Towards sector-based attribution using intra-city variations in satellite-based emission ratios between CO\textsubscript{2} and CO

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Abstract. Carbon dioxide (CO\textsubscript{2}) and air pollutants such as carbon monoxide (CO) are co-emitted by many combustion sources. Previous efforts have combined satellite-based observations of multiple tracers to calculate their emission ratio (ER) for inferring combustion efficiency at regional to city scale. Very few studies have focused on burning combustion efficiency at the sub-city scale or related it to emission sectors using space-based observations. Several factors are important for deriving and interpreting spatially-resolved ERs from asynchronous satellite measurements including 1) variations in meteorological conditions induced by different given mismatch in satellite overpass times, 2) differences in vertical sensitivity of the retrievals (i.e., averaging kernel profiles), and 3) interferences from the biosphere and biomass burning, and 4) mismatch in the daytime variation of CO and CO\textsubscript{2} emissions. In this study, we extended an established emission estimate approach to arrive at spatially-resolved ERs based on retrieved column-averaged CO\textsubscript{2} (XCO\textsubscript{2}) from the Snapshot Area Mapping (SAM) mode of the Orbiting Carbon Observatory-3 (OCO-3) and column-averaged CO from the TROPOspheric Monitoring Instrument (TROPOMI).

To evaluate the influence of the confounding factors listed above and further explain the intra-urban variations in ERs, we leveraged a Lagrangian atmospheric transport model and an urban land cover classification dataset and reported ER\textsubscript{CO} from the sounding-level to the overpass- and city-level. We found that the difference in the overpass times and averaging kernels between OCO and TROPOMI strongly affect the estimated spatially-resolved ER\textsubscript{CO}. Specifically, a time difference of > 3 hours typically led to dramatic changes in the wind direction and shape of urban plumes and urban plume shapes and thereby making the calculation of accurate sounding-specific ER\textsubscript{CO} difficult. After removing those such cases from consideration and applying a simple plume shift method when necessary to account for changes in wind direction and speed, we discovered significant contrasts in combustion efficiencies between 1) two megacities versus two industry-oriented cities and 2) different regions within a city, based on six to seven nearly-coincident overpasses per city.

Results suggest that the combustion efficiency for heavy ER\textsubscript{CO} impacted by the industry in Los Angeles is slightly lower than its the overall city-wide value (< 10 ppb-CO / ppm-CO\textsubscript{2}). In contrast, ERs related to the heavy industry in Shanghai are found to be is much higher than Shanghai’s city-mean and more aligned with city-means of the two industry-oriented Chinese cities (approaching 20 ppb-CO / ppm-CO\textsubscript{2}). Although investigations based on a larger number of satellite overpasses are needed, our first analysis—unique approach (without using sector-specific information from emission inventories) provides
guidance for estimating intra-city gradients in combustion efficiency from future assessing combustion efficiency within a city based on future satellite missions, such as those that will map column CO$_2$ and CO concentration simultaneously with high spatiotemporal resolutions.

1 Introduction

Home to more than half of the total global population, urban areas have been expanding, especially for-in Asia and Africa with an urbanization rate of 1.3% and 1.1% yr$^{-1}$ between 2015 and 2020 (World Urbanization Prospects 2018). Urban regions are also responsible for a significant amount of anthropogenic emissions of greenhouse gases (GHG) and air pollutants into the atmosphere including carbon dioxide (CO$_2$), methane, carbon monoxide (CO), and nitrogen oxides (Duncan et al., 2016; Lin et al., 2018; Super et al., 2017; Plant et al., 2019). To monitor the abundance of a number of atmospheric species in a globally-consistent manner, satellite observations have become indispensable in past years (Yokota et al., 2009; Crisp et al., 2012; Veefkind et al., 2012). For example, carbon-monitoring satellites such as the Orbiting Carbon Observatory-2 (OCO-2, Crisp et al., 2012) have made the quantification of city-scale CO$_2$ emissions and emission trends possible (e.g., Hedelius et al., 2018; Ye et al., 2020; Wu et al., 2020; Shekhar et al., 2020; Lei et al., 2021). Quantifying the spatial gradient of atmospheric concentrations and relating the gradient to emissions within the city domain becomes the next critical yet challenging task. Understanding such spatial heterogeneity in emissions and the environmental consequences can support better decisions in urban planning and pinpointing hotspots for emission mitigation.

To reduce emissions of greenhouse gases and air pollutants, targeting the efficiency during combustion activities given the co-benefit between GHG reduction and improved air quality at various scales (Zhang et al., 2017), controlling the consumption of fossil fuels altogether is the key. Such efficiency Efficiency associated with various combustion activities is linked to the underlying combustion processes and conditions (e.g., oxygen-to-fuel ratio and temperature). For example, the amount of CO$_2$ emitted from coal-fired power plants varies with thermal and pressure conditions, the type of fuel consumed, the technology deployed, and the service duration of power plants (Yuan and Smith, 2011). Modern power generation with distinct scrubbing technology are often regarded as “clean” emitters leading to minimal CO and NO$_x$ enhancements (Lindenmaier et al., 2014). The commonly-used approach in estimating combustion efficiency is to combine atmospheric observations of multiple trace gases. Benefit from the cancellation of the errors in describing the atmospheric transport that carries tracers to the measurement site, the and report the ratio of the total or excess measured concentrations (above a defined background value) between tracers are reported (Silva and Arellano, 2017; Reuter et al., 2019; Park et al., 2021). Such tracer-to-tracer ratio calculation has the benefit that errors in describing the atmospheric transport that carries tracers to the measurement site can be cancelled. A few notable studies further utilized their-derived emission ratios (ERs) from ground or airborne measurements to infer sector-specific emission signals (Wennberg et al., 2012; Lindenmaier et al., 2014; Nathan et al., 2018; Tang et al., 2020).

CO and NO$_x$ often serve as tracers for anthropogenic CO$_2$ due to their overlapping sources of combustion common sources (e.g., Palmer et al., 2006; Wunch et al., 2009; Hedelius et al., 2018). Analyzing remotely-sensed NO$_x$ plumes with relatively
short lifetime can help identify local fossil fuel CO\textsubscript{2} (FFCO\textsubscript{2}) sources that would otherwise be difficult to detect (Reuter et al., 2019; Fujinawa et al., 2021). While at the same time, such reactivity raises the requirement of accurately accounting for chemical transformation and complicates the interpretation of emission signals or ERs from NO\textsubscript{x} observations (Lama et al., 2020; Hakkarainen et al., 2021). CO with a much longer lifetime, on the other hand, CO\textsubscript{2} is much easier to interpret and more likely to be found during incomplete combustion. The emission ratio of CO to CO\textsubscript{2} (ER\textsubscript{CO}) is usually estimated from sparse ground-based measurements within a city (Bares et al., 2018; Chandra et al., 2016; Lindenmaier et al., 2014) and from satellites at the city scale (Park et al., 2021; Silva and Arellano, 2017). Sector-specific activities and ER\textsubscript{CO} such as from the traffic sector have been diagnosed by limited but valuable tunnel studies (Ammoura et al., 2014; Bradley et al., 2000; Popa et al., 2014).

**Figure 1.** ER\textsubscript{CO} [ppb ppm\textsuperscript{−1}] associated with specific processes (a) and ER\textsubscript{CO} integrated over the entire city/region (b) summarized from previous studies. The x-axis indicates the time these estimates were made except for Akagi et al. (2011). 2011 was simply chosen for x-axis since the paper was published in 2011. The error bars represent the uncertainties in estimated ERs and transparent rectangle indicates the range of ERs over multiple years. Paper citations are omitted from the figure but included in Appendix A. ERs related to biomass burning and shipping sectors are derived using EF\textsubscript{CO} and EF\textsubscript{CO\textsubscript{2}}. The range of overpass-specific ER\textsubscript{CO} estimates for Shanghai, LA, Baotou, and Zibo derived from our study are added to the figure (dashed black box).

We performed a literature search on ER\textsubscript{CO} derived from observations (Appendix A) and summarize their values in Fig. 1. Combustion efficiency fluctuates 1) over time (e.g., Turnbull et al., 2011b), likely explained by technological
improvements and 2) between sub-sectors, e.g., gasoline vs. diesel vehicles or moving vs. congestion traffic (Westerdahl et al., 2009; Popa et al., 2014). Despite differences in measurement platforms and analyzing analysis approaches, the observed urban-integrated ER_{CO} values, especially for those in Europe and the United States, are well constrained within the range of 4 to 15 ppb ppm^{-1} (Fig. 1b). ER_{CO} for biomass burning and shipping sectors are estimated based on fuel-specific emission factors, i.e., ER_{CO} = EF_{CO} / EF_{CO2} with proper unit conversions, where emission factor EF_{X} indicates the emission of gas X per kg of fuel burned.

associated with specific processes (a) and integrated over the entire city/region (b) summarized from previous studies. X axis indicates the time these estimates were made except for Akagi et al. (2011). 2011 was simply chosen for x-axis since the paper was published in 2011. The error bars represent the uncertainties in estimated ERs and transparent rectangle indicates the range of ERs over multiple years. Paper citations are omitted from the figure and included in Appendix A. ERs related to biomass burning and the shipping sectors are derived using emission factors of CO and. The range of the overpass specific estimates for Shanghai, LA, Baotou, and Zibo derived from this work are also added to the figure (dashed black box).

The variability in observation-derived ERs among different combustion processes and sectors (Fig. 1a) hinders the generalization and representation of gridded ERs. Many When estimating fossil fuel emissions from a bottom-up emission inventories simulate EF emissions using activity data for spatially allocating sector-based EFs. perspective, most inventories rely on activity data and may involve prior knowledge of emission factors (Gurney et al., 2019; Solazzo et al., 2021). One notable example is Hestia, a high-resolution inventory for the US, which estimates CO\_2 emissions of non-point sources based upon CO emissions from the National Emission Inventory ...and with EFs and carefully evaluates their adopted EFs (Gurney et al., 2019). However, constructing inventories for the entire globe is data demanding and challenging because accurate when constructing emission inventories across regions/nations, the large variability in ERs across combustion processes, sectors, years, and regions (as seen in Fig. 1a) makes the choice of EFs extremely challenging. Accurate bottom-up estimates require emission estimates require accurate activity data and EF_{X} that naturally vary with combustion conditions (e.g., temperature, fuel load, oxygen level) and are generally not well known especially over data-scarce regions. To our knowledge, only a few global inventories, such as the Emissions Database for Global Atmospheric Research (EDGAR, Solazzo et al., 2021), offer global anthropogenic CO and CO\_2 emissions. Considering the challenge in approximating ERs, the certain knowledge derived from atmospheric observations may 1) complement inventory-based ERs (e.g., CO:NO\_x ratio in Lama et al., 2020) and 2) facilitate the emission constraint for a desired species, gas usually with relatively larger uncertainties (Wunch et al., 2009; Palmer et al., 2006; Wang et al., 2009; Brioude et al., 2012; Nathan et al., 2018). Such prior success motivates us to derive ERs from achievements motivate us to examine ERs using satellite observations of multiple tracers.

Most previous studies have existing studies focused on quantifying an integrated ER for the whole city or region. As We take a step forward, we to zoom into an urban area and leverage spatially-resolved satellite observations. Intra-city variations in the satellite-based concentration of a specific air pollutant like NO\_x have been examined analyzed and linked to societal inequality such as of-inequalities regarding the income and educational attainment (Demetillo et al., 2021; Kerr et al., 2021). Yet, no one has attempted to study the intra-urban gradient in combustion efficiency from space and connect such relate such a gradient to a specific combustion process sector. This is now possible by virtue of the Orbiting Carbon Observatory-3 (OCO-3) mounted
on the International Space Station (ISS) that can sample a city-landscape during the Snapshot Area Mapping (SAM) mode (Eldering et al., 2019; Taylor et al., 2020; Kiel et al., 2021). In this effort to arrive at spatially-varying ERs from sensors with asynchronous orbits, we must account for several factors that have not been thoroughly investigated. These include 1) variations in meteorological conditions and emission patterns during different overpass times, 2) discrepancies in the vertical sensitivity of the retrievals (i.e., averaging kernel or AK profiles), and 3) interference from non-anthropogenic sources and sinks, especially from the biosphere.

Motivated by the gaps in prior literature, we conducted an analysis to In this study, we explore the spatial distribution of ER\textsubscript{CO} in four urban areas mainly using XCO\textsubscript{2} observations from OCO-3 and XCO observations from the TROPOspheric Monitoring Instrument on board the Sentinel-5 Precursor (TROPOMI; Veefkind et al., 2012). To avoid relying on prior sectoral information on sector-specific information of ER\textsubscript{CO} from emission inventories, we adopt the urban land cover data from the high-resolution World Urban Database and Access Portal Tools (WUDAPT; Ching et al., 2018). WUDAPT offers the so-called Local Climate Zone (LCZ) that takes into account building structures of the building structure/spacing and along with vegetation coverage (Stewart and Oke, 2012), which can shed light on localized infrastructure within the city-the urban infrastructure.

Our work seeks to answer the following two questions.

1. Is it possible to accurately quantify spatially-resolved ER\textsubscript{CO} from asynchronous satellite measurements?

2. Can the combustion efficiency for a given sector be determined without using prior emission inventories?

In Section Sect. 2, we describe the satellite data and methodology for obtaining emissions, ER\textsubscript{CO}, and associated uncertainties. In Section Sect. 3, we present the results on how intra-city variations in ER\textsubscript{CO} (including ER\textsubscript{CO} tied to heavy industry areas in a megacity) and its sensitivity to several interference factors. In Section how multiple factors may interfere in deriving ER\textsubscript{CO}. In Sect. 4, we discuss the implication and limitation implications and limitations of this analysis.

2 Data and methodology

We targeted two types of cities: 1) industry- and energy-oriented cities (Baotou, China and Zibo, China), and 2) megacities with more diverse emission sectors (Shanghai, China and Los Angeles, US). The four cities are selected considering the amount and quality of XCO\textsubscript{2} data from OCO-3 SAMs and TROPOMI XCO data. The two industry- and energy-oriented cities in China are selected given their considerable large amount of metal production plants for aluminum or iron and steel (Global Energy Infrastructure Emission Database, GID; Wang et al., 2019) and surrounding surrounding coal-fired power plants (Global Energy Monitor, GEM; and the Global Power Plant Dataset; World Resources Institute, WRI, 2018) that support the nearby industries.

Our goal is to calculate ER\textsubscript{CO} from every satellite sounding within an urban plume that is the spatial extent a downwind area affected by urban emissions (Sect. 2.2). Sounding-dependent ER\textsubscript{CO} are calculated as ratios of CO emissions over CO\textsubscript{2} emissions (Eq. 3) that estimated from the are estimated from satellite-derived FF-fossil fuel (FF) enhancements and further re-
...intra-city ERs in June and each two ER, X August and six variations accounts for several mismatches between OCO-2/3 and TROPOMI (Sect. 2.1) and is obtained from an atmospheric transport model (Sect. 2.2.1). Since we do not differentiate emission signals due to biofuel or fossil fuel combustion, the term “FF enhancement” is simply referred to as column enhancement induced by any anthropogenic combustion processes by the target city. Determination of FF enhancements requires an estimate of the background values (Sect. 2.2.2) and “second-order” correction terms for biogenic and pyrogenic sources (see explanations in Sect. 2.2.3). The sounding-specific ERs and their Sounding-specific ERs and uncertainties (Sect. 2.2.4) are aggregated to yield an ER per overpass and per city. After determining the intra-city variations in ER, we illustrate how FF enhancement is retrieved from the urban land cover classification dataset (WUDAPT, WUDAPT).

2.1 Satellite observations and data pre-processing

We screened available data for overpass evaluated all overpasses coincidences between OCO-3 SAM X and TROPOMI XCO observations and TROPOMI observations but only selected those with relatively small differences in overpass times. Considering the limited number of coincidences between sensors, two non-SAM overpasses from OCO-3 and one OCO-2 overpass are added to the analysis. In the end, six to seven As a result, six OCO-TROPOMI coincidences with higher data quality from Oct 2019 to June 2021 were integrated into the final result for each city. Only two every city. Two of the total 25 overpasses (both in June 2021) 24 overpasses fall within the northern hemispheric summer months between June and August (both in June).

2.1.1 OCO-2/3 XCO₂

The column-averaged dry-air mole fraction of CO₂ (XCO₂) is retrieved from the reflected sunlight over two CO₂ bands centered on 1.6 and 2.0 μm and the oxygen-A band for obtaining surface pressure obtained by OCO-3 (Eldering et al., 2019; Taylor et al., 2020). In addition to the standard Nadir, Glint, and Target modes, OCO-3 performs SAMs that collect several adjacent swaths of XCO₂ observations over a spatial area of approximately 80 km by 80 km during its SAM mode, e.g., four individual swaths in an overpass over LA on Feb 24, 2020 (Fig. 2a). Similar to OCO-2, each satellite swath is comprised of eight spatial footprints/soundings and each sounding has an area of ~1.6×2.2 km² at nadir (Fig. 2a). Our analysis only used screened OCO-3 B10r/B10p4r data (Eldering, 2021) with an XCO₂ quality flag of zero (QF = 0). It is worth highlighting that the B10r/B10p4r product is superior to the Early version for of OCO-3 (Taylor et al., 2020) including improved geolocation, advanced radiometric calibration, improved quality filters, and customized post processing bias correction. Because As OCO-3 is mounted on the ISS - International Space Station that is in a precessing orbit, its overpass time varies, for example, from 07:00 to 15:00 local time for the overpasses we examined, unlike OCO-2.
2.1.2 TROPOMI XCO

The TROPOMI column density of CO molecules [mole cm$^{-2}$] is retrieved via the measured radiation from the shortwave infrared wavebands on TROPOMI, centered at $\sim$2.3 $\mu$m (Veeckind et al., 2012). We only selected data—selected soundings with quality assurance $\geq$ 0.5 as recommended by the TROPOMI readme document (Landgraf et al., 2020) and converted the column density to the total column-averaged dry-air mole fraction of CO [XCO in ppb] by calculating the dry-air column density [mole cm$^{-2}$] estimated from retrieved surface pressure and total column water vapor. TROPOMI CO is retrieved at a larger pixel area of $\sim$7$\times$7 km$^2$ at Nadir and reduced to 5.5$\times$7 km$^2$ after Oct 6, 2019 (Fig. 2c). The overpass time of TROPOMI is $\sim$13:30 local time of equatorial overpass for nadir measurements with a time span of 1–2 hours for soundings on the edge of its wide swath (i.e., $\sim$2600 km).

![Spatial maps of FF XCO$_2$ enhancements with corrections of non-FF sources at OCO-3 scale and TROPOMI scale](image)

**Figure 2.** Spatial maps of FF XCO$_2$ enhancements with corrections of non-FF sources at native OCO-3 scale (a, ppm) and aggregated at the TROPOMI scale (b, ppm) along with FF XCO enhancements (c, ppb) over Los Angeles on Feb 24, 2020. Power stations with different primary fuel types are displayed in different white symbols based on the Global Power Plant Dataset (World Resources Institute, 2018). The overall X-STILT column footprint [ppm / ($\mu$mol m$^{-2}$ s$^{-1}$)] from all soundings is drawn in light grey (see explanations for column footprint in Sect. 2.2.1). The underlying hybrid maps were created using the ggmap library in R with the hybrid view of Google Maps over LA (copyright: Map data ©2021 Imagery ©2021 TerraMetrics).

2.1.3 Differences between two sensors/species

Four mismatches between OCO-3 XCO$_2$ and TROPOMI XCO pose challenges in extracting FF enhancements and ER$_{CO}$ from atmospheric observations, which we attempt to account for and assess are accounted for in this analysis:

1. **Satellite pixel area:** We searched for XCO$_2$ enhancements from multiple OCO-2/3 soundings falling within each TROPOMI polygon and averaged the corresponding enhancements to the TROPOMI scale. Given TROPOMI polygon are grouped...
and averaged (Fig. 2a vs. b). For simplicity, we used the centered lat/lon coordinate of an OCO-3 sounding OCO pixel is used to determine its corresponding TROPOMI polygon. Retrieval uncertainties and observation noise (defined as the variability within each TROPOMI polygon) are estimated at the TROPOMI pixel scale and propagated as part of the total observed. The retrieval uncertainty tied to each OCO sounding is also aggregated according to the TROPOMI sampling, contributing to the total observational uncertainty (Sect. 2.2.4).

2. Averaging kernel profile: Within the planetary boundary layer where most emissions occur, TROPOMI XCO retrieval is affected by cloud height/fractions, which yields lower-than-unity AK (Supplementary Fig. ??). OCO-2/3 XCO under cloudy conditions are typically omitted from Lite files and when QF = 0 is applied; thus, its AK normally approaches one near the surface for cloud-free scenes. The mismatch in AKs between sensors must be accounted for as it can affect the interpretation of ERs. In this work, we accounted for AK AKs within an atmospheric transport model (Sect. 2.2.1).

3. Overpass time and upwind times, meteorological conditions, and emission variations: As a result of the sometimes large time difference, meteorological conditions including the overpass time difference between sensors, variations in meteorological conditions (e.g., wind direction and speed) can change significantly, leading to changes in urban plume shapes detected by the two sensors as they pass by. We dealt with changes in wind speed and wind direction separately. The former is resolved by the “scaling factor” generated from the inferred from an atmospheric transport model and the latter undergoes manual evaluations (Sect. 2.3). Besides, CO and CO2 emissions themselves can vary over the course of a day, e.g., driven by road transportation and residential sectors. Given the overpass time difference between sensors, it is likely that such mismatch in the timing of CO versus CO2 emissions may affect the observed ERCO.

4. Non-fossil fuel sources/sinks: The lack of account of influence from the biosphere and biomass burning may affect the calculation of bias ERCO. Given our definition of background regions a local background, the contrast in non-FF concentration anomalies between the urban and background region may interfere the calculation of FF enhancements and (more explanations in the background region needs to be included (for more explanation, see Sect. 2.2.3).

FF enhancements at the native OCO-3 soundings (a, ppm) and aggregated to the TROPOMI scale (b, ppm), and XCO enhancements (c, ppb) over Los Angeles on Feb 24, 2020. Power stations with different primary fuel types are displayed in different white symbols based on the Global Power Plant Dataset (World Resources Institute, 2018). The X-STILT column footprint from all soundings are drawn in light grey (see explanations for column footprint in Sect. 2.2.1). The underlying hybrid maps were created using ggmap library in R that adopted the Google Maps (copyright: Map data ©2021 Imagery ©2021 TerraMetrics).

2.2 Estimates of $E_{gas}$, ERCO and uncertainties

Previous studies (Mitchell et al., 2018; Wu et al., 2020; Lin et al., 2021) proposed an approach to calculate the an overall CO2 or CH4 fluxes flux using atmospheric measurements and atmospheric transport model without, without relying on prior
information from emission inventories. Here we briefly describe this approach to obtain the overall emission of either CO\(_2\) (Eq. 1) or CO (Eq. 2) for each sounding. A single sounding \(S\), modified from Wu et al. (2020):

\[
\langle E_{\text{CO}_2, s} \rangle = \frac{X_{\text{ffCO}_2, s} \langle X_{\text{CO}_2, s} \rangle}{\langle X_{\text{CO}_2} \rangle} = \frac{X_{\text{obsCO}_2, s} - X_{\text{bgCO}_2} - \delta X_{\text{bioCO}_2, s} - \delta X_{\text{bbCO}_2, s}}{\iint X_{\text{CO}_2, s}(x, y) \, dx \, dy},
\]

(1)

\[
\langle E_{\text{CO}, s} \rangle = \frac{X_{\text{ffCO}, s} \langle X_{\text{CO}, s} \rangle}{\langle X_{\text{CO}_2} \rangle} = \frac{X_{\text{obsCO}, s} - X_{\text{bgCO}} - \delta X_{\text{bbCO}, s}}{\iint X_{\text{CO}, s}(x, y) \, dx \, dy}.
\]

(2)

All the \(X\) terms in the numerator contribute to FF-the estimate of FF column enhancements (\(X_{\text{ff}}, \text{Fig. 2}\). In theory, \(X_{\text{ff}}\) at a downwind satellite sounding \(S\) is the sum of its corresponding \(S\) is the net result of FF sources over its corresponding the source region \((x, y)\). To describe and attribute this source region the source region and attribute it to each satellite sounding, we adopted the column version of the Stochastic Time-Inverted Lagrangian Transport (X-STILT) model (Lin et al., 2003; Fasoli et al., 2018; Wu et al., 2018). Using X-STILT, we can From this model, we obtain a “scaling factor” \(\langle X_{\text{ffgas}} \rangle\) that accounts for to account for the sounding-specific AK profile and meteorology (Sect. 2.2.1).

Within the calculation of FF enhancements of either or \(X_{\text{CO}_2}\), \(X_{\text{bg}}\) represents the background values calculated from denotes the local background values using satellite observations uncontaminated by the urban plume city emission, which are normally constant for a group of observations (i.e., not sounding-specific, background observations. The background region is usually chosen over rural region outside the urban plume with consideration of wind direction (Sect. 2.2.2). The From a Lagrangian viewpoint, the air parcels arriving at the sounding in the city center can have different origins and pathways an urban sounding might be traced back to different origins from the air parcels tied to arriving at a rural sounding. These, meaning observations at the two soundings may be influenced differently by biospheric fluxes and biomass burning emissions the surrounding biosphere. Hence, two background correction \(\delta\)-terms are attached to correct account for the urban-background gradient in column anomalies from the concentration anomalies due to net ecosystem exchange (NEE) and biomass burning (Sect. 2.2.3 and Eq. 4).

Similar to, the resultant For a given sounding, the estimated flux \(\langle E_{\text{gas}} \rangle\) with unit of \(\mu\text{mol m}^{-2} \text{s}^{-1}\)–is tied to each sounding. These fluxes represent the total emissions in the source region with respect to a given TROPOMI sounding and represents the average emission over the corresponding source region of that sounding, which should not be confused with the direct emission at that sounding location. The ER\(_{\text{CO}}\) for a given sounding \(S\) is then derived from Eqs. 1 and 2 as follows:

\[
ER_{\text{CO}, s} = \frac{\langle E_{\text{CO}} \rangle}{\langle E_{\text{CO}_2} \rangle} \frac{\langle X_{\text{CO}_2} \rangle}{\langle X_{\text{CO}} \rangle} = \frac{X_{\text{ffCO}} \langle X_{\text{CO}_2} \rangle}{X_{\text{ffCO}_2} \langle X_{\text{CO}} \rangle} = \frac{X_{\text{ffCO}, s} \langle X_{\text{CO}_2, s} \rangle}{X_{\text{ffCO}_2} \langle X_{\text{CO}, s} \rangle} \gamma_{\text{foot}, \text{foot}, s},
\]

(3)

\[
\frac{X_{\text{ffCO}}}{X_{\text{ffCO}_2}}\text{ is the where } \frac{X_{\text{ffCO}, s}}{X_{\text{ffCO}_2, s}}\text{ is the observed enhancement ratio and } \gamma_{\text{foot}, \text{foot}, s}\text{ measures how enhancement ratios without accounting for AKs and meteorology differ from emission ratios. We simply use ppb-CO/ppm-CO\(_2\) for units of ER\(_{\text{CO}}\) (same as mmol-CO/mol-CO\(_2\)).}
2.2.1 The X-STILT model

The X-STILT model is adopted for three purposes: to in this study, 1) to provide the scaling factor \( \langle XF_{gas} \rangle \) that resolves the influences from differences in AK and wind fields between sensors, differences in AKs and changes in wind speeds; 2) identify the overpass-specific urban plume for background determination determining background regions (Sect. 2.2.2), and to; and 3) estimate the sounding level to estimate the sounding-specific biogenic and pyrogenic contributions to the background anomalies for background corrections (Sect. 2.2.3).

STILT releases an ensemble of air parcels from target observations (known as the STILT “receptor”) and tracks the movement of those air parcels backward in time. The source region corresponding for each sounding is informed by the “source-receptor relation” or the STILT “footprint” (Lin et al., 2003; Fasoli et al., 2018). The STILT footprint [ppm / (µmol m\(^{-2}\) s\(^{-1}\))] describes the change in atmospheric concentration [ppm] at a downwind location due to possible upwind sources/sinks [µmol m\(^{-2}\) s\(^{-1}\)].

The magnitude of STILT footprints tends to be higher close to the target observations observation or under steadier wind condition, as conditions, thus, air parcels within the boundary layer can interact more closely with fluxes from the surface.

To accommodate the use of satellite-based column data, X-STILT incorporates the retrieval-specific AK and pressure weighting (PW) profiles in profiles to the footprint calculation (Wu et al., 2018), such that the influence of on air parcels originating from various altitudes of an atmospheric column are weighted by the sounding- and sensor-specific AK vertical profile (Supplementary Fig. ??). The “column footprint” \( \langle \langle X F_{gas} \rangle \rangle \) measures the sensitivity of the total column concentration to upwind fluxes. Because AK profile is specific to the retrieval from the perspective of a specific satellite sensor. For instance, XF\(_{gas}\) for TROPOMI XCO differs from that-XF\(_{gas}\) for OCO-2/3 XCO\(_2\) even for concurrent observations (Eqs. 2, 1). Because the air flow arriving at each satellite observation is unique, the magnitude and spatial distribution of column footprints vary from one sounding to another XF\(_{gas}\) vary across soundings (Supplementary Fig. ??). By taking an average of these sounding-dependent column footprints, as shown in Supplementary Fig. ??, we can identify the source region for all soundings in a SAM as indicated by the (light gray area in Fig. 2b,c). In this work, we only traced air parcels back for 12 hours backward in time for calculating to calculate column footprints, which is sufficient to capture the near-field influence from the target city and better aligned with the local background region outside the city (Sect. 2.2.2).

In summary short, the spatial summation of column footprints \( \langle XF_{gas} \rangle \) is regarded as a scaling factor in addressing the sensor specific to address the sounding-specific meteorological condition and AK profile. The deviation of the term \( \gamma_{foot} \) in Eq. 3 from 1 as derived from Eq. 3 reveals the difference between a simple concentration enhancement ratio and a more robust, model-corrected emission ratio.

2.2.2 Background definition \( X_{bg} \)

Defining accurate background levels to extract urban FF enhancements has always been a challenge in top-down analysis, especially when dealing with column measurements with small signal-to-noise ratio. Wu et al. (2018) compared several approaches to determine the localized XCO\(_2\) background for extracting urban signals from OCO-2, including approaches that 1) solely use satellite observations with statistics like percentile or median (e.g., daily median); 2) solely use atmospheric
transport models an atmospheric transport model (e.g., curtain method and the “curtain method” based on global concentration fields); and 3) combines observations and model. The latter two methods do not involve prior information on emissions combine observations and transport information from models. Here, we expand the third approach to arrive at localized swath-dependent XCO and background values. The broader spatial coverage and multiple swaths of stretching out of the city domain of OCO-3 SAMs improve the determination of the background terms help improve such background determination by introducing spatial variations in the background, compared to the narrow swath of OCO-2. Accurately describing the latitudinal or spatial gradients in background XCO₂ have been emphasized previously has been emphasized recently (Ye et al., 2020; Schuh et al., 2021).

The process of background determination used in this work involves a first step of identifying the urban plume and differentiating soundings as within or outside of the plume. Here we used To outline the urban plume shape at the overpass time, we utilized the forward mode of STILT with the inclusion of wind uncertainty to into atmospheric dispersion. Specifically, 1000 air parcels were released continuously from a rectangle representing the urban extent city domain (dashed black box in Fig. 3) every 30 minutes starting from 10 hours ahead of the overpass time. All air parcels are allowed to travel forward in time for 12 hours from their initial release times. A random wind component typifying model-data wind errors is added to the parcel dispersion (Lin and Gerbig, 2005). We subset the air parcels only during the overpass time and applied a 2-dimensional kernel density estimate (KDE) based on the parcels’ spatial distribution distributions (blue to purple contours in Fig. 3). KDE is carried out using the kde2d function provided by the MASS library in R (Venables and Ripley, 2002). These normalized KDE contours then denote indicate the likelihood and shape of an urban plume when the satellite scans through. The extent of the urban plume is finalized using a normalized KDE contour of 0.15 (black curve in Fig. 3), which is proper to 1) include soundings with possible influence from the target city and 2) exclude observations elevated by another city (e.g., the red polygons centered at around 32°N and 120°E in Fig. 3c). This procedure is carried out separately for OCO-2/3 and TROPOMI to address differences in the urban plume reveal the impact of changing meteorology on urban plumes at different overpass times (see Sect. 3.1). It is worth stressing that only enhancements within the urban plume are selected to yield used for ERCO₂ estimates.
Next, the background value is calculated as the median value of observed \( X_{\text{gas}} \) per swath over the background region. For example, the background region is the area to the east outside the urban plume since southeasterly wind dominates (Fig. 3b,c). Background values vary with swaths if an OCO-3 SAM is examined. We chose the median instead of the mean to minimize the impact of any “outliers” that may be from a second FF source (other than our target cities) in the background region. When analyzing data from OCO-2’s narrow swath (Fig. 3a), the latitude range outside the plume serves as the background region and can be sensitive to the modeled wind bias and number of valid soundings (Wu et al., 2018). Fortunately, modeled wind bias is generally less of an issue when analyzing SAMs, because the broader coverage of valid SAM observations helps evaluate model-based urban plumes. Background uncertainties are estimated and propagated into the ER Background uncertainty is estimated as a component of the total observed uncertainty (Sect. 2.2.4).

Demonstrations of background determination from OCO-2 on Feb 4, 2020 (a), OCO-3 SAM ppm and TROPOMI XCO ppb on Feb 20, 2020 (b, c) over Shanghai. The model-based urban plume (solid black curve) is determined by the normalized 2-D kernel density of the air parcels’ distribution during the overpass time (blue-purple contours). On Feb 20, 2020, measurements to the east outside modeled plumes are identified as the “background measurements”. The underlying maps were created using ggmap library in R that adopted the Google Maps (copyright: Map data ©2021 Imagery ©2021 TerraMetrics).
2.2.3 Background correction terms for non-FF sources/sinks

The swath-dependent local background approach described above explicitly assumes equal contributions from non-FF sources and sinks for soundings in the background versus soundings in the urban plume. We further estimated urban background gradients in resulting - which may not always be the case. We then correct for the spatial gradient in contributions from biogenic and pyrogenic fluxes.

As initially proposed in Wu et al. (2021), rather than the absolute biogenic or pyrogenic absolute biogenic concentration anomalies, it is the contrast in these anomalies between the background versus urban region - the urban plume that is required, given our considering our localized background definition. Specifically, hourly column footprints from X-STILT X-STILT column footprints are convolved respectively with hourly mean NEE from a biogenic biospheric model representation and the daily mean wildfire emissions from the Global Fire Assimilation System (GFAS, Kaiser et al., 2012) to estimate the sounding-specific absolute column anomalies $X^{\text{bio}}_{\text{bg}}$ and $X^{\text{bio}}_{\text{sum}}$ for every sounding. The Solar-Induced Fluorescence (SIF) for Modeling Urban biogenic Fluxes (SMUrF, Wu et al., 2021) model estimates gross primary production (GPP) from a Contiguous SIF product (CSIF trained based on OCO-2 SIF, Zhang et al., 2018) and respiration based on modeled SIF-based GPP, air and soil temperatures.

Next, the urban-background gradient in the anomalies are such anomalies is calculated as the difference between the sounding-specific anomalies and the average anomalies over mean anomaly within the background region -

$$\delta X^{\text{bio}}_{\text{CO}_2}(s) = X^{\text{bio}}_{\text{CO}_2}(s) - \bar{X}^{\text{bio}}_{\text{CO}_2}(s_{\text{bg}})$$

(4)

where $s$ or $s_{\text{bg}}$ represents all the soundings or selected soundings in the background region, respectively. Let us imagine a north hemispheric summer day at noon - when in the north hemisphere, the urban core is normally associated with a weaker biospheric uptake than the surrounding rural region. Biogenic signals $X^{\text{bio}}_{\text{CO}_2}(s)$ for soundings in the city are less negative than the mean biogenic signal over the rural background $\bar{X}^{\text{bio}}_{\text{CO}_2}(s_{\text{bg}})$. Hence, the urban-background biogenic gradient $\delta X^{\text{bio}}_{\text{CO}_2}(s)$ is normally positive and should be subtracted from the observed column to yield the FF enhancement total column (Eq. 1). Modeled sounding-specific Estimated $X^{\text{bio}}_{\text{bb}}$ and their urban-background gradient $\delta X^{\text{bio}}_{\text{bb}}$ and their impacts on are discussed are shown in Sect. 3.1.

Flux exchanges from the ocean and chemical transformation (e.g., CO sink via hydroxyl radical (OH) and source from oxidation of volatile organic compounds, VOCs) are not considered. The average lifetime of CO against OH ranges from a few weeks to several months depending on the season, much longer than the few-hour timescale we care about. Yet, CO can be generated from the oxidation of CH$_{4}$ and non-methane VOCs at various rates, which are discussed in Sect. 4.4.3.

2.2.4 Uncertainty sources

The uncertainty related to emissions should contain uncertainties from 1) the atmospheric transport (i.e., column footprints), 2) the retrieval and measurement, observations, and 3) background, and 4) non-FF gradients. However, we sources and sinks.
assuming each the TROPOMI overpass time. The urban-background gradient in non-FF fluxes remains very small compared to FF enhancements (Sect. 3.1).

Observed uncertainty of We estimated uncertainties of observed FF enhancements following Eq. 5. As previously described, observations from a few screened OCO soundings (~ 5 to 28 OCO soundings depending on the TROPOMI footprint size) are averaged to arrive at mean XCO₂ are comprised of retrieval errors and measurement noise (or at the TROPOMI scale. Due to such averaging/binning process, the XCO₂ variability) as the uncertainty due to binning is considered using the standard deviation of XCO₂ observations (σ²_{x,bin} in Eq. 5) within a TROPOMI polygon. Depending on the TROPOMI sounding size (nadir or not) and the amount of screened OCO-3 soundings, there could be 5 to 28 OCO-3 soundings per TROPOMI polygon

\[ \sigma_{x,obs}^2 = \sigma_{x,bin}^2 + \sigma_{x,bg}^2 + \sigma_{x,ertrv}^2 \]  

(5)

σ²_{x,bin} is not required for estimating XCO uncertainty. Background uncertainty contains (σ²_{x,bg}) contains both the retrieval error and the measurement noise of observations over variability of column observations (as standard deviation) within background regions. Retrieval errors associated with each OCO-3 sounding are aggregated to the polygon. The retrieval uncertainty (σ²_{x,ertrv}) of XCO is available for each TROPOMI sounding, whereas that of XCO₂ is reported for individual OCO-2/3 sounding (as read from Level 2 Lite files), which need to be aggregated at the TROPOMI scale. Due to possible correlations in retrieval errors between nearby OCO soundings, we estimated the error correlation length scale (L_{x}) using exponential variograms as demonstrated in Supplementary Fig. ?? Within a TROPOMI spatial scale in a standard deviation of mean manner. Hence, polygon that contains N numbers of OCO soundings, an error variance-covariance matrix with a dimension of N × N is constructed with its diagonal elements filled with OCO sounding-specific retrieval error variance. Then, L_{x} is used to form the normalized covariance matrix, i.e., \( \exp(-D(S_i, S_j)/L_{x}) \) where \( D(S_i, S_j) \) denotes the distance between each two OCO soundings (1 ≤ i < j ≤ N). Lastly, the fewer OCO-3 soundings in a given TROPOMI polygon, the larger the observed uncertainties will be, which accounts for the unequal OCO-3 sampling in a TROPOMI polygon. Sum of all elements in the error covariance matrix (both variance and covariance elements) is divided by N² to obtain one σ²_{x,ertrv} per TROPOMI grid. As a result, the overall uncertainty of FF enhancement per sounding is often predominated by the background error component.

2.3 Identifying ER_CO for heavy industry within a city

One key objective of this study is to explain the intra-city variability of ER_CO by exploring sector-specific or sector-dominant burning-combustion activities. While certain combustion processes and sectors tend to have higher ERs than others, the sectoral-dependent ER is likely variable within and across cities. Moreover, the ERs determined from atmospheric observations comprise a mixed effect of different sectoral activities activities in the city. Previous attempts
include reducing the number of sectors and relying on prior knowledge of sector-specific ERs in a (joint) Bayesian inversion (Nathan et al., 2018; Brioude et al., 2012) (Brioude et al., 2012; Nathan et al., 2018).

Map of Local Climate Zone (LCZ) from WUDAPT at a grid spacing of 120 m (a and d with zoomed-in images on b and e) and interpolated areal coverage of heavy industry % at 1 km around Shanghai and Los Angeles (e, f). LCZ classifications centered on Wuxi and Shanghai are combined. Power stations based on the Global Power Plant Dataset (World Resources Institute, 2018) are drawn on the map as different symbols. The light gray and white dashed rectangles in the first and third columns indicate the zoomed in region of the second column.

Here, we propose a novel approach to identify ERs associated with heavy industry within the heavy industry in a city. Instead of relying on prior emission inventories that can sometimes be erroneous regarding the magnitude and location of sectoral heavy industry-dominated activities (see discussions in Sect. 4.4), we utilize a utilized an urban land cover classification dataset. The World Urban Database and Access Portal Tools (WUDAPT, Fig. 4a, d) project, WUDAPT that provides Local Climate Zone (LCZ) classifications at a grid spacing of 120 m (Ching et al., 2018). Example As shown in Fig. 4a, d, LCZ categories include street canyons (e.g., compact/open/lightweight, high-/mid-/low-rise), building spacing (e.g., sparsely built, heavy industry), and tree spacing (e.g., dense/scattered trees, low plants, rocks, etc) (Stewart and Oke, 2012). Each LCZ is unique in its thermal, radiative, and metabolic properties. For instance, compact high-rise (LCZ 1) and heavy industry (LCZ 10) categories have the highest anthropogenic heat output of 50–300 W m$^{-2}$ and $>300$ W m$^{-2}$, respectively (Stewart and Oke, 2012). Heavy industry is defined as low-rise and mid-rise industrial structures (towers, tanks, stacks) and mostly paved or hard-packed metal with steel and concrete construction materials with few or no trees in WUDAPT (Ching et al., 2018), which differs from the industry-relevant sectors (e.g., defined by the Intergovernmental Panel on Climate Change). Some industries are also found within the WUDAPT-based heavy industry region (Figure 4, e.g., as used in EDGAR). We clarify that we are not trying to tackle individual industrial processes, but treat some as an entity according to land cover data. Note that WUDAPT which is much more difficult. LCZ maps are only available for a limited number of cities across the globe including Shanghai and Los Angeles LA as of this analysis but have recently been generalized to the entire globe (Demuzere et al., 2022).

To relate ER$_{CO}$ to heavy industry, the percentage of heavy industry is first interpolated at 1 km grid spacing from WUDAPT LCZ maps (%) Fig. 4c, f. Those industry coverage are The industrial coverage map is then convolved with the X-STILT column footprint (Supplementary Fig. ??) to quantify the industrial influence on each TROPOMI polygon $P_{ind}(x,y)$, which is defined as the column footprint-normalized industry fraction (Supplementary Fig. ??). For example, soundings in the city center farther away from the heavy industry in LA are related to smaller influences. Lastly, we sum $P_{ind}(x,y)$ across the space to arrive at $\langle P_{ind}\rangle$, serving as a metric of how much the enhancement observation at a given sounding is affected by heavy industry. Specifically, soundings with $\langle P_{ind}\rangle$ larger than the 75$^{th}$ or 90$^{th}$ percentiles are marked as locations “impacted” or “strongly impacted” by heavy industry within the city. Sensitivity and significance analyses are conducted and presented in Sect. 3.2.2 to test if: 1) the results are subject to the percentile threshold when defining industry-dominant soundings, and; 2) ERs over industry-dominant industry-dominated soundings are statistically significantly different from ERs for the remaining soundings.
3 Results

$\text{ER}_{CO}$ values and uncertainties are reported at multiple spatial scales originating from the spatially-explicit sounding level from the spatially-resolved sounding level (Eq. 3) to the overall overpass- and city-level. Again, only ERs at soundings within the urban plume are selected. Overpasses with too low valid soundings few valid soundings in a plume area are also removed from the results. Before presenting ERs at different spatial scales, we assess the few factors that may influence the derived $\text{ER}_{CO}$.

3.1 Interference factors that modify $\text{ER}_{CO}$

We examine the impacts on $\text{ER}_{CO}$ from the following interference factors: 1) differences in AKs between OCO-2/3 XCO$_2$ and TROPOMI XCO; 2) shifts in wind fields induced by asynchronous between two overpass times; and, 3) urban-background contrast in biogenic and pyrogenic contributions; and, 4) temporal variation in emission themselves. In summary, we found...
that difference in AKs and wind directions between sensors can significantly affect the spatially-resolved ER_{CO}. After removing the overpasses substantially interfered by wind shift from consideration, biogenic and pyrogenic contributions play a minor role in the overall-molar roles in overpass- or city-level ERs.

The sensor-specific AKs and wind speeds were incorporated into the calculation of species-specific column footprint in-speeds were being considered in the sounding-specific column footprint using X-STILT as introduced in Sect. 2.2. By looking at the $\gamma_{foot} = \left( \frac{X_{FCO}}{X_{FCO}} \right)$ (Supplementary Fig. ??d), one can tell the impact on suggested their combined impacts on spatially-resolved ER_{CO} due to mismatches in AKs and wind fields between sensors (Supplementary Fig. ??e). For instance, mean $\gamma_{foot}$ spans from 1.20 to 1.54 over Los Angeles - 1.57 over LA and from 1.02 to 1.38 over Shanghai across different overpasses (printed in Fig. 7a, c). $\gamma_{foot}$ is generally larger than 1 because the TROPOMI XCO-AKs near the surface are less than 1 and smaller than of TROPOMI XCO are smaller than surface AKs for OCO-2/3. Simply using enhancement ratios without accounting for mismatches in AK and wind speed AKs and wind speeds between sensors will likely lead to an underestimation of the emission ratios (Eq. 3). On average, overpass-level ER_{CO} can be about 20% higher than the enhancement ratio for the examined cases: enhancement ratios across our 24 overpasses.

Figure 5. Examples of modeled urban plumes during OCO-3 (red curve) and TROPOMI (blue curve) overpass times in UTC. The likelihood of these meteorology-only urban plumes (no emission involved) is quantified by the normalized KDE binned by 10 intervals of the modeled air parcel distribution (yellow-green-purple contours). Three types of overpasses are shown as follows: 1) “good cases” with almost identical urban plumes at two times, e.g., Baotou on Oct 8, 2019 with $\Delta t$ of 8 mins (a, b); 2) cases to be used with caution where the urban plume shifts from one time to another and requires a simple plume rotation, e.g., Shanghai on Feb 20, 2020 with $\Delta t$ of 1.5 hours (c, d); 3) outliers where two urban plumes change significantly, e.g., for Los Angeles on March 3rd, 2020 with $\Delta t$ of over 4 hours (e, f). The underlying hybrid maps were created using the ggmap library in R with the hybrid view of Google Maps over LA (copyright: Map data ©2021 Imagery ©2021 TerraMetrics).
The second factor is the changes in wind directions between two overpass times, which is evaluated using the same approach for identifying the urban plumes algorithm as the urban plume detection in Sect. 2.2.2. Again, these colored contours and curves in Fig. 5 do not indicate the intensity of concentration concentrations nor flux fields (as no prior emission is used), but rather the likelihood of urban plumes solely determined by atmospheric dispersion with random wind uncertainties. Matching between OCO-3 soundings and TROPOMI polygons as described earlier would be fine for concurrent observations (e.g., “good cases” with almost identical plumes at two times in Fig. 5a, b); but becomes problematic if Δt is large (e.g., becomes large (“outliers” with significant changes in urban plumes in plumes in Fig. 5e, f). Since no simple wind or plume rotation would improve the ER estimates, cases with > 3 hours are removed from this analysis. The cases between the “good cases” and the “outliers” are easier to be used with caution (Fig. 5c, d). By comparing the overlap of plumes at the two times, we then shifted the OCO-3 soundings to better align with the TROPOMI polygons. For example, on Feb 20, 2020, because the modeled plume at the OCO-3 overpass time (06:06 UTC) appears northward compared to the plume at the TROPOMI overpass time (04:44 UTC), soundings at the OCO-3 overpass time were shifted southward by 0 to 2 grids depending on their longitudinal coordinates (Supplementary Fig. ??). In other words, by shifting the observed FF XCO₂ enhancements, we better align the urban plume at OCO-3 time with the plume at TROPOMI time. Every OCO-TROPOMI coincidence has been manually examined and assigned to one of the three categories, which are further summarized in Sect. 4.1. “Outliers” are removed from this analysis, since no simple wind or plume rotation would improve their ERCO₂ estimates.

Examples of modeled urban plumes during OCO-3 (red curve) and TROPOMI (blue curve) overpass times (in UTC labelled on the bottom of each panel). The likelihood of these meteorology-only urban plumes (no emission involved) is quantified by the normalized KDE (10 intervals in the color legend) of modeled air parcel distribution (yellow-green-purple contours). Three types of overpasses are shown as follows: 1) “good cases” with almost identical urban plumes at two times, e.g., Baotou on Oct 8, 2019 with of 8 mins (a, b); 2) cases to be used with caution where the urban plume shifts from one time to another and requires a simple plume rotation, e.g., Shanghai on Feb 20, 2020 with of 1.5 hours (c, d); 3) outliers where the urban plumes change significantly, e.g., for Los Angeles on March 3rd, 2020 with of over 4 hours (e, f). Outliers with of over 3 hours are removed from the final results.

The last factor is the urban background contrast due to non FF sources/sinks. Although LA is surrounded by occasional intense wildfire activities, column anomalies due to biomass burning suggested by the coupling of GFAS and X-STILT are minimal for the dates we examined. However, since fire related. Besides changes in wind directions, CO and CO₂ emissions themselves can vary across daytime hours, likely driven by the road transportation and residential sectors. As a result, variations in the derived ERCO₂ are mostly higher than FF related (across multiple overpasses may reflect not only the variation in combustion efficiencies but also the mismatch in the emission timing. LA may be one of the cities with more distinct daytime changes in emissions compared to industry-centered cities. Fortunately, based on a supplementary sensitivity analysis using measurements from the Total Carbon Column Observing Network in Pasadena (TCCON, Wennberg et al., 2017), by limiting satellite overpasses to those with a smaller time difference, ERCO₂ appear to be less variable (Supplementary Fig. ??).
provide better guidance towards the hourly pattern in urban emissions, especially from the traffic sector with more daytime fluctuations, which have been discovered using surface monitoring networks (e.g., over Chicago; de Foy, 2018).

The last factor is the enhancement important for cities in mountainous and forested areas during the fire season (e.g., Mexico City and LA). The sounding-specific urban-background contrast in contributions from non-FF sources and sinks. The modeled biogenic XCO₂ anomalies anomaly using SMUrF and X-STILT ranges from -0.7 to 0.3 ppm per OCO-3 sounding, depending on the season and the hour of day (i.e., solar zenith angle), season and wind direction (Supplementary Fig. ??) and are further aggregated to the TROPOMI scale. As explained above, strong in Sect. 2.2.2, urban-background gradients in these biogenic anomalies (i.e., δX_{bio}) may alter the FF enhancement and so such gradients were used to correct the constant localized background X_{bg}(Eq. 1). Take the two overpasses with the largest urban-background contrast as examples: as biospheric uptake is normally weaker in urban areas than surrounding rural areas (often as background regions), the urban-rural gradient for locations in the plume region becomes more positive (Supplementary Fig. ??b). Nonetheless, even for the one summertime SAM over Zibo on June 21, 2020, sounding-level δX_{bio} ranges from 0 to 0.4 ppm, which remains small compared to sounding-level FFCO₂ enhancements of 2 to 7 ppm (Supplementary Fig. ??a, b). For most other overpasses, urban-background δX_{bio} remains aggregated to TROPOMI sampling stay low with an absolute value < 0.2 ppm-0.3 ppm (as printed in each panel of Figs. 6 & 7). Even with a bias in the resultant δX_{bio} (resulting from uncertainties in prior NEE resulting from incorrect prior NEE), the effect on derived FF enhancements and ER_{CO} would be small.

Although LA is surrounded by occasional intense wildfire activities, column anomalies due to biomass burning suggested by the coupling of GFAS and X-STILT are minimal for the dates we examined. Yet, since wildfire-related ER_{CO} are usually higher than FF-related ER_{CO} (Fig. 1), the proper account of pyrogenic contributions and gradients between urban and surrounding rural areas is important for cities in mountainous and forested areas during fire seasons. For instance, Crouse et al. (2009) leveraged aircraft measurements of HCN and C₂H₂ over Mexico City as indicators to disentangle CO signals due to biomass burning and urban emissions, respectively.

### 3.2 Intra-city ER_{CO} variations and signal signals from heavy industry

The measured concentration Observed enhancements are the net consequence of associated sources/sinks from source regions. That is, high atmospheric content of CO₂ or CO at the sounding location does not necessarily indicate a high emission rate at this location (Kiel et al., 2021). Our derived emissions and ERs, although reported for each sounding, indicate the overall emission and combustion efficiency over its source region.

In the following subsections, we present ERs from sounding level to the overpass and city level for each sounding and the aggregate for each overpass and city. Since aggregating spatially explicit sounding-level ERs to a single value per overpass or city is sensitive to the adopted method/statistics and the overpass-specific atmospheric movement statistic, we bootstrapped ECO and Ebased on sounding-level emissions and uncertainties 5,000 times and applied linear regression fits (e.g., E_{CO} and E_{CO₂} based on their sounding-specific values and uncertainties to generate a linear regression fit per bootstrap loop (light grey lines in Fig. 6). Specifically, 51,000 random sets of ECO and E_{CO₂} were generated following assumed normal distributions, where sounding-level emissions denote the mean statistic with observed and background uncertainties as the standard
deviation (SD) statistic emission estimates provide mean statistics with observational uncertainties as standard deviations. We used the standardized major axis (SMA) solution for linear regression to minimize the deviation of the data point deviations of data points from the regression line for both axes. Eventually, we obtained 51,000 bootstrapped slopes and only selected slopes with positive values, of which mean values and SDs which yield the overpass-level ER CO\textsubscript{2} values and uncertainties (and uncertainty (e.g., colored dashed lines and text in Fig. 6). Sounding level Besides, sounding-level ER CO\textsubscript{2} values from all overpasses are also presented in histograms which and generally follow a log-normal distribution (Figs Fig. 7b, 7d).

| City            | Total power capacity (MW) and by fuel types | Key industry OR annual crude steel capacity (kt yr\textsuperscript{-1}) |
|-----------------|---------------------------------------------|---------------------------------------------------------------------|
| Los Angeles     | 5,808 MW (95.6% fueled by gas; 0% by coal)  | refinery, shipping                                                  |
| Shanghai        | 16,031 MW (75.2% fueled by coal; 24.4% by gas) | iron & steel (25,099 kt yr\textsuperscript{-1})                     |
| Baotou          | 6,470 MW (100% fueled by coal)              | iron & steel (12,619 kt yr\textsuperscript{-1})                     |
| Zibo (w/ Zouping)| 9,720 MW (100% fueled by coal)             | electrolytic aluminum; iron & steel (2,532 kt yr\textsuperscript{-1}) |

Table 1. A summary of total power generation capacity (Global Power Plant Datasets by World Resources Institute, 2018) and information on heavy industry including annual crude iron capacity (GID, Wang et al., 2019). Power plants are selected from a 0.5° × 0.5° region around each city with percentage generated by the main fuel types.

3.2.1 Baotou and Zibo

Combustion efficiencies are generally poor for these two industry-oriented and energy-oriented cities. The overpass-specific ERs span from 8.49 ± 1.2 to 26.7 ± 3.8 mmol mol\textsuperscript{-1} with an integrated city-level estimate of 48.4 ± 0.6 mmol mol\textsuperscript{-1} for Baotou (Fig. 6a). According to GID, the Baotou iron and steel group is located within the city and contributes to an annual capacity of crude iron of 12,619.91 kt 619 kt yr\textsuperscript{-1} with estimated CO\textsubscript{2} emissions of 20,462 kt per year. The relative low yr\textsuperscript{-1} (Table 1). The slightly lower ER CO\textsubscript{2} and FF enhancements in Feb 2021 coincides with the timing of the Spring Festival in 2021. SDs of the 2021 (~Feb 12). SDs of bootstrapped slopes are higher for overpasses with fewer high-quality satellite soundings, e.g., 3.8 mmol mol\textsuperscript{-1} for overpasses with available urban TROPOMI polygons over Baotou seven available TROPOMI polygons in the urban plume on May 31, 2020, which helps minimize 2020. Utilizing the bootstrap method helps account for the impact of low-sounding numbers on the overall city-level ER estimates estimate.
Interestingly, the ER for Zibo first dropped from 11.0 to 10.1 ± 1.1 mmol mol⁻¹ during Feb 2020 and then gradually rose back to 20.4 ± 1.3 mmol mol⁻¹ by June 2020 (Fig. 6b). In addition to low in Feb and May 2020, their FF enhancements remain low. Such temporal variations in both ER and enhancements agree nicely with the timing of the initial phase of COVID-19 lockdown in China.
We suspect changes in ER CO could be driven by the partial shut-down and re-opening of the multiple coal-fired power plants and metal industries in the area.

3.2.2 Los Angeles and Shanghai

Although OCO-3 has sampled the Los Angeles basin several dozens of times to date, unfortunately, a few of them many overpasses did not pass the quality check (i.e., QF) and were removed from the final result due to their dramatic change in wind direction—noticeable shifts in urban plumes between two overpass times (e.g., >3 hours time difference on March 3, April 15, and May 5, 2020 for LA—see discussion; discussed in Sect. 4.1). The overpass-level ER ranges from 7.27±0.8 to 12.11±1.5 mmol-CO/mol-CO2 with a city-level value of either 9.79±0.5 mmol mol−1 informed by using the regression approach (Fig. 7a) or 9.9±0.7 mmol mol−1 by using the histogram approach (Fig. 7b). Our space-based ER CO values for estimates over LA fall within the reported range of 7.1 to 12.4 mmol mol−1 inferred from several from prior studies (Wennberg et al., 2012; Brioude et al., 2013; Hedelius et al., 2016; Silva and Arellano, 2017) despite the time difference. Small discrepancies in ER CO between studies may be attributed to discrepancies in the time of interest, sampling strategies, and techniques for calculating ER CO calculations (e.g., exact background locations, background definition).

In contrast to LA, where urban plumes are usually well-constrained with the basin, the wind speeds and directions change dramatically among vary across different overpasses over Shanghai—i.e., southeasterly wind on Feb 4 and Feb 20, 2020; southwesterly wind on Feb 24, 2020 and Feb 19, 2021; and northerly wind on April 23 and Dec 30, 2020. Such changes in the wind regimes between overpasses over Shanghai suggest that observations per overpass reflect fluxes soundings from an individual overpass may reflect emission patterns over different source regions, which emphasizes the importance of integrating atmospheric transport in interpreting temporal variations in observation-based ERs. In other words, one cannot simply use all the soundings over a city to calculate ERs, but need to select those soundings that are actually affected by emissions from that city. The overpass-specific ER ranges from 4.74±1.2 to 20.17±7.3 mmol mol−1 with a city-level average of 10.5±1.2 mmol mol−1 based on the linear regression approach (Fig. 7c) or 12.9 mmol mol−1 using the histogram approach (Fig. 7d).

a, c) Same as Fig. 6 but for LA and Shanghai. Only bootstrapped regression lines with positive slopes are presented as light grey lines. b, d) Histogram of all soundings (black bars), soundings impacted or strongly impacted by heavy industry are defined using larger than their 75th or 90thpercentiles (blue or red bars) with corresponding median ERs (vertical dashed lines). The industrial impact is quantified using column footprints from X-STILT (to inform atmospheric transport) together with localized information from the urban land cover data WUDAPT.

Histograms for the Now we focused on the distribution of sounding-level ERs within the LA basin and the greater Shanghai area are shown in Fig. 7bd, respectively for these megacities (Fig. 7b, d) to see if ERs associated with a part of the city (i.e., heavy industry region) can be revealed. As described earlier, to address the overpass-specific meteorology, we coupled the LZC-based industrial coverage with X-STILT column footprints to locate the soundings affected or strongly affected by heavy industry in a city. For example, on Feb 20, 2020 the few soundings with of >75thpercentiles (outlined in black in with the account of overpass-specific meteorology, we coupled the LZC-based industrial coverage (Supplementary Fig. ??4c, f) are...
identified as soundings affected by industry with X-STILT column footprints and quantified the industrial influence \( \langle P_{\text{ind}} \rangle \), at each sounding location.

Heavy industrial regions within the LA basin are concentrated to the south (e.g., near the Port of LA) and to the west of downtown near Los Angeles Airport and the Chevron Refinery in El Segundo (Fig. 4e). The distribution of ERs for industry-dominant soundings tend industry-dominated soundings tends to shift slightly towards the lower end (blue or red bars in Fig. 7b) compared to the distribution for all soundings (black-gray bars in Fig. 7b). Specifically, ERs > 20–15 ppm\(^{-1}\) are less frequently found for industry-dominant soundings (red bars in Fig. 7b). It is worth noting that the industry-oriented soundings generally have slightly lower CO but higher CO\(_2\) enhancements (Supplementary Fig. ??a, 2b, c), compared to all other soundings within the valley basin, resulting in slightly lower ER\(_{\text{CO}}\) (Supplementary Fig. ??c). No iron and steel facilities or coal-fired power plants are found over the heavy industry area in LA according to GID and GEM. We hypothesize that the slight shift of ER\(_{\text{CO}}\) towards the lower end may be explained by the heavy-duty diesel engines and natural gas power plants occupying the Port of LA versus the predominately gasoline vehicles across the city, because ER\(_{\text{CO}}\) for heavy-duty diesel vehicles and non-coal-fired power plants are generally lower than that for light-duty gasoline vehicles. For example, by splitting observations for daytime versus nighttime, a field campaign in 2007 in Beijing suggested that the ER linked to nighttime diesel transportation is much lower than the gasoline sub-sector (Westerdahl et al., 2009, Fig. 1a). Similar to LA, higher fuel efficiency has been found over the ship channel of Houston (ER of \( \sim\) 4 ppm\(^{-1}\)) compared to downtown Houston (ER of \( \sim\) 10 ppm\(^{-1}\)) (Brioude et al., 2012, Fig. 1b). Unfortunately, only two good SAMs are available near Houston from late 2019 to June 2021, but future work can further validate the urban-industry contrast in ERs from space.
For Shanghai, the heavy industry is concentrated to the north of the city center (Fig. 4a). Interestingly, in contrast to LA, ERs strongly concentrated with affected by heavy industry are skewed towards the higher end with medians of 16.8 or 18.4–18.8 ppb ppm⁻¹ (blue or red bars in Fig. 7d), compared against the city-level median of 12.7–12.9 ppb ppm⁻¹ (black bars in Fig. 7d). FFCO and FFCO and CO₂ enhancements and ERₐ for all soundings combined. Such spatial divergence in enhancements and ERs between heavy industry and the entire city may be attributed to substantial CO emissions from iron and steel production. Schneising et al. (2019) also found that many hotspots with high TROPOMI CO enhancements in China and India are tied to iron and steel industries. During such production processes, iron ores are reduced to crude iron and steel where CO is involved. According to the plant level estimate in 2019 from GID, Baoshan Iron & Steel Co., Ltd. located to the north of downtown Shanghai has an annual crude steel capacity of 25,000,000 ton yr⁻¹ (Table 1) and a total CO₂ emission of 32,148.0–148 kt yr⁻¹ for all coke, sinter, iron, and crude steel combined.

Finally, to validate the robustness in such ER shifts related to heavy industry within an urban area, we tested different percentile thresholds other than the default 75th and 95th for determining industry-dominant used to determine industry-dominated soundings (Sect. 2.3). The above statements on industry-impacted ERₐ hold if using alternative thresh-
olds including the 50th, 60th, 80th percentiles. Additional Welch two-sample t-test confirms that ERs from industry-dominant soundings significantly differ from the remaining soundings (i.e., less affected by industry-heavy industry). When the adopted percentile threshold increases from 50th to 95th, divergence in ERs between industrial vs. non-industrial soundings becomes more apparent and the p-value for statistical significance in such difference becomes smaller (with p-values < 0.05). Also for all thresholds. In addition, the average number of OCO-3 soundings in a TROPOMI polygon is roughly the same for industry-affected soundings versus the rest (e.g., 11.8 vs. 10.3 for LA and 7.3 vs. 8.7 for Shanghai).

We note that it acknowledged that although many iron/steel plants may aim at combusting as much CO as possible before releasing CO into the atmosphere, the indispensable role CO played in the iron/steel industry makes it unique when assessing its ERCO and combustion efficiency among various industrial processes. Furthermore, it is difficult to separate individual sectoral signals purely from observations (combustion signals of individual sectors from observations) sectoral contributions, since atmospheric concentration at a given location is comprised of various underlying burning combustion processes spread over the source region. Even using additional co-emitted species, it would be risky to assume that a co-emitted species (e.g., CO or NOx) solely comes from one individual emission sector.

4 Discussion

This study is one of the first to analyze intra-city variations of emission ratios between CO and CO2 using two asynchronous satellite sensors. We describe 1) complications induced by discrepancies between satellite sensors and retrievals and 2) demonstrate methods to mitigate these complications by accounting for species-specific averaging kernels, sounding-specific averaging kernels, atmospheric transport, and urban-background contrast in the contribution from non-FF sources/sinks using an atmospheric transport model.

4.1 Influence from non-FF components and atmospheric transport

The pyrogenic anomalies are minimal for the overpasses we examined, but should be considered for certain cities (e.g. during dry seasons over Mexico City, Crounse et al., 2009) considering the high ERCO from forest wildfires of 35 to 80 ppb ppm−1(Fig. 1a). Most overpasses we analyzed fall within the dormant seasons. For the three overpasses during the growing season, modeled biogenic anomalies using the SMUrF model for a given OCO-2/3 sounding may reach up to 0.5 ppm (Supplementary Fig. ??). Even though modeled NEE and resultant biogenic contributions/gradient can be uncertain, we stress again it is the urban-background biogenic contrast (δXbio in Eq. 1) that should be considered for when is important for estimating FFCO2 enhancements given our setup for a local background value. Satellite missions such as TROPOMI and the upcoming Geostationary Carbon Cycle Observatory (GeoCarb) will also provide the provide Solar-Induced Fluorescence (SIF), which may help improve spatially-explicit SIF-based GPP and NEE estimates (Turner et al., 2020; Wu et al., 2021), specifically by reducing the dependence on other remote sensing products and the assumption of model parameters for each plant functional type.
The biggest challenge interfering the robust estimate of spatially-resolved ER estimates is the wind directional shift induced by the lack of concurrence between sensors. ER estimates is the shift in wind directions between two overpass times. Substantial changes in the wind direction and resultant wind directions and urban plumes (e.g., the “outlier” case in “outliers” in Fig. 5e, f) were mostly found for overpasses when absolute time differences with an absolute time difference $|\Delta t|$ were of > 2 hours (implied by the bars with white strips and asterisk on top attached with an asterisk in Fig. 8). However, if TROPOMI pixel sizes are relatively large (i.e., non-nadir observations) or the wind is steadier, this $|\Delta t|$ constraint can be relaxed—may be relaxed, as long as emissions for a specific city is less driven by sectors with noticeable diurnal cycle (e.g., road transportation). For instance, TROPOMI polygon sizes for Baotou on May 31, 2020, TROPOMI polygon sizes for the industry-dominated city Baotou are sufficiently large compared to the shift in urban plumes despite its $|\Delta t|$ of 3 hours (Fig. 8). Because of this, we decided to exclude overpasses with $|\Delta t|$ > 3 hours. In addition, we manually re-positioned the OCO-3 soundings to TROPOMI polygons for a few cases (bars with non-zero numbers on top in Fig. 8) using a simple wind/plume shift demonstrated in Sect. 3.1. Fortunately, future geostationary satellite satellites will be capable of mapping XCO and XCO$_2$ spontaneously simultaneously at a higher temporal frequency, which will eliminate this issue.

![Wind bias summary](image)

**Figure 8.** A summary figure of the investigation on the wind directional shift between OCO-2/3 versus TROPOMI overpass times. The y-axis denotes the absolute time difference ($|\Delta t|$ in hours) for multiple overpasses per overpass. The color of the bar represents the instantaneous modeled surface wind speed [m s$^{-1}$] provided by OCO-2/3 Lite files. Bars labelled with an asterisk indicate that the urban plumes between two overpass times differ significantly so much that they cannot be brought into agreement with a simple plume rotation fails to fix. The number on each bar (e.g., 0~1) denotes the number of TROPOMI polygons needed to be shifted to align the urban plumes at two times. “Good Cases” For example, 0~1 means that TROPOMI polygons over certain locations are shifted by one grid. Bars labelled with zero on top do not require a manual plume shift (bars with zero labelling). Bars outlined with white indicate that the sampled TROPOMI soundings on that date are non-nadir with larger pixel size.
4.2 ERs per individual sounding, per overpass, city, and per heavy industry region within a city

Contrary to previous work relying on inventory-based sector-based ERs, we attribute the intra-urban gradient to heavy industry using an urban land cover classification dataset. Such high-resolution localized maps help guide the identification of identify the observations strongly influenced by heavy industry. Based on a limited sample size, the heavy industry within the greater Shanghai area is tied to an ER$_{CO}$ higher than the city average reflecting a relatively poorer combustion efficiency (Fig. 7d). Industry-oriented Industry- and energy-centered cities like Baotou and Zibo are less efficient in their burning combustion activities. In particular, industry-dominant industry-dominated ERs over Shanghai (20.9±18.8 mmol mol$^{-1}$ as indicated by the red bars dashed red line in Fig. 7d) align better with the overall city-scale ER over Baotou or Zibo (24.1 or 20 of 17.3 mmol mol$^{-1}$ (Fig. 6). The previously reported urban-integrated ER$_{CO}$ values are mostly constrained within the range of 5 to 20 ppb ppm$^{-1}$ with a few exceptions over 30 ppb ppm$^{-1}$ in east Asia before 2010 (Fig. 1). The order of magnitude of our Our city-level estimates from space agree well with that the range of previously reported ER$_{CO}$ values.

Reporting one city-scale ER$_{CO}$ from spatially-explicit ERs can be subjective subject to 1) the adopted statistics statistic, 2) the overpasses and their associated wind regimes overpass dates and overpass-specific wind conditions, and 3) estimated uncertainties in ER$_{CO}$. For example, overall ER based on derived from all soundings within the urban plume differs from ER derived from a selection of soundings. ERs between overpasses over Shanghai can vary due to changes in the wind fields and source receptor geometry. Even though we begun with all available started with all quantified OCO-2/3 observations in a SAM, only soundings-those located within the urban plumes (black curve in Fig. 3) are selected for ER estimate can be used to estimate ERs, which is an unbiased way to assess different compare ERs from overpasses with different meteorological conditions. The mean or median value of sounding-level ER$_{CO}$ (e.g., 13.4 or 9.6 ppb ppm$^{-1}$ for LA in Supplementary Fig. ??) differs slightly from the city-average when using the regression slope method that take observational uncertainties when observational uncertainties were taken into account (e.g., 10.5±9.6 ppb ppm$^{-1}$ for LA in Fig. 7a). Apart from these bulk quantities, intra-city distributions of ERs are negatively skewed the distribution of ER$_{CO}$ in the linear space are negatively-skewed and roughly follow the normal distribution in natural log space log-normal distribution (Supplementary Fig. ??), where a few observations with higher ER$_{CO}$ are influenced by point sources with poorer combustion efficiency. More observations with finer satellite pixels across the city would improve the robustness in both the spatial distribution and the bulk estimates of ERs.

4.3 Limitation and implications

The main limitation of this work is the relatively low sample size largely constrained by the requirement for small differences in overpass times. When more satellite data or upcoming data from geostationary satellites become accessible, intra-city ERs can be used to more robustly re-assess the temporal variations assess the temporal variation in sector-oriented combustion efficiency, including across different seasons and seasons or times (e.g., business-as-usual scenarios versus pandemic-disturbed time frames). Beyond the sheer number of soundings, uncertainty arises due to the aggregation of when aggregating CO$_2$ enhancements from the finer resolution OCO-3 grid to coarser TROPOMI spatial scale TROPOMI sampling. The centered lat/lon coordinates of OCO-2/3 soundings are used to decide which chosen to decide the corresponding TROPOMI polygons
fall into, while a very few OCO soundings may be located right on the boundary of TROPOMI polygons. Nevertheless, we find no significant bias associated with the number of OCO soundings per TROPOMI polygon. The variability from different OCO soundings within a given TROPOMI polygon serves as the “observational noise” in the uncertainty regarding the heavy industry analysis.

We then discuss the impact on our results given the lack of consideration of the secondary CO source. Another factor that we did not explicitly account for is the secondary CO production from both anthropogenic and biogenic VOCs (AVOCs, BVOCs). Under a cascade of reactions in favorable conditions, VOCs can be emitted from the upwind source location are oxidized to CO at various rates, relying on the amount, speciation, and reactivity of VOCs. The lifetimes of and certain VOCs species against OH radical are long enough compared to our time of interests, i.e., a few hours before overpass time to render their impact negligible in this analysis. BVOCs (e.g., isoprene) and a subset of the anthropogenic VOCs (e.g., alkenes) react quickly and often generate HCHO (e.g., Surl et al., 2018) which subsequently can be photochemically converted to CO in a few hours. For example, isoprene contributed to 21.2% of which result in possible higher CO at the downwind sounding location and a divergence between enhancement ratios and emission ratios. As BVOCs are usually associated with shorter lifetimes compared to many AVOCs (e.g., Surl et al., 2018), we discuss BVOCs and AVOCs separately. BVOCs can contribute significantly to the total CO sources from June to August, but negligible amount from March to April over Alaska (Miller et al., 2008). Most of our overpasses fall within the non-growing season, the CO produced by BVOCs may likely be encapsulated in the background XCO and yield a small impact on our results. Regarding industrial areas with possible higher AVOCs than urban cores, e.g., over Houston in Aug-2000 (Czader et al., 2008), whether AVOCs produce significantly more CO over industrial areas than urban cores within the time period of interest remains unclear. Owing to the lack of observations for the source at the regional scale especially during growing seasons (e.g., Miller et al., 2008; Hudman et al., 2008; Gonzalez et al., 2021). However, since BVOCs like biogenic CO2 come mainly from rural areas outside the city, by subtracting localized CO background using CO observations outside the urban plume, the impact from BVOCs on the derivation of CO enhancements would be minimized.

The lifetime of most AVOCs remains long enough, except for a few species including alkenes (Surl et al., 2018). Without a good observational constraint of the VOC composition and species-specific emissions in the air mixture over different cities and parts of a city, it is group-specific emissions for different cities around the globe over the years, it would be challenging to accurately quantify the intra-city variation in secondary CO production and isolate such variation from the observed XCO variability impact on atmospheric XCO and ER_CO due to AVOCs emitted from urban areas or specifically from industrial areas. More future efforts regarding urban VOCs may include 1) exploring what good proxies can be measured from space that well represent the bulk AVOC characteristics (e.g., formaldehyde, Zhu et al., 2014) and 2) interpreting such observations, e.g., by utilizing chemical transport models for source attribution (Gonzalez et al., 2021). Note that the noise/uncertainty in current daily TROPOMI formaldehyde observations may be too large for daily resolved analyses.

This work also provides some-

4.4 Implications for inventory evaluation
This work provides insights towards estimating emission ratios from future satellite sensors, as ERs help pinpoint hotspots with poor combustion efficiency, can help, which to inform sub-city emission/pollution control efforts.

Satellite-based ER may help evaluate sectoral estimates help evaluate sector-specific emission factors and source locations adopted in bottom-up emission inventory inventories (e.g., Silva and Arellano, 2017). Substantial contrast in both the magnitude and spatial distribution of enhancement ratios can be found between the observations and forward simulations based on (using X-STILT column footprint footprints) and sectoral emissions from EDGARv5. Over Shanghai, for example, enhancement ratios simulated using the industry emissions from EDGAR are located far south (Supplementary Fig. ??c), compared to the observed enhancement ratio in Supplementary Fig. ??a. Additionally, the simulated enhancement ratios (Supplementary Fig. ??b) are generally too high (e.g.,). Take Shanghai as an example, simulated enhancement ratios using prior emissions appear to be much higher (> 50 ppb ppm$^{-1}$) compared to, Supplementary Fig. ??b) than observed ratios (mostly < 30 ppb ppm$^{-1}$), Supplementary Fig. ??a). Regarding the spatial distribution, simulated enhancement ratios using total FF emissions mimic simulated enhancement ratios using only industry-related emissions (Supplementary Fig. ??b versus c); and both simulated ratios differ substantially from observed enhancement ratios. Such model-data mismatch may result from inaccurate activity data and emission factors when constructing the bottom-up flux estimates of EDGAR as well as from uncertainties in the atmospheric transport. The simple example atmospheric transport uncertainties. This preliminary analysis illustrates that satellite observations of trace gases could be used to evaluate emission factors used adopted in bottom up emission inventory inventories. More sophisticated approaches such as flux inversion (Hedelius et al., 2018; Brioude et al., 2011, 2012; Palmer et al., 2006) may better constrain sector-specific CO and CO$_2$ emissions from inventories.

Spatial proxies including nightlight data from the Black Marble (https://blackmarble.gsfc.nasa.gov/) and detailed urban land cover data can not only support support not only the development of emission inventories but also sector-orientated investigations with mapped atmospheric concentrations evaluations with atmospheric observations of CO$_2$ and co-emitted pollutants from space. This work demonstrates the benefit of using high-resolution urban land cover datasets like WUDAPT in informing classifications to provide independent information about locations of various anthropogenic activities, building structures, and vegetation coverage. Yet, such high resolution urban datasets (like WUDAPT and NLCD) are currently only available for a limited number of cities across the globe.

5 Conclusion

We investigated fossil fuel combustion efficiency by quantifying the emission ratio of CO and CO$_2$ across Los Angeles, Shanghai, Baotou, and Zibo (Zouping), using nearly coincident observations of TROPOMI XCO and OCO-2/3 XCO$_2$. The multiple swathes of observations collected by OCO-3 SAMs cover a much broader area relative to OCO-2 swathes, facilitating the determination of background values and the separation of emission signals from different parts of a city. We incorporate spatial gradients in the background values by calculating the background for each per swath and correcting for the urban-background gradient due to non-anthropogenic sources and sinks. Sensor-specific averaging kernel profiles and meteorological conditions
were accounted for using an atmospheric transport model (X-STILT). The ratio between XCO and XCO\textsubscript{2} enhancements without considering such sensor-specific factors is normally lower than the emission ratio. Cases with severe asynchronicity, specifically overpass time differences over 3 hours, are excluded from the final result. Temporal variations in the wind fields may result in different source regions with respect to the satellite soundings. Therefore, properly correspond to significant changes in urban plumes. Properly accounting for the meteorology or the overpass-specific meteorological condition or source-receptor relation and identifying the soundings affected by the relationship and identifying only the soundings influenced by urban emissions is important. Critical for estimating ER for cities, which is the main reason that realized using an atmospheric transport model is. Such model approach is then used to identify soundings strongly affected by heavy industry.

The As a result, the overall city-level ER\textsubscript{CO} for Shanghai (40.5±10.2±0.4 mmol mol\textsuperscript{−1}) is slightly larger than the city-level that for Los Angeles (9.7±9.6±0.5 mmol mol\textsuperscript{−1}). Looking at the sub-city scale, industry-related Industry-related ER\textsubscript{CO} for Shanghai are much larger than the its city-level for Shanghai average; whereas industry-related ER\textsubscript{CO} for LA are slightly lower than the its city-level for LA. This divergence in ERs is likely driven by the distinct industrial processes between the two megacities. ERs average, ERs tied to heavy industry regions in Shanghai (18.4±18.8 mmol mol\textsuperscript{−1}) are approximately equal to the city-level ER\textsubscript{CO} for the industry-orientated city of Baotou (18.4±17.3±0.6±0.5 mmol mol\textsuperscript{−1}). High ERs highlight the poor burning combustion efficiency tied to certain industrial activities, e.g., high CO emissions from metal productionmetal productions (Table 1).

With future satellites (e.g., GeoCarb, TEMPO, CO2M) providing better spatial and temporal coverage of XCO\textsubscript{2}–XCO, and other relevant co-located tracer observations, it may will be possible to monitor and verify temporal trend or variations in combustion efficiencies for and variation in the combustion efficiency over hotspots within an urban area, which have significant implications will provide significant guidance for urban planning and emission control.

**Code and data availability.** OCO-3 L2 B10r XCO\textsubscript{2} data and TROPOMI XCO data were accessed from https://doi.org/10.22002/D1.2046 and 10.5270/S5P-hkp7rp, respectively. X-STILT code has been modified to work with TROPOMI data archived on github branch at https://github.com/uataq/X-STILT. We kindly ask the users to follow the code policy in utilizing and acknowledging the X-STILT code for interpreting TROPOMI column data. Hourly NEE fluxes from SMUrF are archived on Oak Ridge National Lab DAAC at https://doi.org/10.3334/ORNLDAAC/1899.

### Appendix A: List of prior studies collected in Figure 1

| Source or Fig. No. | Location | Year(s) | Reference | Estimated source |
|-------------------|----------|---------|-----------|-----------------|
| Traffic | United States | 2006-2007 | Hiller et al. (2006) | Diesel engines; Estimated from EFs |
| Traffic | Switzerland | 2004-2007 | Hiller and Stocker (2006) | Diesel engines; Estimated from EFs |
| Traffic | Paris | 2012 | Ansmann et al. (2012); Table 1 | Tunnel (urgency vs. moving) |
| Traffic | Switzerland | 2013 | Pope et al. (2014); Table 1 | Tunnel (urgency vs. moving) |
| Traffic | Beijing, China | 2014 | Wang et al. (2014) | Tunnel (urgency vs. moving) |

| Shopping | China | 2013 | Zheng et al. (2013); Table 1 | Tunnel (urgency vs. moving) |
| Shopping | Western Europe | 2006 | Moldanová et al. (2009); Table 5 | Tunnel (urgency vs. moving) |
| Shopping | Taiwan | 2006 | Williams et al. (2009); Figure 2 | Tunnel (urgency vs. moving) |
| Shopping | Global | 2015 | Akagi et al. (2015); Table 1 | Estimated from EFs |

Note: EF = Emission factor; Estimated from EFs.
| Urban areas in Fig. 1b | Observation years | Reference |
|-----------------------|-------------------|-----------|
| Los Angeles (LA)      | 2002 and 2010     | Brioude et al. (2013) |
| LA                    | 2007-2008         | Djuricin et al. (2010) |
| LA                    | 2008 and 2010     | Wennberg et al. (2012) |
| LA                    | 2010              | Silva et al. (2013); Silva and Arellano (2017) |
| LA                    | 2013-2016         | Hedelius et al. (2016) |
| LA                    | 2019-2021         | This study, Figure 7 |
| Pasadena              | 2007              | Wennberg et al. (2012), Table 2 |
| Sacramento            | 2009              | Turnbull et al. (2011a), Sect. 3.2 |
| Indianapolis ( Indy)  | 2012-2014         | Turnbull et al. (2015) |
| Salt Lake City (SLC)  | 2015-2016         | Bares et al. (2018), Table 2 |
| Edinburgh             | 2005              | Famulari et al. (2010), Table 1 |
| Paris                 | 2010              | Lopez et al. (2013) |
| Paris                 | 2010-2014         | Ammoura et al. (2016), Table 1 |
| London                | 2006              | Harrison et al. (2012), Figure 27 |
| London                | 2012              | O’Shea et al. (2014), Table 3 |
| London                | 2016              | Pitt et al. (2019), Table 2 |
| Rotterdam             | 2011              | Super et al. (2017) |
| Germany Alps          | 2012-2013         | Ghasemifard et al. (2019) |
| Hungary               | 2017              | Haszpra et al. (2019), Table 1 |
| St. Petersburg         | 2019              | Makarova et al. (2021) |
| Miyun                 | 2004-2008         | Wang et al. (2010), Table 2 |
| Beijing               | 2006              | Han et al. (2009), Figure 11 |
| Shangdianzi           | 2009-2010         | Turnbull et al. (2011b) |
| Nanjing               | 2011              | Huang et al. (2015), Sect. 3.4.2 |
| Seoul                 | 2016              | Tang et al. (2018), Table 3 |
| Seoul                 | 2019              | Sim et al. (2020), Table 2 |
| Jingdezhen            | 2017-2018         | Xia et al. (2020), Table 3 |
| Zibo, Baotou, Shanghai| 2019-2021         | This study, Figures 6-7 |

**Author contributions.** DW designed and carried out this analysis. JL, POW, and PIP supervised this study. RRN, MK, and AE provided the bias-corrected B10 data for OCO-3 SAMs used in this work. All authors participated in the interpretation of the results and paper writing plus editing.

**Competing interests.** The authors declare no conflict of interests.

**Acknowledgements.** The production of the OCO-3 science data products used in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration [prime contract num-
The research effort was funded by the Jet Propulsion Laboratory Research and Technology Development project R.21.023.106. The analysis is supported by the W.M. Keck Institute for Space Studies and by the National Aeronautics and Space Administration (grant number 80NSSC21k1064). The computations presented here were conducted in the Resnick High Performance Computing Center, a facility supported by Resnick Sustainability Institute at the California Institute of Technology. The first author appreciates the discussion with Joshua Laughner, Eric Kort, Tomohiro Oda, and John Lin. We thank Julia Marshall and the second anonymous referee for their careful read of our submitted manuscript and for their constructive suggestions that have helped improve our study.
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