retrieved at https://ads.atmosphere.copernicus.eu/cdsapp#!/dataset/cams-global-reanalysis-eac4?tab=form, last access: 1\textsuperscript{st} July, 2020) is spatially, temporally and vertically interpolated to the WRF grid. The NO\textsubscript{x} lifetime is derived as follows:

\[
\frac{d\text{NO}_2}{dt} = K_{\text{NO}_2\text{OH}} \cdot [\text{OH}] \cdot [\text{NO}_2] \tag{2}
\]

\[
\text{fact} = \frac{\text{NO}_x}{\text{NO}_2} \tag{3}
\]

\[
\tau_{\text{NO}_x} = \frac{1}{K_{\text{NO}_2\text{OH}} \cdot \text{fact} \cdot [\text{OH}]} \tag{4}
\]

where, \(K_{\text{NO}_2\text{OH}}\) is the International Union of Pure and Applied Chemistry (IUPAC) 2\textsuperscript{nd} order rate constant for the reaction of NO\textsubscript{2} with OH. “fact” represents the fractional contribution of NO\textsubscript{2} to NO\textsubscript{x} (NO\textsubscript{x}/NO\textsubscript{2}). This NO\textsubscript{x} to NO\textsubscript{2} conversion factor is derived from the CAMS reanalysis and re-gridded to WRF, to account for its spatial and temporal variation. \(\tau_{\text{NO}_x}\) is the lifetime of NO\textsubscript{x}.
The components of NOx (NO and NO$_2$) have short lifetimes during daytime because of the photo-stationary equilibrium exchanging NO and NO$_2$ into each other. For this reason, we estimate the lifetime of their sum (NO$_x$) which is determined largely by the reaction with OH. In earlier work with satellite NO$_2$ data, the Jet Propulsion Laboratory (JPL) high pressure limit was used as rate constant to represent the first order loss of NO$_2$ (Beirle et al., 2011; Lama et al., 2020; Lorente et al., 2019). However, we found this approximation to be too crude, and therefore apply the full IUPAC recommended pressure dependent formula for the 2$^{nd}$ order rate constant. Supplement Figure S4 shows the difference between the three rate constants, i.e. JPL high pressure limit, JPL 2$^{nd}$ order and IUPAC 2$^{nd}$ order, confirming the importance of accounting for the pressure dependence.

WRF output for the third domain is interpolated spatially and temporally to the footprints of TROPOMI. The interpolated WRF- NOx tracers are converted to NO$_2$ using the conversion factor derived from the CAMS reanalysis accounting for its spatial and temporal variation (for the names and functions of tracers see Table 1). The averaging kernel available for each TROPOMI CO and NO$_2$ observation is applied to the WRF output, after interpolation to the vertical layers of the TROPOMI retrieval. To compare WRF output to TROPOMI, WRF derived XNO$_2$ (XNO$_2$$_{WRF}$) is calculated by combining the NO$_2$ tracer that accounts for the OH effect (XNO$_2$$_{emis,OH}$) and the CAMS NO$_2$ background (XNO$_2$$_{Bg}$) (see Fig. S5 and S6). Similarly, the CO emission tracer (XCO$_{emis}$) is added to the CAMS CO background (XCO$_{Bg}$) to calculate WRF simulated XCO (XCO$_{WRF}$) (see Fig. S7 and S8).

**Figure 1.** TROPOMI derived XCO (left) and average wind speed and wind direction from the surface to the top of boundary layer (right) derived from the CAMS global reanalysis eac4 data at the TROPOMI overpass time over Riyadh for August 4$^{th}$, 2018. The white star represents the centre of Riyadh. The black box (B1) with a dimension of 300 x 100 km$^2$ is rotated in the average wind direction at 50 km radius from the centre of Riyadh at the TROPOMI overpass time resulting in the red box. For the calculation of cross-directional averaged NO$_2$ and CO, the red box is divided into 29 smaller cells with the width ($\Delta x$) $\sim$11 km. For this TROPOMI derived XCO is gridded at 0.1$^\circ$x0.1$^\circ$. 
2.5 NO₂/CO ratio calculation using box rotation

The variation of the NO₂/CO ratio in the downwind city plume is calculated as a function of distance \( x \) from the city centre in downwind direction. We select days with an average wind speed \( U \) in the range of 3.0 \( \text{ms}^{-1} \) (Beirle et al., 2011) < \( U \) < 8.5 \( \text{ms}^{-1} \) (Valin et al., 2013) within a 50 km radius from the centre of Riyadh (24.63° N, 46.71° E). The horizontal distribution of EDGAR emissions over Riyadh is used within this 50 km radius (Fig S9). Ninety five days in summer and 70 days in winter meet the wind speed criteria over Riyadh for the ratio calculation. The boundary layer average wind speed and direction is calculated using the CAMS global reanalysis eac4 (retrieved at https://ads.atmosphere.copernicus.eu/cdsapp#!/dataset/cams-global-reanalysis-eac4?tab=form, last access: 1st August, 2020) at a resolution of 0.75°x0.75° spatial and 3 hourly temporal resolution. For this, the CAMS wind vector is spatially and temporally interpolated to the central coordinate of TROPOMI pixels.

To compute the NO₂/CO ratio as a function of the downwind distance \( x \), TROPOMI and WRF data have been re-gridded at 0.1°x0.1°. A box (B1) is selected with a width of 100 km, from 100 km in upwind to 200 km in downwind direction of the city centre (see Fig 1a). The dimension of the box is motivated by multiple TROPOMI overpasses over Riyadh showing NO₂ and CO enhancements advected downwind over a ~200 km distance, without other large sources of NO₂ and CO within a 100 km radius of the city centre (see Fig. 1a). Figure 1(b) shows the boundary layer averaged wind speed and wind direction over Riyadh indicating flow towards the northeast on 4th of August, 2018. The box is rotated for every TROPOMI overpass depending upon the daily average wind direction within a 50 km radius from centre of Riyadh as shown in Figure 1(a) and Figure S10. The rotated box B1 is divided into N rectangular boxes, orthogonal to the wind direction with length \( (\Delta x) \approx 11 \text{ km} \) (see Fig. 1 and Fig. S10). The XNO₂ and XCO grid cells that fall within the N rectangular boxes are selected to derive zonally averaged XNO₂ and XCO for summer and winter.

Unlike the enhancements over the city, \( \Delta \text{XNO}_2 \) and \( \Delta \text{XCO} \) become smaller than retrieval uncertainties at large distance from the city, where the ratio \( \Delta \text{XNO}_2/\Delta \text{XCO} \) becomes ill-defined. Therefore, we decided to use the ratio of mean XNO₂ and XCO instead of enhancements over the background. To analyse the influence of atmospheric transport and the OH sink on the WRF derived XNO₂/XCO ratio two different ratios are derived: 1. \( \frac{\text{XNO}_2\text{emis}}{\text{XCO\text{emis}}} \), named “Ratio_{\text{without OH}}”, 2. \( \frac{\text{XNO}_2(\text{emis,OH})}{\text{XCO\text{emis}}} \), named “Ratio_{\text{with OH}}” (see Table 1). The CAMS background accounts for the balance between regional source and sink in CTMs so it is excluded to analyse the influence of atmospheric transport on the ratio. For the comparison between TROPOMI and WRF, the CAMS backgrounds are included in “WRF RATIO” \( \frac{\text{XNO}_2\text{WRF}}{\text{XCO\text{WRF}}} \) (see Table 1). The comparison of WRF RATIO to TROPOMI ratio, and the contribution of its components, is presented in section 3.2.

2.6 OH estimation: satellite data only

In the EMG method, following Beirle et al. (2011), 2D NO₂ column densities maps are assigned to eight equal wind sectors, spanning 360° for summer and winter. 1D column densities per wind sector are computed by averaging in cross wind direction.
This way, average NO\textsubscript{2} column density functions of the downwind distance to the city centre have been constructed for summer and winter (see Fig. S11). Using the EMG method as in Beirle et al., (2011), the e-folding distance x\textsubscript{0} and NO\textsubscript{2} emissions have been estimated. The NO\textsubscript{2} lifetime is derived by dividing x\textsubscript{0} by the average wind speed (5.46 ms\textsuperscript{-1} and 5.24 ms\textsuperscript{-1} for winter and summer, respectively) and is provided in Table 2. The OH concentration is derived from the inferred NO\textsubscript{2} lifetime using the IUPAC second order rate constant (for details see section Text S2 and S3). Rate constants at the time of TROPOMI overpasses are obtained from WRF by averaging the IUPAC second order rate constant from the surface to top of the planetary boundary layer. The PBL height at the time TROPOMI overpass has been taken from WRF. EMG derived NO\textsubscript{2} emissions are also converted to NOx emissions using the CAMS-derived conversion factor. Summer and winter averaged CAMS derived conversion factors for the box of 300 km x 100 km are 1.28 and 1.31, respectively.

2.7 OH estimation: WRF optimization

To jointly estimate the NO\textsubscript{x} and CO emissions as well as the OH concentration from the TROPOMI data, a least squares optimization method is used. This method fits the model to the data by minimizing a cost function (J) (see Text S4 for details). The reaction of NO\textsubscript{2} with OH introduces a non-linearity in the OH optimization. To account for this non-linearity, we linearize the problem around the a priori starting point, using small perturbations (10 \%) \Delta\text{background}, \Delta\text{emission}, \Delta\text{OH}. The non-linear model is fitted to the observations, by optimizing scaling factors f\textsubscript{Bg}, f\textsubscript{emis}, f\textsubscript{OH} to the perturbation functions \Delta\text{background}, \Delta\text{emission} and \Delta\text{OH}, respectively. This process is repeated iteratively, updating the linearization point and re-computing the perturbation functions. The scaling factor f\textsubscript{emis}, f\textsubscript{oh}, and f\textsubscript{bg} represent the modification of the prior in percentage change.

We estimate OH by optimizing WRF with TROPOMI in two ways 1) optimizing the simulated NO\textsubscript{2}/CO ratio using TROPOMI-derived ratios, named as “Ratio optimization” and 2) optimizing NO\textsubscript{2} and CO separately using TROPOMI derived XCO and XNO\textsubscript{2} named as “Component wise optimization”. First the ratio optimization is described followed by the component wise optimization. Optimized ratios are derived as follows:

\[
F_{\text{TROPOMI}} = F + \frac{\Delta F}{\Delta \text{emis} \cdot 10} * f_{\text{emis}} + \frac{\Delta F}{\Delta \text{OH} \cdot 10} * f_{\text{OH}} + \frac{\Delta F}{\Delta \text{B} \cdot 10} * f_{\text{B}} \tag{5}
\]

\[
F = \frac{\text{XNO}_2\text{WRF}}{\text{XCO}_{\text{WRF}}} \tag{6}
\]

\[
\text{XNO}_2\text{WRF} = \text{XNO}_2\text{emis,OH} + \text{XNO}_2\text{B} \tag{6}
\]

\[
\text{XCO}_{\text{WRF}} = \text{XCO}_{\text{emis}} + \text{XCO}_{\text{B}} \tag{7}
\]

\[
\frac{\Delta F}{\Delta \text{emis}} = \frac{\text{XNO}_2\text{emis,OH} \cdot 1.05 + \text{XNO}_2\text{B}}{\text{XCO}_{\text{emis}} \cdot 0.95 + \text{XCO}_{\text{B}}} - F \tag{8}
\]
$$\Delta F_{\Delta OH} = \frac{XNO_2^{(emis,OH+1.1)} + XNO_2^{Bg}}{XCO_{emis} + XCO_{Bg}} - F$$ (9)

$$\Delta F_{\Delta Bg} = \frac{XNO_2^{(emis,OH)} + XNO_2^{Bg} \times 1.05}{XCO_{emis} + XCO_{Bg} \times 0.95} - F$$ (10)

Here, $F_{TROPOMI}$ is the TROPOMI derived NO$_2$/CO ratio, $F$ is the WRF Ratio, $\Delta F_{\Delta \text{emis}}$ is the change in $F$ due to an increase in the NO$_2$ emission by 5 % and a decrease in the CO emission by 5 % ($1.05/0.95 = \sim 10\%$), $\Delta F_{\Delta \text{OH}}$ is the change in $F$ due to an increase in OH by 10 % and $\Delta F_{\Delta \text{Bg}}$ is the change in $F$ due to an increase in the NO$_2$ background by 5 % and a decrease in the CO background by 5 %. $XNO_2^{(emis,OH)}$ is the contribution of city NOx emissions to XNO$_2$ accounting for the OH sink, $XNO_2^{Bg}$ is the NO$_2$ background. $XCO_{emis}$ is the contribution of the EDGAR city CO emissions to XCO and $XCO_{Bg}$ is the CO background derived from CAMS. $XNO_2^{WRF}$ and $XCO^{WRF}$ is the WRF derived XNO$_2$ and XCO respectively. $XNO_2^{(emis,OH+1.1)}$ is the contribution of city NOx emissions to XNO$_2$ after increasing CAMS OH by 10 %. The scaling factors $f_{\text{emis}}, f_{\text{OH}}$ and $f_{\text{Bg}}$ obtained from the ratio optimization have been divided by 10 because $\Delta F_{\Delta \text{emis}}, \Delta F_{\Delta \text{OH}}$ and $\Delta F_{\Delta \text{Bg}}$ are defined as the change in $F$ due to modification of emission, OH and background by 10 %.

Although the ratio optimization is sensitive to the emission ratio and the OH sink of NO$_2$, it is not sensitive to the absolute emissions of CO and NO$_2$. Therefore, we performed component-wise optimizations for XCO and XNO$_2$ to optimize absolute emissions. We also compare the OH factor obtained from the ratio optimization and component-wise optimization to test the robustness of the method. The optimized XNO$_2$ is derived using Eq. (11). XCO is optimized using the same equation but without considering the OH sink (see Appendix B).

$$XNO_2^{TROPOMI} = XNO_2^{WRF} + \Delta XNO_2^{\text{emis}} \times \frac{f_{\text{emis}}}{10} + \Delta XNO_2^{\text{OH}} \times \frac{f_{\text{OH}}}{10} + \Delta XNO_2^{\text{Bg}} \times \frac{f_{\text{Bg}}}{10}$$ (11)

$$\Delta XNO_2^{\text{emis}} = XNO_2^{(emis,OH)} \times 1.10 - XNO_2^{(emis,OH)}$$ (12)

$$\Delta XNO_2^{\text{OH}} = XNO_2^{(emis,OH+1.1)} - XNO_2^{(emis,OH)}$$ (13)

$$\Delta XNO_2^{\text{Bg}} = XNO_2^{Bg} \times 1.10 - XNO_2^{Bg}$$ (14)

Here, $XNO_2^{TROPOMI}$ is the TROPOMI derived XNO$_2$, $XNO_2^{WRF}$ is the WRF XNO$_2$. $\Delta XNO_2^{\text{emis}}$ is the change in XNO$_2$ due to an increase in emission by 10 %, $\Delta XNO_2^{\text{OH}}$ is change in XNO$_2$ due to an increase in CAMS OH by 10 % and $\Delta XNO_2^{\text{Bg}}$ is a change in the background XNO$_2$ by 10 %. The scaling factors $f_{\text{emis}}, f_{\text{OH}}$ and $f_{\text{Bg}}$ are divided by a factor 10, because $\Delta XNO_2^{\text{emis}}, \Delta XNO_2^{\text{OH}}$ and $\Delta XNO_2^{\text{Bg}}$ are defined as 10 % changes in NOx emission, OH and background level.
3. Results and Discussion

3.1. XNO$_2$ and XCO over Riyadh

In this subsection, we compare WRF-derived XCO$_{WRF}$ and XNO$_2$$_{WRF}$ with TROPOMI for summer (see Fig. 2) and winter (see Fig. S6) over Riyadh. TROPOMI and WRF derived XCO and XNO$_2$ are averaged from June to October 2018 for summer and November 2018 to March 2019 for winter in a domain of 500 x 500 km$^2$ centered around Riyadh. The comparison for summer in Figure 2 shows TROPOMI NO$_2$ after replacing the TM5-based tropospheric AMF with WRF profiles as described in Visser et al. (2019). The enhancement of XNO$_2$ and XCO over Riyadh due to urban emissions is clearly separated from the background for TROPOMI and WRF, showing that the city of Riyadh is well suited to investigate the use of the NO$_2$/CO ratio to quantify OH in urban plumes. Due to the longer life-time of CO, the TROPOMI-observed XCO plume extends further in the southeast direction compared to XNO$_2$. Figure 2 shows that our WRF simulations are able to reproduce the TROPOMI
retrieved XNO\(_2\) \((r^2 = 0.96)\) and XCO \((r^2 = 0.78)\) plumes, confirming that WRF-derived \(\frac{XNO_2}{XCO}\) is suitable for the optimization of CTM-derived OH concentrations using TROPOMI data. XNO\(_2\) WRF is higher by 25 % compared to TROPOMI in the city centre. In the background, XCO\(_{WRF}\) shows a similar spatial distribution as TROPOMI XCO, but the values are higher by 5 % to 10 % (see Fig 2.). Close to the city centre, XCO\(_{WRF}\) is ~5.7 % higher than TROPOMI XCO. In EDGAR 2011, emission sources are located in the centre of Riyadh (see Fig. S9). However, as noted by Beirle et al. (2019) they extend to a larger part of the city in reality. This difference in spatial distribution leads to higher XNO\(_2\)\(_{WRF}\) and XCO\(_{WRF}\) close to centre of Riyadh compared to TROPOMI.

In winter, the wind direction is predominantly from the south easterly sector in WRF and TROPOMI (see Fig S12). The spatial distribution of XCO\(_{WRF}\) \((r^2 = 0.73)\) and XNO\(_2\)\(_{WRF}\) \((r^2 = 0.88)\) matches quite well with TROPOMI. Therefore, the difference between summer and winter should offer the opportunity to quantify the seasonality in emissions and OH concentrations over Riyadh. In winter, XCO\(_{WRF}\) is ~5 % to 10 % higher than TROPOMI, while XNO\(_2\)\(_{WRF}\) is higher by 40 % to 50 %. The difference could either point to uncertainties in the NO\(_2/CO\) emission ratio, uncertainties in the NO\(_2\) lifetime, or inaccuracies in the background. By quantifying OH, we can evaluate these explanations (see section 3.3). XNO\(_2\)\(_{WRF}\) is higher by 20 % in winter than in summer. Contrary, TROPOMI NO\(_2\) is lower by ~30 % in winter (Fig S12.) compared to summer (Fig. 2). Again, to disentangle the role of changing sources and sinks, we need an independent estimate of OH.

### 3.2. The XNO\(_2/XCO\) ratio and OH

Before comparing TROPOMI and WRF-derived XNO\(_2/XCO\) ratios, we first analyse the influence of atmospheric transport and the OH sink on the WRF derived XNO\(_2/XCO\) ratio. To do this three ratios are used 1. Ratio\(_{\text{without OH}}\) 2. Ratio\(_{\text{with OH}}\) 3. WRF RATIO (the see Table 1). As seen in Figure 3, S13 and S14, WRF is able to reproduce the TROPOMI-observed downwind evolution of XNO\(_2\) and XCO in summer and winter. The peak of the XNO\(_2\) and XCO plumes is shifted away from the city centre due to the balance between the accumulation of urban emissions in the atmospheric column and atmospheric transport (Lorente et al., 2019).

As expected, Ratio\(_{\text{without OH}}\) shows an approximately straight line when the background is removed, because transport influences NO\(_2\) and CO in the same way and therefore cancels out in the ratio (see Fig. 3b). The Ratio\(_{\text{with OH}}\) however, shows an approximately gaussian relation with distance due to the influence of the sink on NO\(_2\). This comparison demonstrates the sensitivity of the relation between XNO\(_2/XCO\) ratio and downwind distance to the NO\(_2\) lifetime, which we want to exploit to quantify OH. When including the background, the shapes of the functions in Figure 3c change (not shown), because the relative weights of the background and city contributions to the ratio vary with distance of the city centre. In summer, the WRF RATIO is higher by ~15 % close to centre of city TROPOMI due to the overestimation of XNO\(_2\)\(_{WRF}\) in WRF (see Fig. 3d). However in the downwind plume, at a distance of 100 km WRF RATIO is higher by 20 % to 50 % compared to TROPOMI.
In winter, Ratio$	ext{without OH}$ and Ratio$	ext{with OH}$ show relations with downwind distance that are similar to summer, confirming that an OH sink leads to a gaussian structure of the ratio (see Fig. S14). The winter WRF RATIO is 40 % to 60 % higher than TROPOMI due to the overestimation of XNO$_2$ by 40 % to 50 %. The WRF RATIO close to the centre of city is also 20 % higher in winter than in summer, due to higher winter XNO$_2$WRF than in summer (see Fig S12 and S15). In contrast, TROPOMI shows a higher ratio in summer compared to winter (see Fig S15). These differences between TROPOMI and WRF-derived ratios offer an opportunity to address uncertainties in CTM computed urban OH and emission inventories, which will be explored next.

3.3 WRF optimization using synthetic data

To translate the discrepancies between TROPOMI and WRF derived ratios of section 3.2 into implied differences in emissions, OH and background, the least squares optimization method has been used as described in section 2.6. Before optimizing WRF
using TROPOMI, pseudo data experiments in WRF have been carried out to test if the optimization method is capable of recovering true emissions and OH levels. To this end, changes in OH concentrations, emissions and background by known scaling factors have been applied to the WRF prior simulation to create a synthetic dataset. This process is repeated multiple times to create thousands of synthetic datasets. Subsequently, the scaling factors are obtained in the inversion procedure. These tests reveal that the estimation errors for $f_{\text{emis}}$, $f_{\text{OH}}$ and $f_{\text{Bg}}$ are less than 2.5\% (see Fig. S16). This confirms that the least square optimization method works, with two iterations leading to a sufficient accuracy, and can be used to estimate emissions and OH from TROPOMI data. Using TROPOMI data, estimation errors for $f_{\text{emis}}$, $f_{\text{OH}}$ and $f_{\text{Bg}}$ are expected to be higher due to atmospheric transport errors, simplified chemistry, and XCO and XNO$_2$ retrieval uncertainties. These errors did not play a role in the pseudo-data experiments, in which perfect transport and sampling was assumed.

To obtain a more realistic estimate of the uncertainty in least squares optimized OH, TROPOMI data have been replaced by NO$_2$, CO and NO$_2$/CO ratio derived from WRF-chem using the Carbon Bond Mechanism Z (CBM-Z) gas-phase chemical mechanism (Zaveri and Peters, 1999). EDGAR based VOCs, NOx and CO emission have been used in combination with boundary condition for NO, NO$_2$, CO, ozone (O$_3$) from CAMS to run WRF-chem for August 17$^{th}$, 2018 and November 18$^{th}$, 2018 representing a summer and winter day, respectively. For August 17$^{th}$, 2018, the ratio and XNO$_2$ optimization increase the CAMS based prior OH of 1.19x10$^7$ molecules cm$^{-3}$ by 15.7\% and 13.4\%, respectively (see Fig S17). In the fully coupled online chemistry with WRF simulation, the boundary layer averaged OH for the box of 300 km x 100 km amounts to 1.33x10$^7$ molecules cm$^{-3}$, which is <5\% lower than the optimized OH value that is derived using our method. The optimized NOx and CO emissions differ by <11\% from the emission input used in the full chemistry version WRF. In winter, the optimization increases CAMS based OH of 1.03 x 10$^7$ molecules cm$^{-3}$ by 19.4\%. The OH derived from WRF with full online chemistry is 1.07x10$^7$ molecules cm$^{-3}$ and lower by 15.2\% than the optimized OH value. The component wise optimization increases the EDGAR NOx and CO emissions by 23.1\% and 10.5\%, respectively (see Fig S18). Overall, the uncertainty in optimized NOx, CO emission and OH derived from this test is <11\% in summer and 10\% to 23\% in winter. Since the lifetime of NOx is determined by other reactions in addition to the oxidation to HNO$_3$ considered in our method, it is expected to overestimate the real OH value. The test using WRF full chemistry confirms that this is indeed the case. The uncertainty for OH, NOx emission and CO emission are in good agreement with the CLASS computations explained in detail in Text S6.

### 3.4 WRF optimization using seasonally averaged TROPOMI data

The results for summer are summarized in Figure 4, showing the optimized fit to the TROPOMI data as well as the corresponding scaling factors $f_{\text{emis}}$, $f_{\text{OH}}$ and $f_{\text{Bg}}$ that are estimated. The optimized emission, OH and Bg obtained from the 2$^{nd}$ iteration is divided by prior to derive the $f_{\text{emis}}$, $f_{\text{OH}}$ and $f_{\text{Bg}}$ (see Text S5 for details). The convergence of the iterative procedure is shown in Fig S19 and S20. The estimated uncertainties for the scaling factors $f_{\text{emis}}$, $f_{\text{OH}}$ and $f_{\text{Bg}}$ are derived by summing the contribution of wind speed, length and width of the box, NO$_2$ bias, CO bias and the different pathways of NOx loss in quadrature (see Text S6, Tables S1 and S2). For summer and winter, the uncertainties of the optimized OH concentrations is
<17 % and < 29 % respectively. For NOx and CO emissions, the uncertainty is < 29 % in summer and winter. Figure 4a shows WRF ratios for summer in comparison to TROPOMI, before and after optimizing the OH concentration. The optimized WRF ratios fit the TROPOMI ratios well with $\chi^2 = 0.1$ (for the derivation of $\chi^2$ see section Text S7). The prior and optimized emission ratio, OH concentration and background ratio obtained from component and ratio optimization for summer and winter is provided in Table S4. According to the ratio optimization, the emission ratio and CAMS OH are underestimated by 155 ± 26 % and 32 ± 5.3 % respectively (see Table S4). The optimized CAMS background ratio is lower by 70 ± 6.5 % compared to prior. It should be realized here that the ratio optimization does not estimate the absolute emission of NO$_2$ and CO, but only their ratio.

**Figure 4.** Comparison between TROPOMI and WRF, before and after optimization for summer (averaged over June to October, 2018) a) XNO$_2$/XCO ratio, b) XNO$_2$ and c) XCO in comparison to TROPOMI. $f_{OH}$, $f_{emis}$ and $f_{Bg}$ are optimized scaling factors obtained iteratively for OH, emissions and background by least square optimization method. $f_{emis}$, $f_{OH}$ and $f_{Bg}$ are derived by accounting the total change in emission, OH and background using the corresponding scaling factors obtained from 1$^{st}$ and 2$^{nd}$ iterative step. The unit of scaling factor is in percent (%).
To derive the absolute emission, we performed component-wise optimizations of WRF-derived $XCO_{\text{WRF}}$ and $XNO_2_{\text{WRF}}$. Optimized $XCO_{\text{WRF}}$ and $XNO_2_{\text{WRF}}$ fit well to the TROPOMI data (see Fig. 4b and 4c). In the $XNO_2$ optimization, the EDGAR NOx emission is increased by $42.1 \pm 8.4\%$ and the CAMs background is reduced by $75.9 \pm 10.0\%$. CAMS OH is increased by $28.3 \pm 3.9\%$ which is close to the results obtained from the ratio optimization (see Table S4). In the $XCO$ optimization, EDGAR CO emissions are roughly doubled and the background is reduced by $4.5 \pm 0.7\%$ compared to CAMS (see Table S4).

The summer optimized NOx/CO emission ratio derived from the component wise optimization is $0.55 \pm 0.09$. The optimized emission ratio from ratio optimization is larger by factor 3.6 compared to component wise optimization (see Table S4). The difference between two estimates can be explained by different constraints on the solution in the two methods. In particular, the ratio inversion allows emission adjustment in a fixed relation between NO$_2$ and CO emissions whereas the component wise has the full flexibility to adjust CO and NO$_2$ emission. The NO$_2$/CO ratio over a city is the sum of the contributions of the background and the city emission. The relative weight of the two is determined by the absolute background levels and absolute emissions of CO and NO$_2$. Therefore, the emission ratio estimated by ratio optimization is sensitive to the XNO$_2_{\text{Bg}}$. However, the difference between the two estimates is larger than expected but does not affect the OH estimation. Lama et al., (2020) inferred an NO$_2$/CO emission ratio over Riyadh of $0.47 \pm 0.1$ for 2018 from TROPOMI favoring the Monitoring Atmospheric

![Graphs](image)

**Figure 5.** As Figure 4, for Winter (averaged over November, 2018 to March, 2019)
Chemistry and Climate and CityZen (MACCity) emission ratio over that of EDGAR. The optimized emission ratio obtained from component wise optimization is consistent to Lama et al., (2020) and MACCity summer emissions. This shows that for the accurate estimation of the emission and emission ratio, the component wise optimization method is preferable.

Figure 5 presents optimization results for winter, where optimized WRF is in similar good agreement with TROPOMI as for summer with $X^2 = 0.11$. For winter, the ratio optimization increases emission ratio by $58.8 \pm 33\%$ and OH by $52.0 \pm 14\%$. The ratio and component-wise optimizations again show similar OH adjustments, demonstrating the robustness of our method. The background ratio is reduced by $66.8 \pm 11\%$. The XNO$_2$ optimization reduces the EDGAR NOx emission by $15.45 \pm 4.1\%$ and the CAMS background by $70.2 \pm 6.1\%$. For XCO, the WRF XCO$_{Bg}$ is reduced by $1.74 \pm 0.1\%$ in combination with a doubling of the EDGAR CO emission. The optimized emission ratio (NOx/CO) derived from component wise optimization is 0.36 which is lower by 4.0 times than optimized emission ratio obtained from ratio optimization (see Table S4).

Table 2. Overview of WRF optimized OH and NOx emissions for Riyadh and comparison to the EMG method. The estimated uncertainty for EMG and WRF derived NOx emission and OH concentration is the sum of the contribution of wind speed, length and width of box, NO$_2$ bias correction, CO bias and the different pathways of NOx loss provided in Table S1, S2 and S3.

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<th>Winter WRF Optimization</th>
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3.5 WRF optimization using a single TROPOMI overpass

To demonstrate the application of our WRF optimization method to single TROPOMI overpass, results are presented in this subsection for August 18th, 2018. This date was selected for clear sky conditions with most of the TROPOMI NO$_2$ and CO pixels passing the data quality filter. During this day, the urban plume is transported in southwestern direction over Riyadh.

The spatial distribution of XNO$_2$$_{WRF}$ ($r^2 = 0.76$) and XCO$_{WRF}$ ($r^2= 0.65$) matches quite well with TROPOMI (see Fig S21). The optimized ratio, XNO$_2$ and XCO for a single day fit well with TROPOMI ($X^2 = 0.1, 0.3$ and $0.7$) comparable to the
summer averaged plumes indicating that the optimization method can be applied to single TROPOMI overpass. The ratio optimization increases the emission ratio and CAMS OH respectively by $111 \pm 18.4\%$ and $37.9 \pm 6.2\%$ respectively, whereas the background is reduced by $51.5 \pm 5.2\%$ (see Fig S22 a). The XNO$_2$ optimization increases the EDGAR NOx emission by $25.5 \pm 5.1\%$ and CAMS OH by $32.3 \pm 4.4\%$, whereas the NOx background is reduced by $54.4 \pm 7.0\%$ (see Fig S22 b). The CO optimization doubles the EDGAR CO emission and reduces the background by $6.1 \pm 0.97\%$ (see Fig S20 c). The optimized NOx and CO emission for August 18th is $8.9 \pm 1.7$ kg/s and $18.9 \pm 4.0$ kg/s respectively and differs by <25% with the summer optimized emission (see Table 2 and S5). The optimized OH derived from a single TROPOMI overpass is $1.73 \times 10^7 \pm 0.3$ molecules cm$^{-3}$ differs by < 5% from the summer averaged OH i.e. $1.7 \times 10^7 \pm 0.3$ molecules cm$^{-3}$ confirming that the method yields realistic results for a single overpass.

### 3.6 WRF optimization Vs the EMG method

To investigate the consistency between our method and the EMG method, the derived NO$_x$ lifetimes, emissions and OH concentrations using both methods are listed in Table 2 for winter and summer. Our optimization and the EMG method agree well on the seasonal change in NO$_x$ emission and OH concentration. Both methods result in higher NO$_x$ emissions and shorter lifetimes in summer; lower NOx emissions and longer lifetimes in winter. Riyadh has dry and warm summer days and the increase in power consumption due to the use of air conditioning contributes to the higher emission in summer than in winter (Lange et al., 2021). During the summer, EMG and the WRF optimization method both increase the NOx emission and OH concentration compared with the prior. The size of the NO$_x$ emission and OH concentration increase, obtained using the WRF optimization method is higher than the EMG method by 10% to 29%. However, the difference between the EMG method and the component optimization method are smaller compared to the uncertainty of the emission and OH concentration derived for the optimization method. For winter, the difference between the EMG and WRF-optimized results are smaller than the difference between the EMG results and the prior. The NOx emission after optimization differs from the EMG method by 33%. Optimized OH concentration and NOx lifetime differs by <10% compared to EMG method. In general, the difference between the EMG and optimization results is within the uncertainty range of 20% to 30%, confirming their consistency and strengthening the confidence in the estimates that are obtained from TROPOMI data. In contrast to EMG method, the optimization method can be used for a single TROPOMI overpass (see Section 3.6) and does not require yearly averaged NO$_2$ data, allowing analysis of day-by-day OH, NOx and CO emission (see Section 3.3). Segregation and averaging of NO$_2$ urban plume by wind sector is not required in the optimization method. The effect of transport cancels out in taking the NO$_2$/CO ratio and loss of NO$_2$ is mostly governed by OH during the mid-day. In this study, NOx emission and OH concentration is estimated iteratively whereas the EMG method arrives at the solution in a single step. However, since our optimization method requires a WRF model simulation it is computationally more expensive. Uncertainties in transport may create mismatches with the satellite observations, leading to errors in the optimized fit. This influences the quality of derived emission estimates (Dekker et al., 2017). Therefore, finding a simplified approach using satellite data to derive the emission ratio and to estimate
OH concentration in urban plumes will be our focus in the future. In the future, the accuracy of our method can be further improved by accounting other NOx removal pathways.

3.7 WRF optimized emissions and emission trends

It should be realized that the a priori EDGAR emissions and TROPOMI optimized estimates represent different years (2012 and 2018, respectively). To check whether the emission differences that are found may be explained by trends in emissions, we compare EDGARv5.0 2012 NOx and CO emissions with 2018 accounting for seasonal and diurnal emission variations using temporal emission factors by van der Gon et al., (2011). EDGAR 2018 NOx and CO emissions are derived by linear extrapolation using emission from 2000 to 2015 (see Figure S23). For summer mid-day NOx emissions, the EDGAR emissions increased by 16.7 % from 2012 to 2018, which is lower than our optimization results. For winter, mid-day NOx emissions increase in EDGAR by 15.2 % from 2012 to 2018, whereas the WRF optimization yields reductions by 15.6%. In EDGAR, summer and winter CO emissions increased from 2012 to 2018 by 38.5 %. However, the WRF optimization suggests that the EDGAR CO emissions for summer and winter need to be doubled (see Table S4). Borsdorff et al., (2018b) mentioned that EDGAR CO emissions have to be increased significantly to match with TROPOMI CO observations over middle eastern cities such as Tehran, Yerevan, Tabriz and Urmia. Overall, this points to a significant uncertainty in the EDGAR emission inventory at the city scale.

To test the accuracy of the linear extrapolation of EDGAR data, we compare the relative change in NOx and CO emission in 2012 to 2018 using CAMS Global (CAMS–GLOB) anthropogenic v4.2 emission datasets (https://ads.atmosphere.copernicus.eu/cdsapp#!/dataset/cams-global-emission-inventories?tab=overview). CAMS–GLOB shows that for summer and winter NOx emission increases by 26 % from 2012 to 2018, which is higher by a factor 1.7 than EDGAR. CAMS-GLOB based summer and winter CO emission increases by 20 % from 2012 to 2018 which differs by ~40 % compared to EDGAR. In general, the relative increase in CO and NOx emission from EDGAR and CAMS-GLOB is much smaller compared to the difference with our optimization method.

4. Discussion

The TROPOMI retrieved XNO$_2$/XCO ratio is useful for estimating mid-day OH over isolated localized sources, such as the city of Riyadh, showing a clear contrast between the urban plume and the background. Such TROPOMI derived OH estimates offer a new opportunity to evaluate urban photochemistry in chemistry transport models. OH depends non-linearly on NOx and VOC emission, meteorological conditions, etc. (Sillman, 1990), which vary substantially between cities that are monitored by TROPOMI. Therefore, the application of our method to the global and multi-year dataset that is available could contribute substantially to the understanding of urban photochemistry and the development of effective pollution mitigation strategies. In addition, the method requires local sources with NO$_2$ and CO emissions that are large enough to be detected by TROPOMI.
Especially in European cities with lower CO emission where TROPOMI cannot detect the CO enhancement along with NO2 this method cannot be applied.

We realise that our method only considers the first order loss of NO2 by OH forming HNO3. In reality, the NO2 lifetime is influenced by more spatially and temporally varying factors such as temperature, ozone, and radiation (Lang et al., 2015; Romer et al., 2018). In cities, the loss of NO2 via the formation of alkyl and multifunctional nitrates (RONO2) are also important reactions influencing the lifetime of NO2 (Browne et al., 2013; Sobanski et al., 2017). For CO, secondary production from short-lived volatile organic compounds can also play an important role in urban pollution plumes. The application of full chemistry that includes all the sources and losses of NO2 and CO could therefore further improve the accuracy of OH estimates.

For cities at higher latitudes, especially in winter, it becomes more critical to account for the contribution of other pathways of NOx loss than OH oxidation. Isolated tropical and subtropical cities are therefore best suited for application of our current method.

A sensitivity test has been performed in which XNOx,Bg is lost by OH. In this case the optimized NOx emission and OH for summer and winter differ by < 7 % from the default method where the background is treated as an inert tracer (see Table S6). Furthermore, a sensitivity test has been performed in which the prior emission has been changed. The optimized emission varied by < 5 %, demonstrating robustness of the method to the choice of prior (see Fig S24). This also indicates that the optimization method can be used to study emission changes. Figure S25 shows that road transport, power plants and manufacturing industries are the largest pollutant emitter over Riyadh (Beirle et al., 2019). In this study, NOx and CO anthropogenic emissions are introduced at the surface, whereas the emission height of different sources is expected to vary in reality. The different emission heights for NOx and CO emission sources can also influence the result. In the future, realistic emission heights should also be incorporated in WRF for accurate estimation of OH. Moreover, the temporal emission factors that have been used by van der Gon et al., (2011) are based on European countries. The comparison of van der Gon et al., (2011) with the Copernicus Atmosphere Monitoring Service TEMPOral profiles (CAMS-TEMPO) (Guevara et al., 2020) suggests that temporal emission factors for weekend road transport and monthly residential combustion are different in Riyadh compared to European countries. CAMS-TEMPO is expected to provide a more accurate representation of emission variation due to the information on temporal, spatial variations that is included. Road transport, CO emission has the largest contribution ~75 % to the total emission over Riyadh, whereas NOx emission from road contributes by 24 % to the total NOx emission. Residential combustion has the smallest contribution of ~0.3 to 0.4 % to total NOx and CO emissions (see Fig S25). In the future, the application of accurate diurnal emission factors for road transport (see Fig S26) can further improve the accuracy of urban OH concentrations estimated using TROPOMI derived XNO2/CO ratios. In addition, the seasonality for NOx and CO emissions is different in Riyadh than in Europe, which should be accounted for in future studies also.
5. Conclusions

In this study, a new method is presented for estimating OH concentrations in urban plumes using TROPOMI observed $\text{XNO}_2$/XCO ratios in combination with WRF simulations of the downwind pollution plume of large cities. Our new method has been tested for the city of Riyadh using synthetic as well as real TROPOMI data. Seasonal emissions and OH concentrations have been estimated for summer (June to October, 2018) and winter (Nov, 2018 to March, 2019). WRF is well able to reproduce the spatial distribution of TROPOMI retrieved $\text{XNO}_2$ and XCO plumes over Riyadh during the summer and winter seasons. However, before the optimization, WRF overestimates $\text{XNO}_2$ by 15 \% to 30 \% in summer and 40 \% to 50 \% in winter compared to TROPOMI. In both seasons, TROPOMI XCO agrees within 10 \% with WRF. The WRF derived $\text{XNO}_2$/XCO ratio is higher by 15 \% to 30 \% in summer and 40 \% to 60 \% in winter compared to TROPOMI, explained mostly by differences in $\text{XNO}_2$.

The differences between WRF and TROPOMI observations have been used to optimize emissions and the NO$_2$ lifetime. To this end, scaling factors for the city emissions, OH and the background level have been optimized iteratively using a least squares method. Ratio and component wise optimizations have been compared to test the overall consistency of the method. In summer, the ratio and $\text{XNO}_2$ optimization for $\text{XNO}_2$ suggest that the OH prior from CAMS is underestimated by 32 ± 5.3 \%. The OH estimates obtained from the ratio and NO$_2$-only optimization differs by <10 \%, demonstrating the robustness of the method. Summertime emissions of NOx and CO from EDGAR are increased by 42.1±8.4\% and 101 ± 21 \%. For winter, the ratio and component wise optimizations increase OH by ~52 ± 14 \% to fit TROPOMI inferred ratios. In the optimization of winter data, NOx emissions are reduced by 15.5 ± 4.1 \% and CO emissions are doubled. In the future, the remaining differences between TROPOMI observations and WRF simulations could be reduced further by the use of precise temporal and monthly emission factors, emission heights and full chemistry to account for secondary sources and sinks of CO and NO$_2$.

TROPOMI inferred OH concentrations obtained from the least squares optimization method have been compared to the EMG method. For the summer and winter, the optimized OH concentrations differ by 10\% between two methods. These results confirm that urban emissions and OH concentrations can robustly be estimated from TROPOMI data. With our method, single TROPOMI overpasses can be used to estimate OH whereas EMG method requires averaging of urban NO$_2$ plume by wind sector. The iterative approach allows to test the factors i.e. $f_{\text{emis}}$, $f_{\text{oh}}$ and $f_{\text{bg}}$ obtained from optimization method, whereas EMG method does not allows such flexibility.

An important remaining uncertainty is the bias correction of the TROPOMI $\text{XNO}_2$ retrieval. Following the recommended procedure, the air mass factor AMF is recalculated by replacing the tropospheric AMF based on TM5, that is provided with the data, with WRF-chem. The TROPOMI $\text{XNO}_2$ bias correction increases the mixing ratio in the urban plume of Riyadh by 5 \% to 10 \% in summer and 25 \% to 30 \% in winter. The background is less affected by the bias correction. Without TROPOMI $\text{XNO}_2$ bias correction, the uncertainty in scaling factor for OH can vary up to 20 \% and NOx emission to 60 \% over Riyadh.
Appendix A: AMF recalculation

The air mass factor (AMF) used in the retrieval of TROPOMI XNO₂ has been re-calculated by replacing the tropospheric AMF, calculated from the NO₂ column simulated by TM5, with its WRF-chem equivalent, as described by Lamsal et al. (2010) and Boersma et al. (2016) using the following Eq. (15),

\[ M_{\text{trop, WRF}} = M_{\text{trop, TM5}} \times \frac{\sum_{l=1}^{L} A_{\text{trop,l}} x_{l,\text{WRF}}}{\sum_{l=1}^{L} L_{l}} \]  \hspace{1cm} (15)

where, \( M_{\text{trop, WRF}} \) and \( M_{\text{trop, TM5}} \) are the tropospheric air mass factors derived from WRF and TM5, respectively. \( A_{\text{trop,l}} \) is the tropospheric averaging kernel, ranging from the surface to the uppermost layer of the troposphere in the TM5 model (l). \( x_{l,\text{WRF}} \) is the equivalent NO₂ column density in model layer l, based on WRF. \( A_{\text{trop}} \) in Eq. (15) is derived using \( A_{\text{trop}} = A \times \frac{M}{M_{\text{trop}}} \), where M and \( M_{\text{trop}} \) are the total and tropospheric AMF’s respectively. Finally, the bias corrected NO₂ vertical column density is computed using,

\[ \text{NO}_2, \text{bias corrected} = \frac{M_{\text{trop, TM5}}}{M_{\text{trop, WRF}}} \times \text{NO}_2 \]

where, \( \text{NO}_2 \) is the TROPOMI tropospheric NO₂ vertical column density and \( \text{NO}_2, \text{bias corrected} \) is the bias corrected TROPOMI tropospheric NO₂ vertical column density.

Appendix B: XCO component wise optimization

The component wise optimization of XCO_{WRF} to estimate the emission and background of CO uses the following equation,

\[ \text{XCO}_{\text{TROPOMI}} = \text{XCO}_{\text{WRF}} + \Delta \text{XCO}_{\text{emis}} \times \frac{f_{\text{emis}}}{10} + \Delta \text{XCO}_{\text{Bg}} \times \frac{f_{\text{Bg}}}{10} \]

\[ \text{XCO}_{\text{WRF}} = \text{XCO}_{\text{emis}} + \text{XCO}_{\text{Bg}} \]

\[ \Delta \text{XCO}_{\text{emis}} = 0.10 \times \text{XCO}_{\text{emis}} \]

\[ \Delta \text{XCO}_{\text{Bg}} = 0.10 \times \text{XCO}_{\text{Bg}} \]

Here, \( \text{XCO}_{\text{TROPOMI}} \) is TROPOMI XCO, \( \text{XCO}_{\text{WRF}} \) is the WRF simulated XCO accounting for emissions and background CO, \( \text{XCO}_{\text{emis}} \) is the XCO contribution from the urban CO emission and \( \text{XCO}_{\text{Bg}} \) is the CAMS-derived XCO background. \( \Delta \text{XCO}_{\text{emis}} \) is the change in XCO due to emission and \( \Delta \text{XCO}_{\text{Bg}} \) is the change in the XCO background level.

Author contributions. SL performed the data analysis, data interpretation, and wrote the paper. SH supervised the study. SH, FKB, IA, MK and HACDG discussed the results. All co-authors commented on the paper and improved it.

Competing interests. The authors declare that they have no conflict of interest.

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