Understanding the influence of combustion on atmospheric CO$_2$ over Europe by using satellite observations of CO$_2$ and reactive trace gases

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Abstract. We assess how nitrogen oxides (NO$_x$=NO+NO$_2$), carbon monoxide (CO) and formaldehyde (HCHO) can be used as proxies to determine the combustion contribution to atmospheric carbon dioxide (CO$_2$) using satellite observations. We focus our analysis on 2018 when there is a full complement of column data from the TROPOspheric Monitoring Instrument (NO$_2$, CO, and HCHO) and the Orbiting Carbon Observatory-2 (CO$_2$). We use the nested GEOS-Chem atmospheric chemistry model to relate high-resolution emission inventories over Europe to these atmospheric data, taking into account scene-dependent averaging kernels. We find that that NO$_2$ and CO are the better candidates to identify incomplete combustion and fingerprints of different combustion sectors, but both have their own challenges associated with properly describing their atmospheric chemistry. The secondary source of HCHO from oxidation of biogenic volatile organic compounds, particularly over southern European countries, compromises its use as a proxy for combustion emissions. We find a weak positive correlation between the CO:CO$_2$ inventory ratio and observed column enhancements of $\Delta$CO:$\Delta$CO$_2$ (R<0.2), suggesting some consistency and linearity in CO chemistry and transport. However, we find a stronger negative correlation between the NO$_x$:CO$_2$ inventory ratio and observed column enhancements of $\Delta$NO$_2$:$\Delta$CO$_2$ (R<0.5), driven by non-linear photochemistry. Both of these observed ratios are described well by the GEOS-Chem atmospheric chemistry transport model, providing confidence of the quality of the emission inventory and that the model is a useful tool for interpreting these tracer-tracer ratios. Our results also provide some confidence in our ability to develop a robust method to infer combustion CO$_2$ emission estimates using satellite observations of reactive trace gases that have up until now mostly been used to study surface air quality.

1 Introduction

Mitigating the worst effects of future climate relies on our ability to reduce rapidly increasing atmospheric levels of gases emitted by human activities that effectively absorb outgoing infra-red radiation, and subsequently influence the warming of Earth’s surface. Atmospheric carbon dioxide (CO$_2$) is the predominant trace gas that continues to affect Earth’s contemporary global climate. Inventories of CO$_2$ that describe human activities, primarily derived from national-scale information about fuel
combustion and the amount of CO$_2$ released per unit of fuel burned, provide invaluable information the spatial and sectoral emission distributions. Assumptions embedded in the nationally-reported data and consequently the inventories can sometimes result in substantial uncertainties in the reported emissions. A complementary and independent approach to estimate CO$_2$ emissions is to use atmospheric CO$_2$ data that reflect the net cumulative result of emissions, atmospheric transport, and surface uptake. Quantifying the influence of fresh emissions on atmospheric CO$_2$ is an ongoing and pressing science objective. Here, we explore the relationships between CO$_2$ and reactive trace gases, co-emitted with CO$_2$ during combustion processes, to help isolate the combustion CO$_2$ from the biospheric fluxes.

Carbon-based fuels have historically dominated global energy use. Extracting energy from these fuels relies on breaking apart atomic bonds that form the molecular structure of the fuel, thereby releasing energy. This is achieved by combustion in which the fuel, composed primarily of hydrogen-carbon bonds, is oxidized by molecular oxygen (O$_2$). Generally, more energy can be released during combustion for fuels with a higher H:C ratio. The primary combustion products are CO$_2$ and water vapour, but as the combustion becomes more inefficient (e.g. insufficient O$_2$ to react completely with the fuel) a wider range of compounds are released, determined by the composition of the fuel being burned. For many combustion processes, air is used to provide O$_2$. While molecular nitrogen (N$_2$) in air does not take part in the combustion reaction, the high temperatures involved can thermally dissociate N$_2$ to facilitate the production of NO (and to a lesser extent NO$_2$) subject to the availability of O$_2$. Carbon monoxide (CO) is therefore a proxy for incomplete combustion of carbon-based fuel while the amount of NO$_x$ (NO+NO$_2$) released during combustion is also associated with the combustion temperature.

Recent work has highlighted that biofuel combustion can represent a significant fraction of fuel burned over Europe, typically 10% for cities and power plants over western and southern Europe but up to 50% over Nordic cities that use more biomass for domestic heating (Ciais et al., 2020). However, as discussed later, we do not distinguish between combustion of fossil fuel and biofuel, instead focusing on isolating the combustion contribution to CO$_2$. We also do not attempt to determine emissions from individual sectors, which is currently limited by the data density of atmospheric CO$_2$ and co-emitted trace gases released by specific combustion processes.

The impetus for our study is the burgeoning capacity to observe accurately gradients of atmospheric CO$_2$ using satellites and to attribute those signals to specific regional fluxes. To separate the combustion emission portion of that signal, a growing number of studies have used NO$_2$ as a proxy for fossil fuel combustion to help infer CO$_2$ emissions (Reuter et al., 2019; Liu et al., 2020; Hakkarainen et al., 2021; Ialongo et al., 2021) while others have demonstrated current capabilities to infer emissions of NO$_x$, e.g., Fortems-Cheiney et al. (2021a, b), that can be used to develop post hoc estimates of CO$_2$ via sector-based emission factors. The main advantage of using NO$_2$ as a tracer of combustion is its atmospheric e-folding lifetime, which ranges from hours to a day in the lower troposphere. Consequently, any major surface emissions will result in an observable plume close to the point of emission. The other advantage of using NO$_2$ is that it is observed by a range of current satellite instruments, although independent of current instruments observing CO$_2$. More importantly, CO$_2$ and NO$_2$ will be observed by the same instruments in the near future, including the Copernicus CO$_2$ Monitoring (CO2M) mission (Kuhlmann et al., 2021) and the Japanese Greenhouse Gases Observing Satellite Greenhouse gases and Water cycle (GOSAT-GW). The value of using satellite column observations of NO$_2$ as a global tracer of anthropogenic CO$_2$ emissions has recently been outlined by
Finch et al. (2021) who used a deep learning method to identify every NO2 plumes observed by the TROPOspheric Monitoring Instrument (TROPOMI) over a two-year period. They showed these plumes effectively mapped out most of the expected hotspots across the world, including large urban centres, oil and gas production, major power plants, and shipping routes.

Researchers have used CO as a proxy for incomplete combustion, e.g. (Kasibhatla et al., 2002; Palmer et al., 2006; Wang et al., 2009; Konovalov et al., 2014, 2016), which has similar advantages to using NO2 but has a longer e-folding lifetime (weeks to months depending on season and latitude) and a large, seasonally varying secondary source from the oxidation of volatile organic compounds (VOCs). Some of these shortcomings will be overcome as measurements progressively have the capability to resolve smaller spatial scales that are closer to the scale of the responsible point sources. Formaldehyde (HCHO) is another proxy for incomplete combustion (e.g., Fu et al. (2007a); Gonzi et al. (2011)) but the secondary source of HCHO and its uncertainty from the oxidation of biogenic VOCs, particularly over southern Europe (Curci et al., 2010), is sufficiently large to compromise this measurement from being used effectively to isolate combustion.

Recent studies have used satellite observations and emission inventories to analyze enhancements of atmospheric CO2 and co-emitted species (CO and NOx) over individual megacities (Hakkarainen et al., 2019; Berezin et al., 2013; Silva et al., 2013) and large urban areas (Silva and Arellano, 2017; Labzovskii et al., 2019; Lama et al., 2020; Park et al., 2021) but have not critically assessed the efficacy of using these data together to isolate the combustion contribution to CO2, which will eventually be needed to support more formal Bayesian inference methods. In this study, we explore the agreement between model and observed ratios of NO2, CO, and HCHO with CO2 by taking advantage of a new, high-resolution self-consistent European emission inventory for these gases (Super et al., 2020), a high-resolution chemistry transport model centred over Europe, and co-located satellite column measurements of CO2, NO2, CO, and HCHO. We combine this information to interpret model and observed ratios at the model grid-scale resolution and at the national scale over Europe.

In the next section, we describe the nested version of GEOS-Chem that we use to study the relationships between emissions and corresponding atmospheric ratios of CO2 and NO2 and CO over Europe. We also describe the satellite data we use to evaluate these model relationships. In Sect. 3 we present our analysis and critically assess the efficacy of these ratios to isolate the combustion contribution of CO2. We conclude the paper in Sect. 4.

2 Data and Methods

Here we describe the nested GEOS-Chem atmospheric chemistry transport model and the satellite data we use to explore the relationships between CO2, NO2, and CO. For the purposes of this study, we focus on contrasting summer (July) and winter (December) months during 2018 when there are data from all relevant satellite instruments.

2.1 GEOS-Chem atmospheric chemistry transport model

We use v12.6.1 of the GEOS-Chem 3-D atmospheric chemistry transport model (www.geos-chem.org) to describe the relationship between surface fluxes and atmospheric concentrations of CO, NO2, and CO2. We drive the GEOS-Chem model with
Goddard Earth Observing System, forward processing (GEOS-FP) meteorological analyses from the Global Modeling and Assimilation Office (GMAO) at NASA Goddard Space Flight Center.

For the experiments presented here, we use the nested version of GEOS-Chem to study atmospheric CO, NO\(_2\), and CO\(_2\) over Europe (broadly defined as 15° W–40° E, 30°–70° N, taking into account a buffer zone that helps to absorb any discontinuities associated with the coarser lateral boundary conditions), driven by the GEOS-FP meteorological analysis at its native spatial resolution of 0.25° (latitude) × 0.3125° (longitude). To provide time-dependent lateral boundary conditions for the nested model, we use a self-consistent version of GEOS-Chem at a coarser resolution of 4° (latitude) × 5° (longitude). For both models we use 47 hybrid-sigma levels from the surface to 0.01 hPa, of which 30 lie below the dynamical troposphere.

We use a GEOS-Chem simulation that includes HO\(_x\)-NO\(_x\)-VOC-ozone-halogen-aerosol tropospheric chemistry, which is coupled with stratospheric chemistry via the unified tropospheric-stratospheric Chemistry eXtension (Eastham et al., 2014). For our global run, we use anthropogenic emissions of chemically reactive gases (CO, CH\(_4\), NH\(_3\), NO\(_x\), SO\(_2\), non-methane volatile organic compounds (VOCs)), carbonaceous aerosols (including black carbon and organic carbon), and CO\(_2\), from the Community Emission Data System (CEDS) global emission inventory (Hoesly et al., 2018). Offline dust aerosol, lightning and soil NO\(_x\), biogenic VOCs and sea salt aerosols emissions (Weng et al., 2020) are used in both global and regional simulations. We use Global Fire Emissions Database version 4 (GFED4, http://globalfiredata.org) to describe pyrogenic emissions. The GFED inventory provides monthly dry matter emissions based on satellite observations of fire activity and vegetation coverage from MODIS (Moderate Resolution Imaging Spectroradiometer, van Marle et al. (2017)). The GEOS-Chem model calculates biomass burning emissions of trace gases and aerosols by applying vegetation-specific emission factors (Akagi et al., 2011) to the dry matter burned data.

For our nested European domain, we replace our global inventory anthropogenic emissions of CO, NO\(_x\), CO\(_2\) with the TNO-GHGco inventory (Netherlands Organization for Applied Scientific Research (TNO), greenhouse gas and co-emitted species emission database, Super et al. (2020)). This inventory is based on national emissions submitted to the United Nations Framework Convention on Climate Change for CO\(_2\) and to the European Monitoring and Evaluation Programme/Centre on Emission Inventories and Projections for NO\(_x\) and CO. National totals are distributed across individual countries on a 0.05° latitude × 0.1° longitude grid by using proxies such as the location of large industrial point sources, industrial area land cover maps for industrial emissions, and road networks derived from Open street map and Open transport map for road transport emissions (Super et al., 2020). Annual emissions are distributed in time using temporal emission profiles according to month, day of the week, and the hour of day for every GNFR (Gridded Nomenclature For Reporting) sector code, based on the sector specific emission data reported by each country, and long-term mean activity data and/or socio-economic characteristics. The TNO-GHGco inventory includes 16 sectors (code - sector): A - Public Power, B - Industry, C - Other Stationary Combustion, D - Figutives, E - Solvents, F - Road Transport (F1–F4), G - Shipping, H - Aviation, I - Off-road transport, J - Waste, K - Agriculture Live Stock and L - Agriculture Others. The TNO-GHGco inventory also separates fossil fuel and biofuel emissions of CO\(_2\) and CO. Emissions of NO\(_x\) are converted to units of kg NO\(_2\) m\(^{-2}\) s\(^{-1}\) for both the global (CEDS) and the regional (TNO-GHGco) inventories, and used as such in the GEOS-Chem model simulations. Consequently, we report NO\(_x\) emissions in the same units. We combine emissions from ten GNFR sectors (public power, industry, other stationary combustion, fugitives, all three...
types of road transport, shipping, aviation and off road transport) that involve the combustion of fossil fuel and biofuel to form combustion emissions. This step is in recognition that we cannot separate emissions from different sectors or the combustion of two fuel types, in terms of their contribution to observed atmospheric CO$_2$ and NO$_2$ columns.

Figure 1 shows the European distribution of TNO-GHGco combustion emission estimates (kg m$^{-2}$ s$^{-1}$) of CO$_2$, NO$_2$, and CO for July and December 2018. Combustion emissions are high over major cities (e.g., London, Paris, Madrid), industrial areas, and over major land and ocean transportation networks, as expected. Figure 2 shows monthly sector contributions to national total combustion emissions of CO$_2$, NO$_2$, and CO during July and December 2018 from the six highest emitting European countries, including the United Kingdom. In general, differences in the spatial distributions of emissions (Fig. 1) of these three trace gases and between July and December reflect the relative national importance of individual sectors (Fig. 2) that contribute to our combustion emission. Combustion emissions during December are generally higher than July, due primarily to a contribution from residential heating (C: Other Stationary Combustion) during the colder month (Fig. 2). We find that the six top CO$_2$ emitting countries for these three gases are consistently Germany, United Kingdom, France, Italy, Poland, and Spain. Germany is the largest emitter of NO$_x$, CO, and CO$_2$, except for CO during December 2018. The largest contributing sectors for these top CO$_2$ emitting countries for NO$_x$, CO, and CO$_2$ are usually public power, industry, residential heating and transportation (Fig. A1). In terms of fuel type, the majority of CO$_2$ emissions comes from fossil fuel combustion in both July and December for the top 14 CO$_2$ emitting countries in the domain (Fig. A2), while for CO more than 50% of the emissions during December comes from biofuel combustion for France, Italy, Spain, Austria, Sweden and Portugal (Fig. A3).

2.2 Satellite observations of CO$_2$, NO$_2$, and CO

We use dry-air column CO$_2$ (XCO$_2$) observations retrieved by the NASA Orbiting Carbon Observatory-2 (OCO-2), launched in July 2014 into a sun-synchronous orbit with a local equatorial crossing time of 13:30 in its ascending node (Eldering et al., 2017). The dimensions of the ground footprint of XCO$_2$ is nominally 1.25 km across track and $\approx$2.4 km along track, determined by the instrument field of view, the orbital speed of the satellite, and the measurement integration time. OCO-2 includes three spectrometers that measure two CO$_2$ bands (1.61 and 2.06 $\mu$m) and the O$_2$ A-Band (0.765 $\mu$m) (Crisp et al., 2004). For this study, we use OCO-2 Version 10 "Lite" (v10r) data, which is a bias-corrected and quality filtered Level 2 XCO$_2$ retrievals. First, the bias correction procedure maps the raw XCO$_2$ retrievals of the OCO-2 Level 2 algorithm to the best available estimate of XCO$_2$, using multi-model mean and TCCON measurements as training data sets (O’dell et al., 2018). Then, additional outlier filtering is applied to screen out low quality data based on parameters such as albedo, aerosol optical depth and cloud fraction (Crisp et al., 2021). On monthly timescales, 7 to 12 % of these measurements are considered clear-sky data (cloud and aerosol free) that pass all quality tests, with single measurement random errors between 0.5 and 1 ppm at solar zenith angles smaller than 70° (Eldering et al., 2017).

We also use satellite column observations of CO, NO$_2$, and HCHO from the TROPOMI, aboard the European Space Agency’s Sentinel-5 Precursor satellite. TROPOMI satellite was launched in 2017 into a sun-synchronous orbit with a local equatorial overpass time of 13:30 in its ascending node. TROPOMI is a nadir viewing instrument that contains four spectrometers that cover UV-Vis-NIR-SWIR wavelengths. With a cross-track swath of 2600 km and a high spatial ground footprint
resolution of $7 \times 7 \text{ km}^2$, TROPOMI has near-daily global coverage, subject to cloud-free scenes (Veefkind et al., 2012). Its operational level 2 trace gas data products include NO$_2$, CO, CH$_4$, O$_3$, HCHO, and SO$_2$). For the purposes of brevity, we refer the reader to dedicated studies that describe the retrieval of CO (Vidot et al., 2012; Landgraf et al., 2016), NO$_2$ (Boersma et al., 2010; Van Geffen et al., 2015; Lorente et al., 2017; Zara et al., 2018; Van Geffen et al., 2020), and HCHO (Platt and Stutz, 2008; Smedt et al., 2018). Tropospheric column retrieval biases of CO, NO$_2$, and HCHO are $<10\%$, 25–50\%, and 80\%, respectively. We use TROPOMI satellite retrievals that have a quality assurance flag with a value $>0.5$ for CO, $>0.75$ for NO$_2$ and $>0.5$ for HCHO, which removes cloud-covered scenes, partially snow/ice covered scenes, errors and problematic retrievals, as recommended by respective technical descriptions (https://sentinels.copernicus.eu/web/sentinel/technical-guides/sentinel-5p/products-algorithms, last accessed 14th July 2021)

3 Results

Here we report our analysis of TNO-GHGco emissions estimates of CO, NO$_x$, and CO$_2$ and their ratios, and the corresponding model atmospheric column concentrations and their ratios, which we compare with observed values calculated from OCO-2 and TROPOMI. We do not consider emission ratios that include HCHO because the direct emission is small compared to the contribution from methane and non-methane VOCs.

3.1 Inventory emission ratios of combustion NO$_x$:CO$_2$ and CO:CO$_2$

Figure 3 shows the inventory combustion emission ratios, described as mole fractions, of NO$_x$:CO$_2$ and CO:CO$_2$ during July and December 2018, corresponding to values shown in Fig. 1. These gridded ratios represent the net combustion efficiency of total emissions weighted by the influence of individual sectors. Generally, higher values of CO:CO$_2$ and NO$_x$:CO$_2$ denote a lower combustion efficiency, with higher NO$_x$:CO$_2$ values also associated with higher combustion temperatures. We find that the NO$_x$:CO$_2$ ratio is higher in July than December, but CO:CO$_2$ ratio is generally higher in December than July, which is reflected in the national mean values (Fig. 4). This is due to a larger contribution from residential heating (C: Other Stationary Combustion) to net emissions during December (Fig. 2) for which NO$_x$:CO$_2$ values (0.49–1.95) are lower and CO:CO$_2$ values (0.60–4.25) are generally higher than for other sectors (Fig. 4).

Figure 4 shows a heatmap of combustion emission mole ratios from eight major sectors (A: Public Power, B: Industry, C: Other Stationary Combustion, F1: Road Transport Gasoline, F2: Road Transport Diesel, F3: Road Transport LPG Gas, G: Shipping and H: Off Road, two sectors excluded here are D: Fugitives and H: Aviation) in the top 14 CO$_2$ emitting countries (in descending order). We find NO$_x$:CO$_2$ values are higher in shipping, off-road transport and diesel road transport. CO:CO$_2$ values are generally higher in off-road transport, residential heating and gasoline road transport. These ratios are assumed to be the same in different months of the year (Super et al., 2020), hence total combustion ratios in July and December only differ in the relative contribution from each sector (Fig. 2 and A1). In terms of NO$_x$:CO$_2$, Portugal, Norway and Spain are higher than neighbouring European countries, with Germany having the lowest value. In terms of CO:CO$_2$, Germany has a lower values than its neighbouring countries. The differences between countries for the two months reflect the relative importance of
individual sectors (Fig. 2, 4 and A1), in particular, the relative importance of transport, domestic heating and shipping emission. Closer inspection of Fig. 1 reveals hotspots of CO$_2$ that correspond to cities, large point sources, and transport network. These CO$_2$ hotspots manifest themselves as low values of the emission ratios (Fig. 3). Emissions in the marine troposphere are mainly due to ship exhaust, which emits more NO$_x$ and less CO than land-based sectors, resulting in the rapid gradient of the ratios between land and ocean.

Figure 4 also shows the corresponding nationwide mean combustion emission ratios of NO$_x$:CO$_2$ and CO:CO$_2$ during July and December 2018. Generally, CO:CO$_2$ ratios are higher than NO$_x$:CO$_2$ (note the different scaling factor), reflecting higher fossil fuel emission factors for CO than for NO$_x$. We find that national values of NO$_x$:CO$_2$ show a smaller dynamic range than corresponding values of CO:CO$_2$, particularly during July. This will have implications for using these ratios to determine combustion CO$_2$ emissions from individual countries, particularly those that are geographical neighbours. Portugal has the highest NO$_x$:CO$_2$ value in the domain, mostly determined by large industrial sources, shipping and off-road transportation. Norway has the highest value for CO:CO$_2$, mostly contributed by emissions from large industries, residential heating and off-road transportation.

### 3.2 Comparison of observed and model column variations of CO$_2$, CO, NO$_2$ and HCHO

Figure A4 shows typical column averaging kernels for OCO-2 CO$_2$, and TROPOMI CO, NO$_2$, and HCHO, which describe the sensitivity of the retrieved columns to changes in these gases as a function of altitude through the atmosphere. Model output, sampled at the time and location of each observation, is convolved with scene-dependent averaging kernels so it can be directly compared with observed columns. These averaging kernels generally show that the retrieved columns of all four gases are sensitive to varying degrees to changes in the lower troposphere where surface emissions have the largest impact. Differences between the vertical sensitivities may result in the misinterpretation of the ratios that we attempt to avoid by applying the kernels to the model output.

#### 3.2.1 Satellite column observations

Figure 5a, b and c shows monthly OCO-2 CO$_2$, TROPOMI NO$_2$ and CO columns during July 2018, gridded on the GEOS-Chem nested model $0.25^\circ \times 0.3125^\circ$ grid. We find that NO$_2$ has the largest spatial variability across Europe, mainly reflecting its much shorter atmospheric lifetimes compared with CO and CO$_2$. Tropospheric NO$_2$ columns are generally elevated over major cities (e.g., London, Paris, Madrid), conurbations (e.g., Manchester, Liverpool) and industrial areas (e.g., Po Valley, northern Italy) across Europe (Pope et al., 2018; Griffin et al., 2019; Finch et al., 2021). We do not consider December 2018 because the distribution of CO$_2$ used below to examine atmospheric trace gases ratios is too sparse due to cloudy scenes (Fig. A5).

Elevated columns of HCHO (Fig. A6) during July 2018 mainly reflect the oxidation of biogenic VOCs (Curci et al., 2010), particularly over southern European countries where Mediterranean vegetation are emitters of isoprene, which rapidly produces HCHO with a large molar yield (Palmer et al., 2006; Surl et al., 2018). There are also small direct emissions and contributions from industrial activity via the oxidation of anthropogenic VOCs (e.g., Po Valley). The rate at which HCHO is produced from
the oxidation of anthropogenic VOCs tends to be much larger than biogenic VOCs so that the resulting HCHO column is smeared over neighbouring grid boxes (Palmer et al., 2003; Abbot et al., 2003; Fu et al., 2007b). Given the limited use of HCHO as a tracer of combustion we do not pursue this tracer any further.

In contrast to TROPOMI that has a wide cross-track swath, OCO-2 data are sparse that also reflects much stricter filtering criteria. With the exception of large point sources, the large, inhomogeneous and slowly varying background values of CO precludes any meaningful attribution of elevated values to individual source regions without the use of an atmospheric transport model.

3.2.2 Satellite columns of CO₂, NO₂, and CO simulated by the GEOS-Chem model

We use the GEOS-Chem model (Sect. 2), driven by emission inventories (Sect. 2), to describe TROPOMI CO, NO₂, and OCO-2 CO₂. To compare model columns with observations, we first sample the model at the local time and location of each observation, map the modeled 3-D concentration field onto the satellite retrieval levels (20 for OCO-2 and 34 for TROPOMI), and then compute the modeled columns using scene-dependent averaging kernels. The GEOS-Chem model then become an intermediary that relates the TNO-GHGco emission inventories (Sect. 2) to the satellite observations.

For OCO-2 column CO₂, the equivalent model XCO₂\text{m} is calculated using:

\[
XCO₂\text{m} = XCO₂\text{a} + \sum_i \eta_i a_i (F(x) - y_{a,i}),
\]

where \(F(x)\) denotes the GEOS-Chem model that relates \(a\ priori\) flux estimates \(x\) to a scene-dependent CO₂ profile and the log-linear interpolation of those values on the model pressure levels to \(i\) pressure levels used by the XCO₂ retrieval algorithm, which uses its own \(a\ priori\) values denoted by \(y_a\) (corresponding to the the column XCO₂\text{a}). The pressure weighting function \(\eta_i\) includes the pressure intervals assigned to the satellite retrieval levels, and \(a_i\) denotes the scene-dependent averaging kernel that describes the sensitivity of the instrument to CO₂ as a function of altitude (e.g., Fig. A4). For TROPOMI columns of CO and NO₂, we use a similar method to translate the model into observation space. For NO₂, we consider only the tropospheric column. A detailed description of the method is given by Van Geffen et al. (2020).

Figure 5 shows OCO-2 and TROPOMI measurements and GEOS-Chem model values for CO₂, CO and NO₂ during July 2018. The model generally reproduces well the observed monthly spatial variations for CO₂ (\(R=0.67\)), CO (\(R=0.28\)) and NO₂ (\(R = 0.18\)) across Europe, but has a relative bias of -0.33%, -14.6% and +50.8%, respectively. In addition to capturing the major NO₂ column hotspots, e.g., southern England, Belgium, Netherlands and northern Italy, Fig. 5 shows that elevated NO₂ columns are more widespread in GEOS-Chem than TROPOMI. Higher model values over land likely reflect over-reporting of NOₓ emissions from rural areas of France, Germany, Poland and other eastern European countries, i.e., errors in emission inventory, temporal profile and errors in vertical mixing and lifetime of NOₓ against chemical oxidation. This positive model bias could also be due to the mismatch between emission timing and satellite overpass. Overestimation of NO₂ columns over the Bay of Biscay and the northern Mediterranean Sea reflect errors in the modelling of lightning (influencing the upper troposphere), vertical mixing over water, NOₓ lifetime, over-reporting of NO₂ shipping emission, and challenges in detecting surface concentrations of NO₂ from shipping (Laughner et al., 2016) (Fig. 1). The lifetime of NOₓ is of the order of hours and
changes with the chemical environment, including the NO\textsubscript{x} concentration itself, e.g. Laughner and Cohen (2019). GEOS-Chem fails to capture the highest values in TROPOMI NO\textsubscript{2} columns, especially over London, Paris, Madrid, Belgium, Netherlands and western Germany, which is due to some combination of underestimating emissions from these large urban sources, errors in the model description of NO\textsubscript{x} photochemistry, and the low sensitivity of averaging kernels to lower levels of the atmosphere (Fig. A4).

Figure 5 also shows there is better relative agreement between GEOS-Chem and TROPOMI for CO than for NO\textsubscript{2}, with a mean percentage bias of -14.6\% compared with 50.8\% for NO\textsubscript{2}, and a better spatial correlation. This reflects the longer atmospheric lifetime for CO (weeks during summertime) against oxidation by the hydroxyl radical so that atmospheric distributions are less influenced than NO\textsubscript{2} columns by immediate and local surface emissions. Observed variations of CO columns represent the sum of direct emissions from incomplete combustion and a secondary source from the oxidation of methane and non-methane VOCs (Duncan et al., 2007). The secondary source is usually assumed to be a diffuse source of CO because of the time it typically takes to produce CO. Using GEOS-Chem, we find that the secondary source is typically 10–20\% of the total CO source in winter months but in July can be as much as 75\% of the total CO source over Europe. This secondary source will therefore need to be considered if CO is to be used to isolate combustion CO\textsubscript{2}.

Large model bias for CO (negative) and NO\textsubscript{2} (positive), as reported above, limits our ability to infer directly combustion CO\textsubscript{2} from these data. However, the reasonably high spatial correlation between GEOS-Chem and TROPOMI (\(R=0.60\) for NO\textsubscript{2} and \(R=0.82\) for CO) provide us with some confidence in our ability to use enhancement ratios of column CO and NO\textsubscript{2} (\(\Delta\text{NO}_2\) and \(\Delta\text{CO}\)). To calculate these enhancements, we first determine latitude-dependent background values of the satellite data and then subtract those from the data. We calculate these background values (i.e., not directly influenced by urban enhancements) using monthly mean values over the remote Pacific Ocean (175\° W to 165\° W) in 10\° latitude bins. Mean monthly observed background levels of XCO\textsubscript{2}, column NO\textsubscript{2} and column CO over the remote Pacific Ocean are 390 ppm, 2.46 \(\mu\) mol m\textsuperscript{-2} and 20578 \(\mu\) mol m\textsuperscript{-2}, respectively. We compute the corresponding background levels for GEOS-Chem model by adjusting the satellite observed background levels with the model bias (domain mean) in Fig. 5, assuming that model bias is mostly caused by the background level (boundary condition simulated by the global full chemistry simulation). We subtract these values from the observations and the GEOS-Chem model to determine \(\Delta\text{XCO}_2\), \(\Delta\text{XCO}\) and \(\Delta\text{XNO}_2\). In the next section, we explore the relationship between \(\Delta\text{NO}_2\) and \(\Delta\text{CO}\) and the corresponding value of \(\Delta\text{CO}_2\).

### 3.3 Observed and model atmospheric variations of CO\textsubscript{2}, NO\textsubscript{2}, and CO columns

Figure 6 shows monthly means and the associated standard deviations of observed and model XCO\textsubscript{2}, NO\textsubscript{2}, and CO enhancements over Europe during July 2018 across the top 14 CO\textsubscript{2} emitting countries. During July 2018, observed XCO\textsubscript{2} enhancements over our European study domain have a mean enhancement of 14.8±1.86 ppm. Belgium, Spain and Portugal have the highest XCO\textsubscript{2} enhancement values, but differences between countries and variations within each country are relatively small. Within our European study domain, observed column NO\textsubscript{2} and column CO enhancements have mean values of 52.3±33.6 pptv and 22.0±7.4 ppbv during July 2018, respectively. Countries with the highest column NO\textsubscript{2} enhancements are Belgium, Netherlands, Germany and UK, while differences in column CO enhancement between countries are relatively small. Model en-
hancements agree reasonably well with observed enhancements on national spatial scales ($R=0.85$ for CO$_2$, $R=0.78$ for NO$_2$, $R=0.96$ for CO), except for column NO$_2$ enhancement in Netherlands, Belgium and Ireland (relative bias $>20\%$).

Figure 7 shows observed and model $\Delta$XNO$_2$:$\Delta$XCO$_2$ and $\Delta$XCO: $\Delta$XCO$_2$ ratios during July 2018. We find that observed monthly mean $\Delta$XNO$_2$:$\Delta$XCO$_2$ show higher values over Germany, Netherlands, Belgium, Northern Italy, UK and Poland, corresponding with the hotspots of NO$_2$ column measurements. The same ratios simulated by GEOS-Chem show high values over the same countries and France, Serbia, Romania and Bulgaria. We generally find that values of $\Delta$XCO:$\Delta$XCO$_2$ show higher values over Eastern Europe than western European countries, both in observed and model values. These ratios are the atmospheric equivalent of the ratios determined by the emission inventory shown in Fig. 3. We find that model fails to capture $\Delta$XNO$_2$: $\Delta$XCO$_2$ hotspots such as Madrid and Paris due to failure to capture hotspots in column NO$_2$ concentration in Figure 5. To understand the relationship between the emissions and corresponding atmospheric values, we correlate the two sets of ratios at grid cell level and at national level for July 2018.

Figure 8a show the relationships between the national emissions ratios of CO:CO$_2$ and NO$_2$:CO$_2$ (Fig. 4) and the corresponding model and observed atmospheric ratios of $\Delta$XCO:$\Delta$XCO$_2$ and $\Delta$XNO$_2$: $\Delta$XCO$_2$. We find only a weak positive correlation ($R=0.15$) between the emission-based ratios, reflecting the importance of different sectors (with varying emission factors) within countries across Europe. Figure 8b shows observed and model national mean values for $\Delta$XNO$_2$: $\Delta$XCO$_2$ and $\Delta$XCO: $\Delta$XCO$_2$ ratios. We find that, on national level, both observed and model ratios are positively correlated, with correlation coefficients of $R=0.60$ and $R=0.66$, respectively. This suggests both observed and model columns reproduce the positive relationship based on the inventory estimates. The comparatively strong correlations found for the observed and model atmospheric ratios reflect the atmospheric mixing of spatially heterogeneous emissions. Observed and model slopes from the linear regression of the the two ratios are 5.90 and 2.57 (unitless), respectively. Slope values reflect the co-enhancement of column NO$_2$ with CO, with the model having a smaller enhancement of NO$_2$ per unit of column CO enhancement. This suggests that the inventory is in error and that the NO$_2$:CO should be smaller, and/or there is a larger NO$_2$ chemical loss than we describe in GEOS-Chem (or a smaller chemical loss of CO).

Figure 9 shows the model and observed relationship between the emission-based ratios of NO$_2$:CO$_2$ and CO:CO$_2$ and the corresponding atmospheric ratios of $\Delta$XNO$_2$: $\Delta$XCO$_2$ and $\Delta$XCO: $\Delta$XCO$_2$. Figures A7 and A8. show the grid-cell resolution analysis for the nine countries with the most amount of data. Figure 9 shows good agreement between model and measurements in terms of the variation of the atmospheric ratio. The situation for the NO$_2$-based ratio (Fig. 9a) is more encouraging. Model and observed $\Delta$XNO$_2$: $\Delta$XCO$_2$ ratio are both negatively related to the inventory based NO$_2$:CO$_2$ ratio, with correlations of -0.69 for GEOS-Chem and -0.50 for the satellite observations. At the grid-scale resolution, the United Kingdom, Italy and Norway demonstrate the similar negative correlation. These countries do not differ significantly from other countries in terms of relative contribution from different sectors (Fig. 2 and Fig. A1), or national mean combustion ratios (Fig. 4). Hence, the negative relationships between the inventory-based and atmospheric-based ratios reflect a strong non-linearity between NO$_2$ emissions and NO$_2$ concentration. This is most likely due to NO$_x$ photochemistry, since other factors are generally similar between our CO and NO$_2$ based ratios, e.g., meteorology. This strong negative correlation in NO$_2$ based ratios requires further investigation to understand how to best use this information to interpret combustion CO$_2$. Nevertheless, good (negative) correlations between
emission-based ratios and the observed and model atmospheric column ratios could indicate the feasibility to infer combustion
CO$_2$ from satellite measurements and GEOS-Chem model using co-emitted CO and NO$_x$.

For CO (Fig. 9b), there is only a weak correlation between combustion CO:CO$_2$ and $\Delta$XCO:$\Delta$XCO$_2$ for both GEOS-Chem and the satellite observations, at national (Fig. 9) and at grid-cell resolutions (Fig. A8). Generally, we find there is more national variation between the inventory-based CO:CO$_2$ ratio than the corresponding atmospheric ratio, which is due to atmospheric mixing of CO that has an e-folding lifetime much longer than the transport time over Europe. Similar to the NO$_2$ based ratios, GEOS-Chem overestimates the column enhancement ratio (Fig. 7b and d).

4 Concluding remarks

We assessed how three reactive trace gases, nitrogen dioxide (NO$_2$), carbon monoxide (CO) and formaldehyde (HCHO), can be used as proxies to determine the combustion contribution to atmospheric CO$_2$ in July and December, two contrasting months in terms of sector emissions and photochemical environment, in 2018. Our choice to focus on combustion emissions reflects varying contributions of biofuel combustion to national CO$_2$ emission budgets across Europe. We use satellite column measurements of CO$_2$ from the NASA Orbiting Carbon Observatory (OCO-2) and satellite tropospheric column data products of CO, NO$_2$, and HCHO from the European TROPospheric Ozone-Monitoring Instrument (TROPOMI) aboard Sentinel-5P. We focus our analysis on 2018 when there is a full year of data from OCO-2 and TROPOMI. We use a nested atmospheric chemistry transport model (GEOS-Chem) driven by self-consistent combustion emissions of CO$_2$, nitrogen oxides (NO$_x$), CO, and volatile organic compounds (VOCs) that are precursors to HCHO.

We found that HCHO as a tracer of incomplete combustion is compromised during the summer by biogenic VOC emissions, particularly over the Mediterranean, and during the winter when the lifetimes of parent anthropogenic VOCs are too long to relate elevated HCHO columns to anthropogenic activity. Based on our assessment, we conclude that HCHO is unlikely to play a substantive role in quantifying the combustion contribution to CO$_2$.

Combustion emission estimates for CO$_2$, CO and NO$_x$ in July and December 2018 show different spatial distribution due to different dominating emission sectors for these trace gases and also in contrasting months, which resulted in spatial variation in CO:CO$_2$ and NO$_x$:CO$_2$. Hence, we find that NO$_2$ and CO are the better proxies for combustion, but both have their own challenges. When using satellite measured $\Delta$XNO$_2$ and $\Delta$XCO as a way to identify characteristic $\Delta$X:$\Delta$XCO$_2$ ratios (where X = NO$_2$ or CO and $\Delta$ denotes elevated values above a regional background value) that correspond to combustion, we find that photochemistry must be taken into account. In the case of NO$_2$, rapid cycling with NO (the sum of which is known as NO$_x$) must be considered, which varies with latitude and season. Similarly, any additional production or loss of NO$_x$ reservoir species, e.g., peroxyacyl nitrate (PAN), could significantly alter the ratio. CO is made up of direct anthropogenic and biomass burning emissions, in addition to a secondary production source from the oxidation of VOCs and methane that can contribute up to 75% of the total source in summer months. Neglecting atmospheric chemistry will compromise the ability to use these tracers to determine combustion CO$_2$. 

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When investigating corresponding ratios in reported emission data, we find a weak positive relationship between CO:CO$_2$ and NO$_x$:CO$_2$ ratios on national levels ($R<0.4$), which suggests that combustion efficiency in terms of co-emitting CO and NO$_2$ are weakly correlated within a country. We also find a weak positive correlation between emission-based ratio CO:CO$_2$ and satellite observed column enhancement $\Delta$XCO:$\Delta$XCO$_2$ ($R<0.2$), which suggests the consistency and linearity in CO chemistry and transport. Conversely for NO$_2$, we find a stronger negative correlation between NO$_x$:CO$_2$ and enhancement $\Delta$XNO$_2$:XCO$_2$ ($R<0.50$), which suggests nonlinearity in NO$_x$ photochemistry. Both of these relationships are described reasonably well (similar R values) by the atmospheric chemistry transport model, providing confidence that the model is a useful tool for interpreting these tracer-tracer ratios.

Some of the challenges we faced in our study, in particular the coincidence of TROPOMI and OCO-2 data, will be partly addressed with upcoming missions that measure both NO$_2$ and CO$_2$. These missions currently include the Copernicus CO$_2$ Monitoring (CO2M) mission (Kuhlmann et al., 2021) and the Japanese Greenhouse Gases Observing Satellite Greenhouse gases and Water cycle (GOSAT-GW). The proposed CO2M mission is temporally staggered three-satellite constellation, resulting in better spatial coverage of the globe per day than currently provided by OCO-2. Developing virtual constellations, i.e. integrating measurements from independent missions, is an ongoing key objective but relies on rigorous calibration of data collected by different sensors. Another current challenge is understanding how to use together CO$_2$ and reactive trace gases to infer robust combustion emission estimates of CO$_2$. Our work has shown that even over Europe, where our knowledge of emissions should be relatively good compared to many parts of the world, we find there are sometimes large differences between model photochemical calculations and satellite observations. Addressing this issue will need an integrated approach that draws together the atmospheric chemistry and carbon cycle communities.

**Code and data availability.** GEOS-Chem model code and input data are free and available from the GEOS-Chem website (www.geos-chem.org). NASA OCO-2 retrievals were produced by the OCO-2 project at the Jet Propulsion Laboratory, California Institute of Technology, and obtained from the OCO-2 data archive maintained at the NASA Goddard Earth Science Data and Information Services Center. TROPOMI NO$_2$, CO and HCHO data are freely available on TROPOMI project website (http://www.tropomi.eu/data-products/)

**Author contributions.** MS and PIP designed experiments and wrote the paper. MFL and LF contributed to the processing and analysis of satellite measurements. IS, SNCD and HACdvdG provided the TNO-GHGco emission inventory and advice on its usage. All co-authors helped to revise the paper.

**Competing interests.** The authors declare that they have no conflict of interest.
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Figure 1. Combustion emissions of (left columns) CO$_2$, (middle columns) NO$_x$, and (right columns) CO (kg m$^{-2}$ s$^{-1}$) over our European study domain from the TNO-GHGco inventory during (top row) July and (bottom row) December, 2018, described on the original 0.05° latitude × 0.1° longitude horizontal resolution.
Figure 2. Sector contributions to national total combustion emissions (Tg month$^{-1}$) of CO$_2$, NO$_x$ and CO for the top six CO$_2$ emitting countries across our European study domain. The two columns reported for each country denote values for (left) December and (right) July, 2018.

Figure 2. Sector contributions to national total combustion emissions (Tg month$^{-1}$) of CO$_2$, NO$_x$ and CO for the top six CO$_2$ emitting countries across our European study domain. The two columns reported for each country denote values for (left) December and (right) July, 2018.
Figure 3. Spatially distribution of combustion emission mole ratios (mole/mole) of (top row) NO$_x$:CO$_2$ and (bottom row) CO:CO$_2$ from the TNO-GHGco inventory during (left column) July and (right column) December 2018, described on the original 0.05° latitude × 0.1° longitude horizontal resolution.
Figure 4. Heatmap of national-scale combustion emission mole ratios (mole/mole) for (a) NO$_x$:CO$_2$ and (b) CO:CO$_2$ from eight major sectors in the top 14 CO$_2$ emitting countries: A: Public Power; B: Industry; C: Other Stationary Combustion; F1: Road Transport Gasoline; F2: Road Transport Diesel; F3: Road Transport LPG Gas; G: Shipping; and I: Off Road) and two contrasting months (July and December). Sector D - Fugitive and H - Aviation are excluded due to relatively smaller contribution to the total combustion emission in the domain.
Figure 5. Satellite measurements and GEOS-Chem model columns of CO$_2$ (ppm), CO ($\mu$mol m$^{-2}$), NO$_2$ ($\mu$mol m$^{-2}$), described on 0.25° latitude $\times$ 0.3125° longitude resolution. The top row shows observed distributions from OCO-2 and TROPOMI, the middle row shows the corresponding GEOS-Chem distributions, and the bottom row shows GEOS-Chem minus observed distributions. Domain-mean values and units are shown in the titles of each panel.
Figure 6. Observed and GEOS-Chem monthly mean and standard deviation of (a) $\Delta X_{\text{CO}_2}$ (ppm), and (b) $\Delta \text{NO}_2$ (ppt) and (c) $\Delta \text{CO}$ columns (ppb) during July 2018 for the top 14 CO$_2$ emitting countries, in descending order. Correlation coefficients from linear regression are shown on sub-panel title.
Figure 7. Observed and GEOS-Chem monthly mean European distributions of (left) $\Delta X_{\text{NO}_2}:\Delta X_{\text{CO}_2}$ and (right) $\Delta X_{\text{CO}}:\Delta X_{\text{CO}_2}$ ratios during July 2018, described on 0.25° latitude × 0.3125° longitude resolution.
Figure 8. European country relationships of a) emission inventory ratios of CO:CO$_2$ and NO$_x$:CO$_2$ and b) (blue) observed and (red) GEOS-Chem ratios of $\Delta$XNO$_2$:XCO$_2$ during July 2018. Correlation coefficients and slopes from linear regression are shown inset of each panel.
Figure 9. European country relationships of inventory estimates of combustion NO\textsubscript{x}:CO\textsubscript{2} and CO:CO\textsubscript{2} and observed and GEOS-Chem atmospheric ratios of $\Delta$XNO\textsubscript{x}:$\Delta$XCO\textsubscript{2} and $\Delta$XCO:$\Delta$XCO\textsubscript{2}. Correlation coefficients and slopes from linear regression are shown inset of each panel.
Figure A1. Sector percentage contribution to national total combustion emission of CO₂, NOₓ and CO in (left) December and (right) July 2018 for six European countries.
Figure A2. Fuel type contribution to national total combustion emissions (Tg month$^{-1}$) of CO$_2$ and CO in (left) December and (right) July 2018 for 14 European countries.

Figure A2. Fuel type contribution to national total combustion emissions (Tg month$^{-1}$) of CO$_2$ and CO in (left) December and (right) July 2018 for 14 European countries.
Figure A3. Fuel type percentage contribution to national total combustion emission of CO₂ and CO in (left) December and (right) July 2018 for 14 European countries.
Figure A4. Example averaging kernels of NO$_2$, CO, HCHO from TROPOMI and CO$_2$ from OCO-2, on July 5$^{th}$, 2018 over London, UK.
Figure A5. Monthly mean dry air column concentration of CO\textsubscript{2} (XCO\textsubscript{2}) retrieved by OCO-2 during (left) July and (right) December 2018. Values are gridded on the GEOS-Chem model spatial resolution of 0.25°(latitude) × 0.3125°(longitude).

**Figure A5.** Monthly mean dry air column concentration of CO\textsubscript{2} (XCO\textsubscript{2}) retrieved by OCO-2 during (left) July and (right) December 2018. Values are gridded on the GEOS-Chem model spatial resolution of 0.25°(latitude) × 0.3125°(longitude).
Figure A6. Monthly mean column density of CO, NO$_2$ and HCHO observed by TROPOMI in (top row) July and (bottom row) December 2018, only data points with $q_{\text{value}} > 0.75$ are selected. Values are gridded on the GEOS-Chem model spatial resolution of 0.25° (latitude) × 0.3125° (longitude).
Figure A7. Relationship between combustion emission NO$_x$:CO$_2$ and satellite measured ΔXNO$_2$:ΔXCO$_2$ (blue) and GEOS-Chem simulated ΔXNO$_2$:ΔXCO$_2$ (red) for nine European countries. Correlation coefficient value of simple linear regression analysis is shown on the sub-panel figure.
Figure A8. Relationship between combustion emission CO:CO$_2$ and satellite measured $\Delta$XCO:$\Delta$XCO$_2$ (blue) and GEOS-Chem simulated $\Delta$XCO:$\Delta$XCO$_2$ (red) for nine European countries. Correlation coefficient value of simple linear regression analysis is shown on the sub-panel figure.