

Development of the United States GR²ES and Air Pollutants Emissions System (GRA²PES)

Key Points:

- GRA²PES provides consistency between fossil-fuel carbon dioxide (ffCO₂) and air quality (AQ) species at high spatial and sectoral resolution
- The air pollutants best correlated with ffCO₂ are nitrogen oxides (NO_x), sulfur dioxide (SO₂), and carbon monoxide (CO)
- The GRA²PES inventory is evaluated with observations in Los Angeles and within ~19% of radiocarbon (¹⁴C)-derived ffCO₂ and AQ/ffCO₂ ratios

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract In the U.S., emissions of greenhouse gases and air pollutants are often developed independently. Here, we describe the GR²ES and Air Pollutants Emissions System (GRA²PES), which provides gridded emissions of fossil-fuel carbon dioxide (ffCO₂) and 93 air quality (AQ) species for 17 combustion and non-combustion sectors at 4 km × 4 km spatial resolution across the contiguous US. We find that the AQ emissions most spatially correlated with ffCO₂ are nitrogen oxides (NO_x, $\rho = 0.67$), followed by sulfur dioxide (SO₂, $\rho = 0.51$), carbon monoxide (CO, $\rho = 0.44$), and fine particulate matter (PM_{2.5}, $\rho = 0.38$). We evaluate GRA²PES ffCO₂ emissions with an ensemble of publicly available regional and global inventories at national (Normalized Mean Bias (NMB) = +1.4%), state (NMB = +1.5%, $R^2 = 0.98$), and urban (NMB = +11.5%, $R^2 = 0.97$) scales. Nationally, the differences of publicly available inventories from the ensemble average range from −10.0% to +5.7%, and consistency diverges at state and urban scales. We simulate GRA²PES ffCO₂ in a particle dispersion model and compare to measurements of radiocarbon (¹⁴C)-derived ffCO₂ collected in Los Angeles (August 2021), with results suggesting that GRA²PES ffCO₂ may be low by 19% for this city, but well within model-observation differences for other publicly available inventories (−43% to +94%). GRA²PES AQ/ffCO₂ ratios converted to concentration space generally agree with field observations (NMB = +4%, log $R^2 = 0.90$). Lastly, we present a method by which to utilize GRA²PES to derive AQ emission fluxes from ffCO₂ emissions.

Plain Language Summary We developed a fossil-fuel carbon dioxide (ffCO₂) emissions inventory over the contiguous U.S. that uses spatiotemporal information consistent with that for air pollutants emissions known as the GR²ES and Air Pollutants Emissions System (GRA²PES). We examined the performance of GRA²PES by evaluating estimated emissions with respect to six publicly available ffCO₂ inventories, radiocarbon (¹⁴C)-based ffCO₂ measurements, and AQ/ffCO₂ ratios observed in Los Angeles. GRA²PES enhances research analyses of combustion-related impacts on air quality from national to state and urban scales.

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1. Introduction

Carbon dioxide (CO₂) emissions from fossil fuel combustion and non-combustion processes are the dominant source of anthropogenic fossil-fuel CO₂ (ffCO₂) to the atmosphere (Friedlingstein et al., 2023), and the single largest contributor to total radiative climate forcing (Hofmann et al., 2006). Co-emitted air pollutants, include nitrogen oxides (NO_x), carbon monoxide (CO), sulfur dioxide (SO₂), volatile organic compounds (VOCs), and

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fine particulate matter (PM_{2.5}), which impact human health (Jerrett et al., 2009; Penha & Werthamer, 1974; Turner et al., 2016) and ecosystems (Ainsworth et al., 2012; Roberts, 1984). Due to different monitoring requirements and reporting frameworks, GHG and AQ emission inventories are often developed independently, even though species are often co-emitted during fossil fuel combustion and various non-combustion industrial processes, such as natural gas systems, cement production, and lime production (EPA GHGI, 2017). Furthermore, it is challenging to integrate greenhouse gas (GHG) and air quality (AQ) emissions inventories (Smith et al., 2022), due to differences in legal requirements, end uses, available resources, key emission sectors, and reporting conventions, including time requirements, emissions units, and emissions uncertainty.

As an example of the challenge to integration, within the US, there are four key GHG and AQ data sets reported by the United States Environmental Protection Agency (US EPA). The National Emissions Inventory (NEI) is reported every 3 years, which covers criteria and hazardous air pollutants and other photochemically reactive species in the atmosphere (EPA NEI, 2017). For GHGs, the US Greenhouse Gas Emissions and Sinks Inventory (EPA GHGI, 2017) reports national and state-level estimates annually. At the facility-level, the US Greenhouse Gas Reporting Program (EPA GHGRP) requires industrial facilities emitting over 25,000 metric tons of CO₂ equivalent per year to report their GHG emissions (EPA GHGRP, 2017). For AQ, facility-level emissions are reported through the NEI and thresholds vary by state. Lastly, Continuous Emissions Monitoring System (EPA CEMS) data report CO₂ and select AQ emissions (NO_x and SO₂) on a monthly basis for Electric Generating Units (EGUs) that have power generation capacity over 25 MW (EPA CEMS, 2017). Given the different cadences and spatial scales at which each of these four key GHG and AQ data sets are reported, careful consideration is needed on how to integrate them for a more holistic GHG and AQ inventory.

Academic and research institutions also have been working on global and regional GHG and AQ emission inventories. Globally, the Open-Data Inventory for Anthropogenic Carbon dioxide (ODIAC) provides estimates of ffCO₂ emissions at 1 km × 1 km spatial resolution from 2000 to 2023 and is updated annually, combining space-based nighttime light data and individual power plant emissions and location profiles (Oda et al., 2018). Integrated GHG and AQ inventories have also been developed at global scale, including the Community Emissions Data System (CEDS; Hoesly et al., 2018) and the Copernicus Atmosphere Monitoring Service (CAMS) global anthropogenic inventory (Soulie et al., 2024). CEDS is a framework of global historical emission estimates that traces emissions levels of GHGs and AQ species back to 1750 (Hoesly et al., 2018). Similar to CEDS, the CAMS global anthropogenic inventory also provides sectoral emissions for both GHG and AQ species, and CAMS further advances the speciation of VOCs into 25 distinct chemical bins (Soulie et al., 2024). These combined AQ and GHG global inventories allow for integrated analysis of climate and air quality. However, the 0.1° spatial resolution, lack of diurnal and day-of-week temporal resolution, lack of vertically-resolved emissions (e.g., plume-rise), and the relatively few VOC speciated bins, are less than ideal for modeling GHG and AQ at the urban scale where atmospheric modeling is typically performed at 4 km × 4 km spatial resolution or less and hourly temporal resolution or finer. Regionally, two U.S. ffCO₂ inventories, including the Vulcan Project and the Anthropogenic Carbon Emission System (ACES) are publicly available. The Vulcan Project, begun in 2004, estimates hourly sectoral ffCO₂ emissions over the U.S. at 1 km × 1 km spatial resolution from 2010 to 2022 (Gurney et al., 2009, 2019, 2024). ACES is a sectorally-resolved U.S. ffCO₂ emissions inventory from 2012 to 17 also at 1 km × 1 km spatial resolution (Gately & Hutyla, 2022). Unlike the global scale products, integrated and gridded GHG and AQ inventories are typically not available at the U.S. regional scale.

Other research-based sector-specific emission inventories for the U.S. have also been developed with some of them covering both CO₂ and AQ. The Fuel-based Inventory of Vehicle Emissions (FIVE; Harkins et al., 2021; McDonald et al., 2014, 2018b) estimates emissions of CO₂ and co-emitted AQ species for on-road and nonroad transportation using taxable fuel sales for on-road engines from the U.S. Federal Highway Administration, and off-road fuel sales data reported by the U.S. Energy Information Administration (US EIA; Kean et al., 2000), respectively. A similar fuel-based method is used in the Fuel-based Oil and Gas (FOG) inventory (Francoeur et al., 2021; Gorchoff Negron et al., 2018) to estimate CO₂ and co-emitted AQ species from onshore oil and natural gas extraction. However, for completeness, AQ inventories must also attempt to include non-combustion sources of emissions to the atmosphere. A significant source of anthropogenic non-methane volatile organic compounds (NMVOCs) are volatile chemical products (VCPs), which have been estimated nationally through a mass balance of petrochemical feedstocks (McDonald, de Gouw, et al., 2018), estimated over time (Kim et al., 2022) and gridded utilizing population density as a spatial surrogate (Gkatzelis et al., 2021b). A recently developed residential and commercial cooking emissions inventory provides estimates of NMVOCs derived from

atmospheric observations in Las Vegas, Nevada (Coggon et al., 2024; Stockwell et al., 2025). These sector-specific emission inventories covering CO₂ and/or AQ for the U.S. lay the foundation for creating a complete CO₂ and AQ emission inventory covering all major sectors for the U.S.

Here, we describe the GREENhouse gas And Air Pollutants Emissions System (GRA²PES). We have designed GRA²PES to be a self-consistent sectorally-resolved ffCO₂ and AQ emissions inventory capturing 17 sectors (74 sub-sectors), 94 species, gridded at 4 km × 4 km over the contiguous US (CONUS), temporally resolved to capture key timescales (monthly, day-of-week, diurnal), and vertically resolved to capture processes such as plume-rise from large point sources. The baseline year is 2017 and can be updated to other months and years following a near real-time emissions estimate approach presented by He et al. (2024). Compared to existing integrated GHG and AQ global inventories, GRA²PES provides more sectoral detail, more AQ species, and greater spatiotemporal resolution. Comparing with the publicly available U.S. regional ffCO₂-only inventories, GRA²PES includes emissions estimates for an additional 93 AQ species. Thus, GRA²PES greatly enhances the integrated analysis of GHG and AQ at urban scales. To evaluate the reliability of GRA²PES, including rigorous evaluation by comparison with atmospheric observations, the objectives of this study are:

1. Comparing GRA²PES to other commonly used ffCO₂ inventories on scales ranging from national to urban;
2. Evaluating GRA²PES ffCO₂ emissions using radiocarbon (¹⁴C)-based ffCO₂ measurements collected in Los Angeles in the summer of 2021;
3. Evaluating GRA²PES AQ/ffCO₂ emission ratios using observations from the same field campaign, and then using observed AQ/ffCO₂ ratios and optimized GRA²PES ffCO₂ to calculate AQ emissions for the Los Angeles area.

In addition, ¹⁴C-based ffCO₂ observations have been used to estimate ffCO₂ emissions at the U.S. national scale (Basu et al., 2020), but the application of such observations in an urban environment is uncommon and presented in this study.

2. Methods

2.1. Bottom-Up Inventory Development

2.1.1. Overview of GRA²PES Processing

Table 1 summarizes the data sources for both ffCO₂ and AQ by 17 sectors. Maintaining consistent spatiotemporal allocation between ffCO₂ and AQ species, GRA²PES integrates emission data sets from the US EPA, including the NEI, CEMS, GHGRP, and the US EIA's State Energy Data System (EIA SEDS, 2017), along with previously published inventories in the literature. Emissions are gridded for CONUS at 4 km × 4 km spatial resolution utilizing the same domain as the gridded NEI. GRA²PES also provides monthly, day-of-week, and diurnal emissions, as well as vertically-resolved emissions from point sources that account for stack plume-rise. GRA²PES uses 2017 as the base year and emissions can be extrapolated to more recent years.

The NEI provides AQ emissions for point and areawide sources of emissions. Areawide emissions are reported at a county-level and can be downscaled to 4 km × 4 km grids utilizing the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system (<https://www.cmascenter.org/smoke>). For Electric Generating Units (EGUs), point source or facility-level CO₂, NO_x, and SO₂ emissions are provided by CEMS utilizing stack monitors. The GHGRP reports facility-level GHG emissions only for facilities above a threshold of 25,000 metric tons CO₂ equivalent per year. SEDS provides state-level energy consumption data by fuel type and sector, and ffCO₂ emissions can be estimated utilizing EPA emission factors (EPA CO₂ EF, 2017). Previously reported inventories are included to capture major components of the petrochemical industry life cycle and critical urban air pollution sources, and described below. The base year of GRA²PES is 2017 because the NEI is only reported every 3 years. The 2020 NEI has impacted activities associated with the COVID-19 pandemic, complicating the representativeness of 2020 as a baseline year. To extrapolate GRA²PES to more recent years, we employ economic and energy scaling factors that capture month-to-month variations of emissions during the COVID-pandemic and recovery-phases as described by He et al. (2024). The first release of GRA²PES is for the calendar year 2021, which is the year of field observations that we utilize to evaluate the inventory. However, our methods and data sources will be applied in the future to develop a long-term reanalysis. Sectoral definitions are listed in Table S1 using the US EPA Source Classification Codes (SCC) corresponding to 74 sub-sectors, specific to fuel types and processes, which are then aggregated to the 17 sectors listed in Table 1. GRA²PES tracks ffCO₂, 7 criteria air

Table 1
Summary of GRA²PES Sectors and Data Sources for ffCO₂ and AQ Emissions

Sector code	Sector	ffCO ₂ data		AQ data source	Reference
		NRT	source		
RES	Residential	✓	SEDS, EPA	NEI17	EIA SEDS, (2017), EPA CO ₂ EF (2017), EPA NEI (2017)
COMM	Commercial	✓	SEDS, EPA	NEI17	EIA SEDS (2017), EPA CO ₂ EF (2017), EPA NEI (2017)
INDF	Industrial fuel	✓	SEDS, EPA, GHGRP	NEI17, GHGRP	EIA SEDS (2017), EPA CO ₂ EF (2017), EPA GHGRP (2017), EPA NEI (2017)
INDP	Industrial processes	✓	GHGRP	NEI17, GHGRP	EPA GHGRP (2017), EPA NEI (2017)
RAIL	Railroad	✓	EIA	NEI17	EPA NEI (2017), U.S. EIA (2017)
EGU	Electric Generating Units (EGU)	✓	CEMS (CO ₂)	NEI17, CEMS (NO _x , SO ₂ only)	EPA CEMS (2017), EPA NEI (2017)
AVIATION	Airport	✓	–	NEI17	EPA NEI (2017)
FUG	Fugitives	✓	–	NEI17	EPA NEI (2017)
WASTE	Waste	–	–	NEI17	EPA NEI (2017)
AG	Agricultural	–	–	NEI17	EPA NEI (2017)
ONROAD_GAS	On-road Gasoline	✓	FIVE	FIVE	Harkins et al. (2021), McDonald et al. (2014, 2018b)
ONROAD_DSL	On-road Diesel	✓			
OFFROAD	Nonroad	✓			
OG	Oil and Gas	✓	GHGRP, FOG	GHGRP, NEI17, FOG	EPA GHGRP (2017), EPA NEI (2017), Francoeur et al. (2021), Gorchov Negron et al. (2018)
VCP	Volatile Chemical Products (VCP)	✓	–	VCP	McDonald, de Gouw, et al. (2018)
COOKING	Cooking	–	–	Observations, gridded population	Coggon et al. (2024)
SHIPPING	Shipping	–	CAMS v4.2	CAMS v4.2	Granier et al. (2019)

pollutants species (CO, NH₃, NO_x, SO₂, primary PM₁₀, primary PM_{2.5}, and total NMVOC), 19 speciated PM species, and 67 speciated NMVOC species (Table S2). The speciation of PM follows EPA's Speciate 5.0 tool (<https://www.epa.gov/air-emissions-modeling/speciate-2>). The speciation of NMVOC utilizes the State-wide Air Pollution Research Center version 11 (SAPRC-11) chemical mechanism and Speciate 5.0 VOC profiles.

Figure 1 provides an overall schematic of the GRA²PES emissions processing system, which consists of four modules that: (a) integrate AQ and ffCO₂ emissions for NEI-based sectors using consistent spatiotemporal information between ffCO₂ and AQ (CO), (b) incorporate previously developed inventories, (c) perform near real-time emission adjustments to scale base year estimates to relevant months and years, and (d) add in year- and month-specific point source emissions from CEMS and GHGRP. Modules (a, b) output areawide and point source emissions of ffCO₂ and AQ species at 4 km × 4 km gridded spatial resolution and hourly temporal resolution. Module (c) scales gridded emissions by sub-sector utilizing energy and economic data sets available at monthly time-resolution. As a last step, module (d) adds in year- and month-specific point source emissions from CEMS and GHGRP. A more detailed version of Figure 1 is provided as Figure S1 in Supporting Information S1. Below are more information on how sectoral emissions are processed utilizing these four modules.

2.1.2. NEI-Based Emissions Sectors

2.1.2.1. Residential and Commercial Fuel Combustion

We employ module (a) (Figure 1a) to process emissions for the residential and commercial fuel combustion sectors. Specifically, the annual total state-level ffCO₂ emissions are estimated by multiplying sector- and fuel-specific energy end-use reported in EIA SEDS (coded by Mnemonic Series Names, i.e., MSN) with EPA CO₂ emission factors. The MSN codes included in the calculations and their CO₂ emission factors are provided in Table S3. Three fossil fuel types are considered for this sector in GRA²PES, which are coal, natural gas, and petroleum products. The mapping from MSN to each GRA²PES sector and fuel type is provided in Table S1.

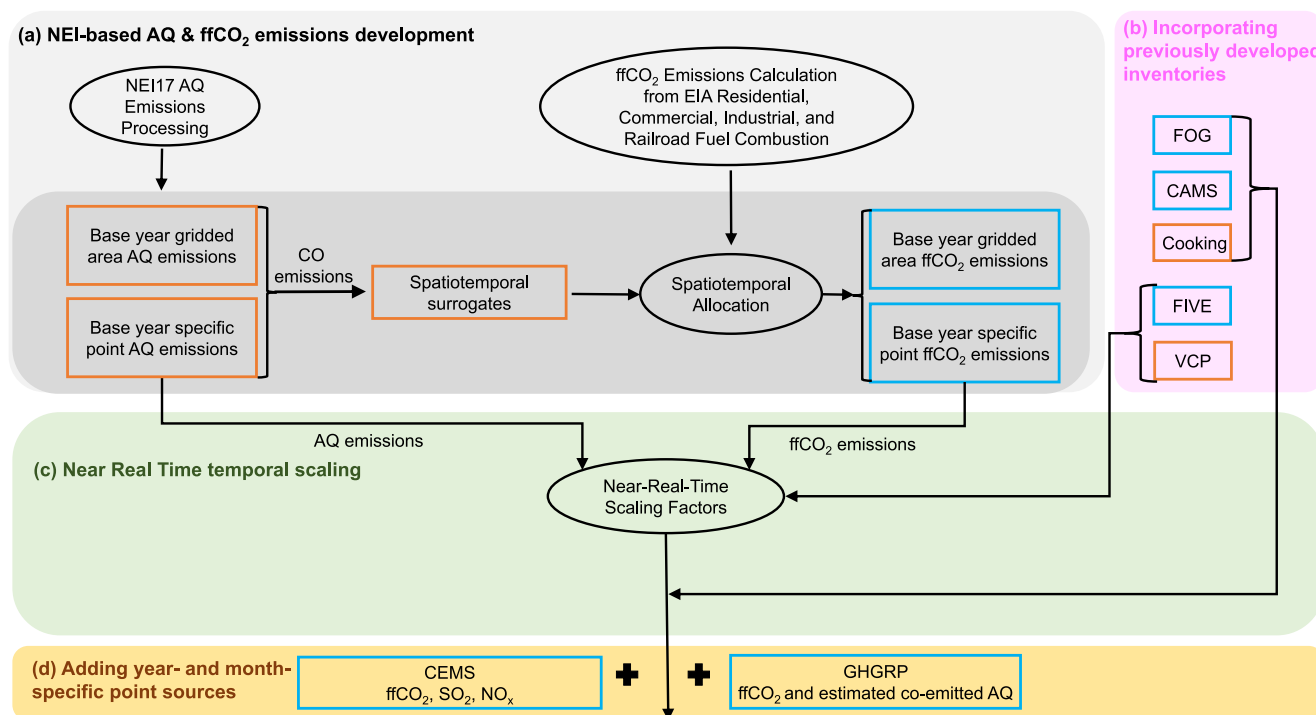


Figure 1. GRA²PES emissions processing overview. Rectangles represent data and ellipses represent emissions processing procedures. Orange outlines indicate AQ emissions-only, blue outlines indicate inclusion of ffCO₂ emissions. Data and emissions processing procedures are grouped into four modules, which are (a) NEI-based AQ & ffCO₂ emissions development, (b) incorporation of previously developed inventories, (c) near real-time (NRT) temporal scaling, and (d) adding year- and month-specific point sources.

These are the same approaches as EPA's GHGI, including the same adjustment to SEDS energy end-use activity data (Text S1 in Supporting Information S1), and as a result, our annual total fossil fuel combustion CO₂ emissions for the residential and commercial sectors are the same as EPA's GHGI by state. This step is represented by the ffCO₂ emissions calculation from EIA SEDS circle in Figure 1a and the blue boxes in the top right corner of Figure S1a in Supporting Information S1.

To get spatially-gridded and temporally-resolved (month, day-of-week, and hourly) emissions, the state-level estimates are downscaled utilizing CO emissions from the spatially and temporally processed NEI17 as a surrogate for ffCO₂ (Text S2, Figure S2 in Supporting Information S1). The NEI17 is processed and gridded by sector, fuel type, month, day-of-week, and hour-of-day utilizing a tool that replicates the functionality of SMOKE. The state-level ffCO₂ emissions are then downscaled with the same spatiotemporal patterns as the gridded NEI17 CO emissions by sector and fuel type. This step is represented by the Spatiotemporal Allocation circle in Figure 1a. Since CO emissions can be influenced by combustion efficiency (Westbrook & Dryer, 1984), which mainly varies by combustion conditions (Aydin & Boke, 2010; Lee & Jou, 2011) and fuel types (Frye et al., 1999; Kaewboonsong et al., 2006), using sector- and fuel type-specific CO emissions limits the variations in combustion efficiency. NO_x emissions are also highly spatially correlated with ffCO₂ emissions (Gao et al., 2022), and we found NO_x emissions-based surrogates to be very similar to CO emissions-based surrogates for the sectors and fuel types we downscale state-level ffCO₂ emissions (Figure S3 in Supporting Information S1). Since residential and commercial fuel combustion largely occur in buildings, most of the emissions are gridded as areawide sources.

2.1.2.2. Industrial Fuel Combustion and Processes

In GRA²PES, industrial fuel combustion is separated between coal, natural gas, and petroleum energy consumption. The state-level ffCO₂ emissions calculation for the industrial fuel combustion utilizes the same approaches as the residential and commercial fuel combustion. Industrial processes include manufacturing for chemical, food, metals and mining, refinery, pulp and paper, electrical equipment, automotive, apparel,

photographic film, pharmaceutical, machinery, and miscellaneous processes. Industrial emissions are divided between areawide and point source or facility-level emissions, which adds complexity to the emissions processing system. GHGRP provides valuable facility-level ffCO_2 emissions from large industrial facilities for both fuel combustion and non-combustion processes. To incorporate GHGRP facility-level ffCO_2 emissions while avoiding double-counting these emissions with the state-level ffCO_2 calculated from EIA SEDS and integrate ffCO_2 emissions with AQ emissions reported by NEI17, we combine modules (a, d) (Figures S1a and S1d in Supporting Information S1), the details of which are provided in Text S3 in Supporting Information S1.

2.1.2.3. Railroad

For rail transport, ffCO_2 emissions are initially calculated utilizing EIA fuel use and EPA CO_2 emission factor for diesel combustion. Diesel is the predominant fossil fuel utilized by rail. We calculated ffCO_2 emissions at the national level prior to downscaling because of the high throughput of goods movement across state boundaries. Similar to other areawide sectors, CO emissions from the NEI17 are utilized as a spatiotemporal proxy to downscale ffCO_2 , while gridded AQ emissions are processed directly from the NEI17. The relative module used for railroad emissions is module (a) (Figure 1a).

2.1.2.4. Electric Generating Units (EGU)

Both AQ and CO_2 emissions from EGUs in the U.S. have decreased steadily since 2000 (de Gouw et al., 2014) due to transitioning of coal-fired to natural gas combined cycle power plants and increasing energy production from renewable sources (Saundry, 2019). Given the change in EGU facilities and emissions over time, we utilize year- and month-specific unit-level EGU emissions from stack monitors provided from EPA CEMS, which reports CO_2 , NO_x and SO_2 emissions. Since CEMS only provide these three species, emissions of other AQ species are still provided by the NEI. To harmonize these two data sources, modules (a, d) are used, which are described into details in Text S4 of Supporting Information S1.

2.1.2.5. Other AQ-Only Sectors (Airport, Fugitives, Waste, Agriculture)

For 4 out of the 17 sectors (airports, fugitives, waste facilities, and agriculture), we include only AQ emissions from the NEI17, which are also processed using module (a) (Figure 1a). In the NEI, the airport sector is defined as emissions during taxiing, takeoff, and landing, and also does not include CO_2 . We recommend that vertically-resolved and gridded aviation emissions that are publicly available (Teoh et al., 2024) be used to replace the airport emissions in GRA²PES for integrated GHG and AQ assessments of aviation. Here, we categorized construction and road dust emissions as fugitives, which are not expected to be co-emitted with CO_2 . While waste and agricultural sources are expected to be significant sources of methane, they comprise only 0.4% of ffCO_2 emissions according to the US GHGI. The ffCO_2 emissions in the waste category are mostly from waste gas flares on landfills and wastewater treatment plants. Currently, GRA²PES does not include methane or fluorinated gases, but these will be considered in future research.

2.1.3. Previously Reported Inventories

For 7 out of the 17 sectors, ffCO_2 and/or AQ are from previously published inventories in the literature and added in module (b) (Figure 1b) with the NEI-based emissions sectors (Figure 1a). All inventories are available or projected onto the NEI 4 km $\times$ 4 km grid prior to addition. Some sectors do not include ffCO_2 emissions, but are important for simulating air pollution, including NMVOCs from VCPs and cooking. A brief description of the published inventories is provided below, although more details on the methodologies can be found in the references listed in Table 1.

2.1.3.1. On-Road and Off-Road Vehicles

On-road and off-road vehicle emissions are from the FIVE inventory (Harkins et al., 2021; McDonald et al., 2014, 2018b). On-road emissions are separated between heavy-duty diesel and light-duty gasoline. The U.S. Federal Highway Administration tracks taxable fuel sales of on-road engines by state, which are downscaled to the roadway-level using vehicle counts from the Highway Performance Monitoring System (<https://www.fhwa.dot.gov/policyinformation/hpms.cfm>). In the process of downscaling fuel to the road-way level, around 80% of light duty traffic (used as a spatial proxy for gasoline consumption) and 70% of heavy-duty traffic (used as a proxy for

diesel consumption) can be accounted for at the roadway level, with the rest (occurring primarily on smaller road types) being distributed spatially based on population density (Harkins et al., 2021). Fuel-based emission factors are used to estimate co-emitted air pollutants from mapped fuel use, and summarized from roadside measurements and laboratory studies (McDonald et al., 2013, 2015; Yu et al., 2021). Day-of-week and diurnal activity factors are applied to estimate hourly emissions for light- and heavy-duty vehicles separately (McDonald et al., 2014). Non-road engine emissions are also included in FIVE, with EIA reported state-level off-road fuel sales data allocated to end uses (Kean et al., 2000). AQ emission factors for non-road engines are taken from the EPA NONROAD model or literature values (McDonald et al., 2015). The FIVE inventory has been evaluated in various regions with atmospheric models and ground, airborne, and satellite observations, and updated to reflect rapid changes in human activity such as those due to the COVID-19 pandemic (He et al., 2024; Kim et al., 2016; Li et al., 2021; McDonald, McKeen, et al., 2018). Lastly, since GRA²PES is evaluated with atmospheric observations that can distinguish fossil and non-fossil components of CO₂, we account for the fraction of finished motor gasoline and diesel blended with fuel ethanol and biodiesel, respectively. We estimate 93.3% of gasoline and 97.2% of diesel CO₂ emissions are of fossil origin based on an analysis of EIA data (<https://www.eia.gov/totalenergy/data/monthly/pdf>).

2.1.3.2. Oil and Gas

The FOG inventory includes CO₂ and co-emitted AQ species from areawide drilling and production equipment utilized for extracting oil and natural gas in onshore shale basins, and similarly evaluated with airborne and satellite observations (Dix et al., 2020, 2022, 2023; Francoeur et al., 2021; Gorchov Negron et al., 2018). Several important updates have been made to the original FOG inventory (Francoeur et al., 2021) and incorporated into GRA²PES (Text S5 in Supporting Information S1). Point source emissions from natural gas processing plants are integrated between the GHGRP for ffCO₂ and NEI17 for AQ species similar to industrial sources using modules (a, d) (Figures 1a and 1d). We also utilize the NEI17 for offshore O&G, and for storage (e.g., bulk terminals), transport, and evaporative gasoline emissions, as well as other onshore point sources.

2.1.3.3. Volatile Chemical Products

VCPs are defined as everyday consumer products, as well as industrial uses, of coatings, inks, adhesives, personal care products, cleaning agents, and pesticides. As described in the introduction, these emissions have been estimated nationally (McDonald, de Gouw, et al., 2018), estimated over time (Kim et al., 2022), gridded (Gkatzelis et al., 2021b), and input into chemical transport models to simulate air quality (Coggon et al., 2021; Kim et al., 2022; Zhu et al., 2024). While VCP emissions do not directly emit CO₂, the NMVOCs emitted to the atmosphere undergo chemical reactions that can be oxidized to CO₂. Because GRA²PES is also intended to be utilized in air quality models, we provide VCP emissions only as NMVOCs, recognizing that these petrochemical feedstock emissions can be converted to CO₂ for full carbon accounting purposes.

2.1.3.4. Cooking

VOC emissions from commercial and residential cooking are added based on atmospheric observations made in Las Vegas, Nevada (Coggon et al., 2024). Residential and commercial cooking emissions are the non-combustion portion only, as fuel combustion emissions are already accounted for in the residential and commercial fuel combustion sectors. Cooking NMVOC emissions are calculated per capita and are distributed onto a grid using population. Non-combustion cooking emissions of PM are under development, and will be included into GRA²PES in our next version update.

2.1.3.5. Shipping

GRA²PES takes both domestic and international shipping emissions of all species from the Copernicus Atmosphere Monitoring Service (CAMS) Global Anthropogenic Inventory v4.2 (Granier et al., 2019). To avoid double counting, NEI17 emissions from commercial marine vessels are removed. CAMS shipping emissions, which are provided at 0.1° × 0.1° resolution globally, are projected onto the NEI 4 km × 4 km Lambert Conformal grid.

2.1.4. Near Real-Time Scaling

The COVID-19 pandemic challenged the development of bottom-up inventories, which often have a few years lag, to account for abrupt changes in human behavior. Review studies of the pandemic showed that reductions in air pollutant emissions were tied to shelter in place measures and the level of reductions depended on the strictness of measures (Gkatzelis et al., 2021c; Sokhi et al., 2021). Here, we employ near real-time (NRT) scaling factors that are year and month-specific (YYYYMM) and illustrated in module (c) (Figure 1c). The full methodology can be found in the work of He et al. (2024) and is briefly described in Text S6 of Supporting Information S1. Table 1 identifies which sectors have NRT scaling factors applied to estimate years and months beyond the 2017 baseline year. We did not attempt to compute waste and agriculture NRT scaling factors, and for these sectors emissions are left as is from the NEI17. However, all sectors that include ffCO₂ emissions have been adjusted to be year and month-specific. In addition to identifying economic and energy data sets for NRT updating, He et al. (2024) simulated atmospheric O₃ and PM_{2.5} precursors distributions based on the NRT emissions utilizing the Weather Research Forecasting with Chemistry (WRF-Chem) model. Atmospheric abundances were then evaluated with spaceborne observations of nitrogen dioxide (NO₂) and formaldehyde (an observational constraint on NMVOC emissions). In general, the NRT inventory (a predecessor to the GRA²PES inventory described here), was able to capture observed changes over urban areas, industrial and power plant point sources, and oil and gas producing regions during the COVID-19 lockdown period and post-recovery phases. The main advance in this work is that the NRT scaling has been applied to ffCO₂ emissions along with AQ species within GRA²PES, whereas He et al. (2024) only updated AQ species. Unless otherwise specified, sectoral emissions in GRA²PES outside of the baseline 2017 years have employed NRT scaling factors. The biggest exception is facility-level emissions from CEMS for EGUs and GHGRP for industrial sources. For these large point source emissions, year and month-specific data is utilized when available and is the last step of the emissions processing system (Figure 1d).

2.2. Inventory Inter-Comparisons

We compare GRA²PES ffCO₂ emissions with several common CO₂ emissions inventories, which are Vulcan v4.0 (Gurney et al., 2024), ACES v2 (Gately & Hutrya, 2022), CEDS v2021_04_21 (Ahsan et al., 2021), CAMS v4.2 (Granier et al., 2019), ODIAC v2020b (Oda et al., 2021), and EPA GHGI. We note that there are many more CO₂ inventories on the global scale available, such as the Emissions Database for Global Atmospheric Research (EDGAR; Crippa et al., 2020), CDIAC (Gilfillan & Marland, 2021), FFDAS (Rayner et al., 2010), etc. We choose CEDS, CAMS, and ODIAC in our inventory inter-comparisons to not overly-weight global inventories versus regional inventories, and because these three global inventories span representative methodologies. CEDS is a global inventory with regional information, CAMS is mostly based on EDGAR (Crippa et al., 2020) emissions with trends from CEDS, and ODIAC uses satellite information. These inventories, including GRA²PES, can be divided into three categories based on whether they are gridded and whether they provide sectoral information. The first category is gridded inventories with sectoral information (GRA²PES, Vulcan, ACES, CEDS, and CAMS). The second category is gridded inventories without sectoral information (ODIAC). The third category is spatially-aggregated inventories at the state-level with sectoral information (EPA GHGI). We compare total and sectoral ffCO₂ emissions from these inventories at multiple spatial levels, including national, state, and urban levels, based on the availability of sectoral and spatial information. Specifically, we calculate ensemble means of these publicly available inventories at multiple spatial and sectoral levels, and compare each inventory to the ensemble means to estimate the range of variability. By comparing the deviations of GRA²PES from the ensemble means, we can evaluate if GRA²PES ffCO₂ emissions are within reason.

The gridded inventories have varying spatial and temporal extents and resolutions (Table 2). We compare all the inventories within the spatial extent of CONUS for 2017, our baseline year. We project all gridded inventories onto the 4 km × 4 km CONUS Lambert Conformal grid native to GRA²PES using a Python-based re-gridded for the Earth System Modeling Framework (xESMF; Zhuang et al., 2024) on a conservative mode, which guarantees mass conservation. One exception is Vulcan v4.0, which is generated onto the GRA²PES 4 km × 4 km CONUS grid by the Northern Arizona University team directly. For consistency in comparisons, we apply a spatial mask for CONUS when summing up the national total. Some emissions can occur outside of the continent, such as from shipping and offshore O&G production.

Comparing emissions by sectors requires aligning sectoral definitions across inventories, which is challenging due to varying definitions. Close-to-perfect alignment of sectors across several inventories can only be achieved

Table 2
Summary of Publicly Available Gridded CO₂ Inventories and Characteristics

Inventory	Version	Spatial extent	Spatial resolution	Temporal extent	Temporal resolution
GRA ² PES	v1.1	Contiguous U.S.	4 km × 4 km	2017 and 2021	Hourly
Vulcan	v4	Contiguous U.S. ^a	1 km × 1 km ^b	2010–2022	Hourly
ACES	v2	Contiguous U.S.	1 km × 1 km	2012–2017	Hourly
CEDS	v2021_04_21	Global	0.1° × 0.1°	1980–2019	Monthly
CAMS	v4.2	Global	0.1° × 0.1°	2000–2020	Monthly
ODIAC	v2020b	Global	1 km × 1 km	2000–2019	Monthly

^aAlaska and Hawaii are also available for Vulcan. ^bPoints/Lines/Polygons gridded to 1 km × 1 km.

when the underlining emissions at ultra-fine sectoral definitions (sub-sectors) are made available, which is usually not the case due to excessive data processing and storage needed. For example, GRA²PES is developed from 74 sub-sectors and aggregated into 17 publicly available sectors. Common inventories usually have around 10 native sectors made publicly available, and the sectoral definitions varies from inventory to inventory. To overcome the challenge given the available data, we define five broad sectors, which are mobile sources, power, residential and commercial, industry, and miscellaneous categories (Table 3). The native sectors with higher sectoral resolution are grouped into these five broad sectors to mitigate challenges in aligning sectors at too high of granularity. A challenging sector is Nonroad, which in GRA²PES is defined as off-road vehicles, such as diesel trucks and mobile machinery on construction sites, lawn mowers, and recreational vehicles, consistent with EPA inventories. However, Nonroad can be grouped into industry and commercial sectors in other inventories, such as CEDS, which does not have a dedicated non-road sector. Among the five broad sectors, the first four sectors account for 98%–100% of ffCO₂ emissions in the six inventories. The miscellaneous category contributes less than 2% of ffCO₂ emissions, and whose emissions are more important for methane and NMVOC emissions.

Table 3
Alignment of Sectoral Definitions Across ffCO₂ Inventories

Broader sectors	GRA ² PES	ACES	VULCAN	CEDS	CAMS	GHGI
Mobile	On-road Gasoline	On-road	On-road	Transportation	On-road	Transportation
	On-road Diesel					
	Nonroad	Non-road	Non-road		Off-road	
	Railroad	Railroad	Railroad		–	
	Airport	Airport	Airport		–	
	Shipping	Commercial Marine Vessel	Commercial Marine Vessel	Shipping	Shipping	
Power	EGU	Electricity Generating Facilities	Electricity production	Energy	Power Generation	Electric Power
Residential and Commercial	Residential	Residential	Residential	Residential & Commercial	Residential & Commercial	Residential
	Commercial	Commercial	Commercial			Commercial
Industry	Industrial fuel	Industrial, Oil and Gas	Industrial, Cement	Industrial	Industrial, Fugitives	Industrial fuel, Industrial processes, Oil and Gas
	Industrial processes					
	Fugitives					
	Oil and Gas					
Misc.	Waste	–	–	Waste	Solid waste	Incineration of Waste
	Agricultural	–	–	Agricultural	Agricultural	–
	VCP	–	–	Solvents	Solvents	–
	Cooking	–	–	–	–	–

2.3. Field Campaign Observations

The Southwest Urban NO_x and VOC Experiment in Summer 2021 occurred in Las Vegas and Los Angeles (SUNVEx, <https://csl.noaa.gov/projects/sunvex/>), consisting of coordinated ground and mobile laboratory measurements. In this work, we rely on three sites in the Los Angeles basin that measured the radiocarbon (¹⁴C) composition of atmospheric CO₂, and a single site at Pasadena that measured both radiocarbon and a wide range of AQ species simultaneously.

During SUNVEx, air samples were collected daily around 2 PM local standard time between August 2nd and 5 September 2021, using the NOAA Global Monitoring Laboratory's Programmable Flask Packages (PFPs; Sweeney et al., 2015). The air samples were collected at three sites in the Los Angeles basin: Pasadena (34.1403°, −118.1254°), Fullerton (33.8802°, −117.8845°), and the University of Southern California (34.0216°, −118.2891°). CO₂ from PFP air samples was cryogenically extracted and subsequently converted to elemental C (graphite) and then analyzed offline for its ¹⁴C:C ratios by accelerator mass spectrometry (AMS; Lehman et al., 2013). AMS allows for very high relative precision (~0.2%) ¹⁴C:C measurement on samples containing ~4 × 10^{−17} mol ¹⁴C. The ¹⁴C:C ratio of atmospheric CO₂ is a widely used tracer for ffCO₂ because emissions of ffCO₂ contain no radiocarbon (¹⁴C) owing to fossil fuels being millions of years old and compared to the half-life of ¹⁴C of 5730 years. Consequently, the larger the ffCO₂ fraction in the atmosphere, the smaller the ¹⁴C:C ratio. ¹⁴C:C ratios referenced to a standard ratio (and after other scalings, expressed as Δ¹⁴C) can be translated to ffCO₂ mole fractions considering observed CO₂ mole fraction and Δ¹⁴C and CO₂ background mole fractions (Miller et al., 2020; Turnbull et al., 2006). The ¹⁴C-derived ffCO₂ mole fractions allow for evaluation of GRA²PES (after transport by FLEXPART-WRF) without needing to consider biospheric CO₂ fluxes. Overall one-sigma uncertainty of ffCO₂ is ~1 μmol/mol, which is dominated by ¹⁴C measurement errors (Lehman et al., 2013).

At the Pasadena site, observations of ¹⁴C-derived ffCO₂ were co-located with a wide range of AQ species. Among the species available, we selected a few representative alkanes (ethane, propane, butanes, and pentanes), alkenes (ethene and propene), alkynes (ethyne), aromatics (benzene, toluene, and xylenes), total reactive nitrogen (NO_y), and carbon monoxide (CO) for our evaluation, because they are typical markers of key emission sources (von Schneidemesser et al., 2023). For example, CO and NO_x are tracers of combustion, mobile, and industry (Hassler et al., 2016), ethane is a marker of natural gas pipeline leaks (Ma et al., 2024), and benzene is closely associated with gasoline (Gkatzelis et al., 2021a). Most of the NMVOCs were measured in situ by gas chromatography-mass spectrometry (GC-MS; Gentner et al., 2014; Gilman et al., 2013, 2015; Lerner et al., 2017) with a sampling frequency of every 20 min and duration of 4 min. The total uncertainties of GC-MS measurements vary by measured species in the range of ~6% to ~17% +0.6 pmol/mol by volume (Lerner et al., 2017). Xylenes were measured with a proton transfer reaction-time-of-flight-mass spectrometer (PTR-ToF-MS), which enables precise quantification of VOC concentrations at high time resolution and sensitivity (de Gouw et al., 2003) and has an accuracy of ±20% for directly calibrated compounds. CO was measured by a commercial cavity ring-down spectrometer, which measures gases including CO at a ± (16 nmol/mol +2%) uncertainty (Gilman, 2023). Reactive nitrogen measurements were made with a custom-built four-channel instrument, which measures NO₂, NO_x, NO_y, and O_x (O_x = O₃ + NO₂) by laser diode-based cavity ring-down spectroscopy (CRDS), with measurement uncertainties, at 1 Hz, of: ±6% for NO₂, ±9% for NO_x, ±15 for NO_y, and ±6% for O_x (Wild et al., 2014). Data from all four AQ instruments, along with ffCO₂ were time-aligned.

Here, we explore the utility of applying AQ/ffCO₂ tracer-tracer ratios to estimate AQ emissions relative to ffCO₂ emissions (Miller et al., 2012) using the GRA²PES inventory. Since we have higher time-resolution AQ/CO observations (sampled continuously across day) than for AQ/ffCO₂ (sampled once-a-day), we first estimate observed AQ/CO ratios and multiply with the observed CO/ffCO₂ ratio to arrive at an AQ/ffCO₂ tracer-tracer ratio. The CO/ffCO₂ enhancement ratio is derived using the slope of orthogonal distance regression (ODR) between CO enhancement and ¹⁴C-based ffCO₂ mole fractions measurements. We force the intercept in this regression to zero after removing CO background values, which were derived for the SUNVEx campaign (Gilman, 2023). One challenge with relating tracer-tracer ratios of AQ species with emission inventories is atmospheric chemistry. Here, we employ approaches to correct bias associated with chemistry in the inventory-observation comparison. First, we evaluate GRA²PES NO_x emissions with atmospheric concentrations of NO_y, which accounts both for NO_x emissions and their photochemical products (McDonald, McKeen, et al., 2018). Most combustion-related NO_x emissions are as NO with a small fraction of NO₂ and nitrous acid (HONO; Wild et al., 2017). Fresh NO emissions rapidly undergo interconversion with NO₂ as part of the NO_x

cycle and are further oxidized to other reactive nitrogen species, including nitric acid (HNO_3), HONO, particulate nitrates, etc., which together with the fresher NO_x species comprise NO_x . In addition to NO_x , NMVOCs also react with the hydroxyl radical (OH) and other radicals in the atmosphere. Here, we employ a photochemical age method to infer fresh emissions from VOC/CO observations. The basic premise is that a reactive VOC will decrease relative to CO with increasing exposure to OH. One can regress the VOC/CO ratio measured at the Pasadena ground site as a function of OH exposure or photochemical age, and the intercept ($t = 0$) is interpreted as the fresh emissions ratio (Borbon et al., 2013; de Gouw et al., 2005). Lastly, CO in the denominator of AQ/CO ratios and the numerator of CO/ffCO₂ ratio is defined as the urban enhancement above background, which was estimated to be 143 nmol/mol by volume during the SUNVEx campaign, with an additional 84 nmol/mol by volume to account for days impacted by wildfire smoke (8/21/2021 19:30 to 9/3/2021 19:29 PDT; Gilman, 2023).

2.4. Lagrangian Inversions

For Lagrangian transport, we run the FLEXible PARTicle dispersion model driven by WRF meteorology (FLEXPART-WRF; Brioude et al., 2013), with updated vertical turbulent mixing (Verreyken et al., 2019) in backward mode (Seibert & Frank, 2004). The back-trajectories are simulated for three Los Angeles Basin sites measuring ffCO₂ to generate a source-receptor matrix, which is referred to as a footprint, and quantifies the relationship between surface fluxes and atmospheric mole fraction changes at the receptor (i.e., flask-sampling) location. Thus, multiplying the footprint of an observation with emissions of a passive tracer results in an estimated mole fraction at the observation site, which is often referred to as convolution. The back-trajectory footprints are produced for 24 hr backward in time from the time of the measurement were taken. For meteorology, we utilize WRF version 4.2, configured with the Mellor–Yamada–Nakanishi–Niino (MYNN) boundary layer scheme, combined with the Eddy Diffusivity Mass Flux (EDMF) scheme. This meteorology was simulated at 4 km × 4 km spatial resolution with 50 vertical levels, utilizing initial and boundary conditions sourced from the High-Resolution Rapid Refresh model (HRRR) described by Verreyken et al. (2025). This WRF configuration has been utilized previously to model the Los Angeles Basin during the SUNVEx campaign (Yu et al., 2023).

Here, we evaluate GRA²PES ffCO₂ emissions against ¹⁴C-derived ffCO₂ mole fractions at the three measurement sites during the SUNVEx campaign (73 samples for August 2021 in total). Since the measurements cover August 2021, we update the GRA²PES inventory to the same month and year with our NRT emissions scaling methodology (He et al., 2024) from the base year of 2017. When evaluating GRA²PES with atmospheric observations, we also take into account day-of-week and diurnal variability of the emissions. In addition to evaluating GRA²PES ffCO₂ emissions against observations, we also performed a three-dimensional variational (3DVar) inversion of ffCO₂ treating the GRA²PES emissions as a first-guess (prior) and then optimizing it to get the posterior. The details of this inversion framework setup (Brioude et al., 2011) and mathematical equations can be found in the supplement (Text S7 in Supporting Information S1). This inversion first applies a domain-wide scaling factor calculated as the reciprocal of the ODR slope of prior versus ¹⁴C-derived ffCO₂ observations, and performs 3DVar inversion from the pre-scaled prior. Even though, we have limited spatial (3 sites) and temporal (one observation per day) coverage of the available ¹⁴C-derived ffCO₂ observations, we still perform this inversion, so that we can estimate a top-down observationally-constrained fluxes of both GRA²PES ffCO₂, and then in a second step, the AQ species. The top-down AQ emissions are estimated for Los Angeles and Orange counties by multiplying observed AQ/ffCO₂ enhancement ratios described in the previous section with the GRA²PES ffCO₂-posterior emissions. Lastly, we evaluate ratios of AQ species to ffCO₂ from the unadjusted GRA²PES inventory with atmospherically observed AQ:ffCO₂ ratios, by multiplying the gridded emissions with the footprint, and fitting the convolution products through the ODR in the same way as described in Section 2.3.

3. Results and Discussions

3.1. GRA²PES Emissions of CO₂ and Air Pollutants

We compare GRA²PES ffCO₂ emissions with publicly available ffCO₂ emissions inventories for 2017, including two U.S. regional inventories ACES (version 2), Vulcan (version 4), and three global inventories CEDS (version 2021), ODIAC (version 2020b), and CAMS (version 4.2). We also include U.S. EPA's GHGI in the state and sectoral-level comparisons where possible. Inter-comparisons of these ffCO₂ emissions inventories provide insights into uncertainties associated with different methodologies, especially at sub-national state and urban scales. To facilitate comparisons, all gridded inventories are projected or gridded to our 4 km × 4 km CONUS domain

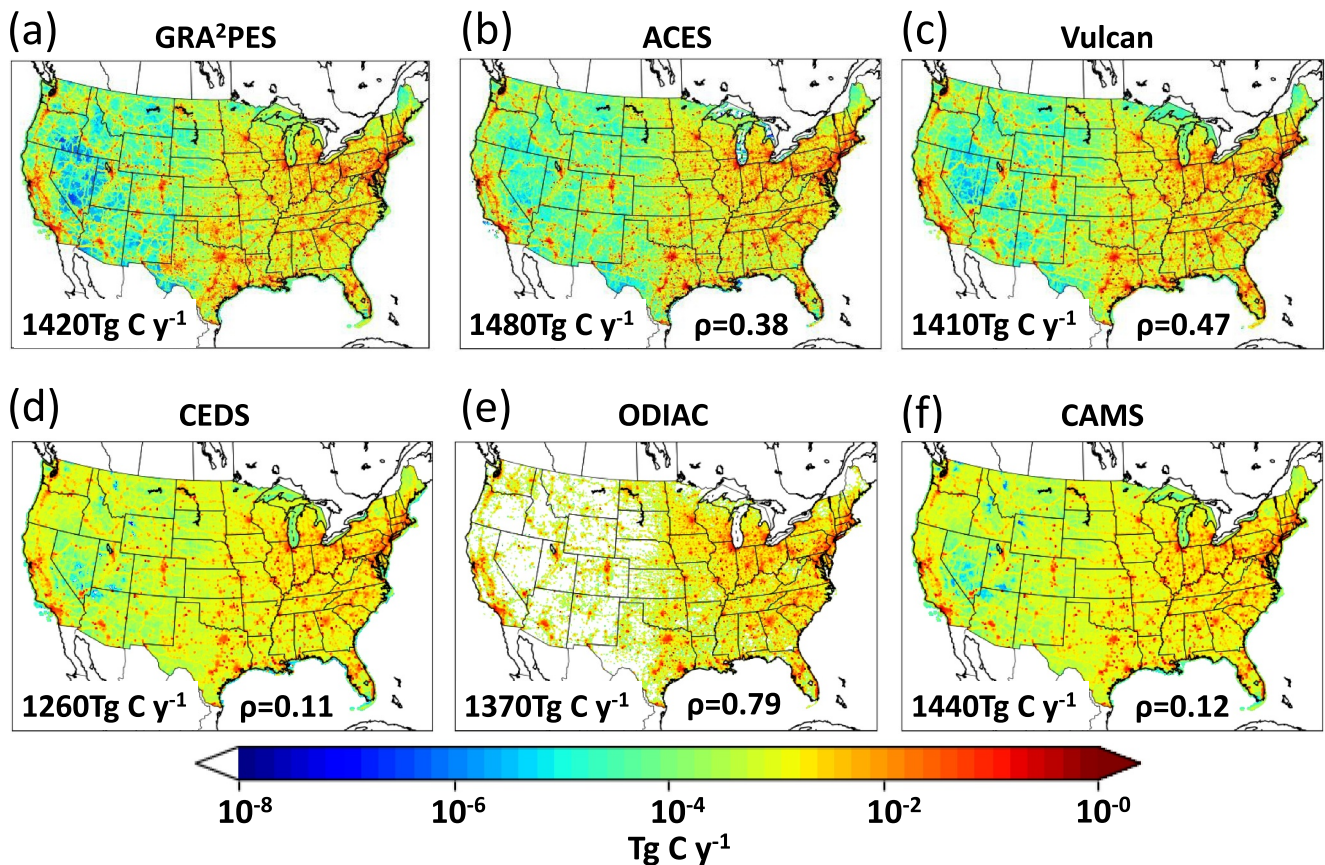


Figure 2. CONUS ffCO₂ emissions maps for: (a) GRA²PES (urban = 40%), (b) ACES (urban = 37%), (c) Vulcan (urban = 36%), (d) CEDS (urban = 26%), (e) ODIAC (urban = 36%), (f) CAMS (urban = 29%). All inventories are shown for calendar year 2017. CONUS totals are shown in the bottom-left of each panel, and Pearson correlation coefficient for each of the other gridded inventories relative to GRA²PES is shown in the bottom-right.

(Figure 2) as described in Section 2.2. The EPA GHGI is plotted as state-level ffCO₂ emissions totals (Figure S4 in Supporting Information S1). Figure 2 shows spatial patterns, aggregate CONUS ffCO₂ emissions, and report the fraction of emissions over urbanized areas and urban clusters defined by the U.S. Census Bureau (U.S. Census Bureau, 2012). Urbanized areas are defined as areas that contain 50,000 or more people and urban clusters are defined as areas that contain at least 2,500 people, but fewer than 50,000 people. The two regional inventories (ACES, Vulcan) generally have spatial ffCO₂ emission patterns similar to GRA²PES. We find all three regional inventories have urban emission shares of 36%–40% using urban boundaries defined previously, and grid cell level Pearson correlation coefficients of 0.38 (ACES) and 0.47 (Vulcan) relative to GRA²PES (Figure 2). The global inventories, CEDS and CAMS, have lower correlations to GRA²PES ($\rho = 0.11$ and 0.12) and smaller urban emission shares (26% and 29%). ODIAC is an exception as a global inventory—it has a similar urban emissions share as the regional inventories at 36%, and the highest Pearson correlation coefficient with GRA²PES at 0.79. The Pearson correlation coefficients between other inventories and GRA²PES are much higher at the aggregated state level as compared to the grid-cell level (Text S8 in Supporting Information S1).

For the inventories with sectoral information, the sectors are aggregated (Table 3) to mobile sources, power, residential and commercial, and industry (Table 4). Across CONUS, GRA²PES ffCO₂ can be compared with all the inventories, regardless of gridding or sectoral information. The ensemble average, inclusive of GRA²PES and all the publicly available ffCO₂ emissions inventories is 1400 Tg C yr⁻¹ for calendar year 2017. The GRA²PES ffCO₂ emissions total is within 1.4% of the ensemble average, and within the range of relative differences versus the ensemble average across inventories (−10.0% to +5.7%). For three of the four aggregate sectors, GRA²PES is within 10% of the national-scale ensemble average (mobile = −2.5%, power = −7.6%, residential and commercial = −5.9%). Industry emissions range from −42% to +34% around the ensemble average, with GRA²PES occupying the upper bound. However, GRA²PES industrial emissions are close to those reported by the US EPA

Table 4
CONUS Sector-Specific ffCO₂ Emissions by Inventory for 2017 (Units in Tg C yr⁻¹)

Broader sectors	GRA ² PES	ACES	VULCAN	CEDS	CAMS	GHGI	Ensemble average
Mobile	477	587	530	406	451	481	489
Power	471	485	523	559	554	470	510
Residential and Commercial	143	154	146	145	183	143	152
Industry	328	249	213	141	232	304	244
Misc.	0	0	0	7	23	4	–
Total	1420	1480	1410	1260	1440	1400	1400

GHGI (+8%), with slight differences due to incorporating GHGRP facility-level emissions and the accounting of the O&G sector. The large variation in industrial ffCO₂ emissions among the inventories illustrate the challenges in uniformly defining and quantifying emissions for this sector.

Inventories diverge to a greater degree when total ffCO₂ emissions are compared at the state level as compared to the national level. State-level ensemble averages are estimated and we compare each individual inventory (GRA²PES, GHGI, Vulcan, CAMS, ACES, ODIAC, and CEDS) with the ensemble means (Figure S5 in Supporting Information S1). The differences between GRA²PES and the ensemble means at the state level are in the range of −26% to +28% (normalized mean bias; NMB = 1.5%, $R^2 = 0.98$). The overall differences across all inventories are in the range of −39% to +52% (NMB = −9.8% to +5.6%, $R^2 = 0.93$ to 0.99). We also compare ffCO₂ emissions at an urban-level (Figure S6 in Supporting Information S1), where we choose the 50 most populated urban areas, based on the US Census. The EPA GHGI is not available as a gridded ffCO₂ product, so it is excluded in the urban level ensemble and comparison. At the urban scale, the differences of GRA²PES ffCO₂ with the ensemble average ranges from −33% to +77% (NMB = 11.5%, $R^2 = 0.97$), while the overall range across all inventories is from −49% to +87% (NMB = −27.8% to +15.8%, $R^2 = 0.92$ to 0.98). Overall, the urban-level differences are larger than the state-level differences by 10%–40%. These results demonstrate variations among inventories at various spatial scales, and are consistent with prior inventory inter-comparison analyses in the U.S. showing greater disagreement at higher spatial resolutions and sub-national scales (Gately & Hutyra, 2017; Gurney et al., 2019, 2020, 2021; Kato et al., 2023).

For the four main emissions sectors (mobile sources, power, residential and commercial, and industry), we compare sector-specific state-level ffCO₂ emissions between GRA²PES and ensemble averages (Figure 3). GRA²PES mobile sources has the greatest agreement with the ensemble average (Figure 3a: NMB = −2%, $R^2 = 0.99$) at the state-scale. Mobile source emissions are from FIVE, which is a well-developed and studied emissions product used in GRA²PES (Harkins et al., 2021; Li et al., 2021; McDonald et al., 2014, 2018b). Though there is broad state-to-state agreement, discrepancies do grow for individual states as exhibited by the large error bars for Texas, California, and Florida. For the power sector, GRA²PES incorporates all of the CEMS EGU emissions. Surprisingly, there are some differences between inventories despite availability of CEMS data, with GRA²PES EGU emissions being slightly lower than the ensemble average (Figure 3b: NMB = −8%, $R^2 = 0.98$). The residential and commercial sector has similar consistency (Figure 3c: NMB = −6%, $R^2 = 0.95$). The largest discrepancies are with the industrial sector (Figure 3d: NMB = +34%, $R^2 = 0.98$). The divergence in the NMB with the regression fit (slope = +51% in Figure 3d) indicates the impact of outlier states, including Texas and Louisiana, which are the states with the highest industrial ffCO₂ emissions (Figure 3d). The major contributor to why these two states exhibit such large differences in the industrial sector between GRA²PES and the ensemble average is the inclusion of more industrial processes and oil and gas emissions in GRA²PES (Text S9 in Supporting Information S1). More field observations of ¹⁴C-derived ffCO₂ in these states would help to better assess their uncertainties in industrial emissions. If Texas and Louisiana are left out of the analysis, the level of agreement across states improve (Slope = +26%, NMB = +23%, $R^2 = 0.95$). We note, GRA²PES has attempted to incorporate as much point source information as possible for the industrial sector, from both the GHGRP and NEI17, including for refineries, manufacturing of chemicals, minerals and metals, and natural gas processing plants. Together, these facility-level emissions account for ~78% of the industrial ffCO₂ emissions.

The seasonal, day-of-week, and diurnal patterns of GRA²PES ffCO₂ emissions by sector are provided in Figure S7 in Supporting Information S1. In general, the seasonal, day-of-week, and diurnal patterns are consistent with

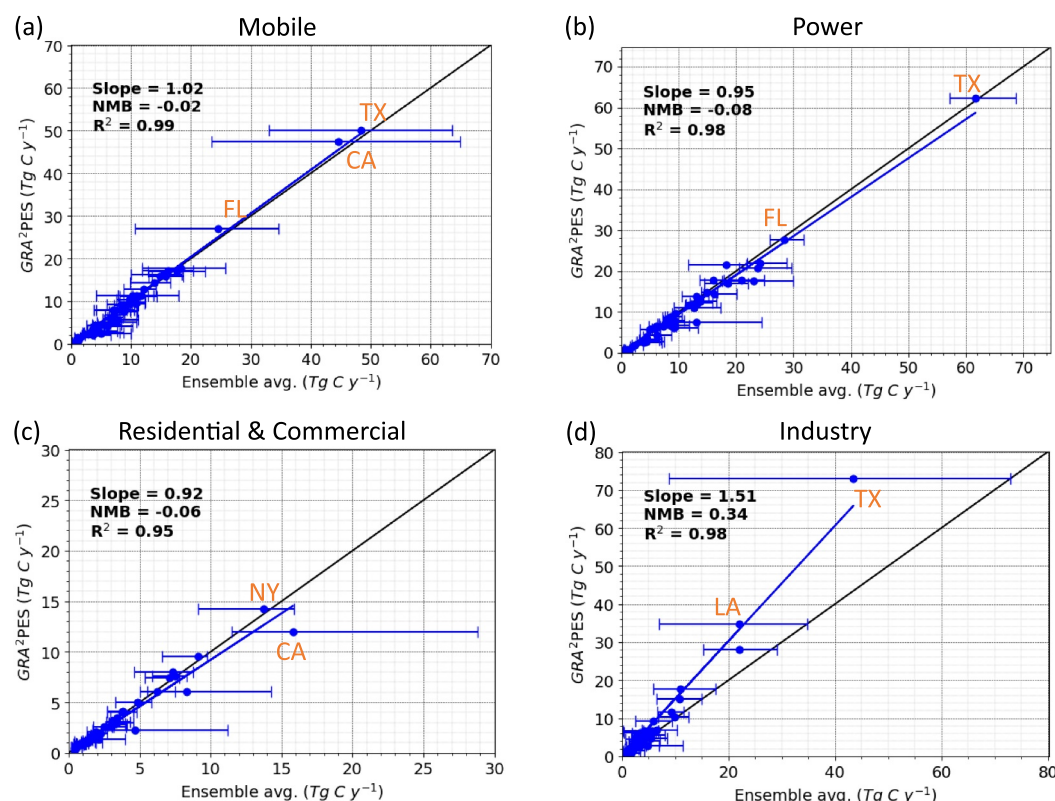


Figure 3. Scatter plots of GRA²PES versus the ensemble average for (a) mobile, (b) power, (c) residential and commercial, and (d) industry sectors. Each data point represents a state-level total. Error bars represent the minimum and maximum ffCO₂ emissions for the six inventories at the state-level for each compared sector. The blue regression line in each panel shows a simple linear regression, and the black represents the 1:1 line. The slope of the blue regression line, normalized mean bias (NMB), and R² value is shown in each panel. Largest states are denoted by orange labels.

expectations (Text S10 in Supporting Information S1). In summary, GRA²PES ffCO₂ is within the range of publicly available inventories for the US at a national to urban-scales, and by sector.

The key advancement of GRA²PES is the integration of ffCO₂ and AQ species. The emissions of ffCO₂ and AQ species were integrated for 74 number of sub-sectors (Table S1), that have been aggregated to 17 sectors (Table 1) for feasibility in sharing the emissions data set. For 11 out of 17 GRA²PES sectors there are ffCO₂ emissions, which are plotted in Figure S9 in Supporting Information S1, and discussed in Text S11 in Supporting Information S1. In addition, over 62,000 stack-level point sources in GRA²PES have both ffCO₂ and AQ emissions, and every point source provides vertically resolved emissions as a result of plume-rise. Another added benefit is that GRA²PES has a robust accounting of non-combustion emissions that are important for AQ, including recent advances of NMVOC emissions from volatile chemical products (McDonald, de Gouw, et al., 2018), cooking (Coggon et al., 2024), and oil and gas development (Francoeur et al., 2021). Lastly, no other ffCO₂ emissions inventory provides 93 co-emitted species with such detailed gas and aerosol composition necessary for modeling urban ozone and PM.

In Figure 4, we show the emissions of key air pollutants along with ffCO₂, including for CO, NO_x, NH₃, SO₂, NMVOCs, PM_{2.5}, and PM₁₀. The spatial patterns of AQ emissions can differ significantly from ffCO₂ (Figure 4a). We calculate the Pearson correlation coefficient (ρ) as the 4 km × 4 km grid-level spatial correlation between each species and ffCO₂. A surprising result is that ffCO₂ and CO emissions are only moderately correlated, $\rho = 0.44$ (Figure 4b). This is due to the non-road sector (e.g., lawn equipment, recreational vehicles, and other off-road two- and four-stroke engines), which is now becoming a dominant source of CO emissions, but contributes a relatively small amount of ffCO₂ (McDonald, McKeen, et al., 2018). NO_x emissions have the highest spatial correlation with ffCO₂ ($\rho = 0.67$; Figure 4c), supporting the idea that NO_x is potentially a reasonable proxy for ffCO₂ (Goldberg et al., 2019; Miyazaki & Bowman, 2023; Yang et al., 2023). Another

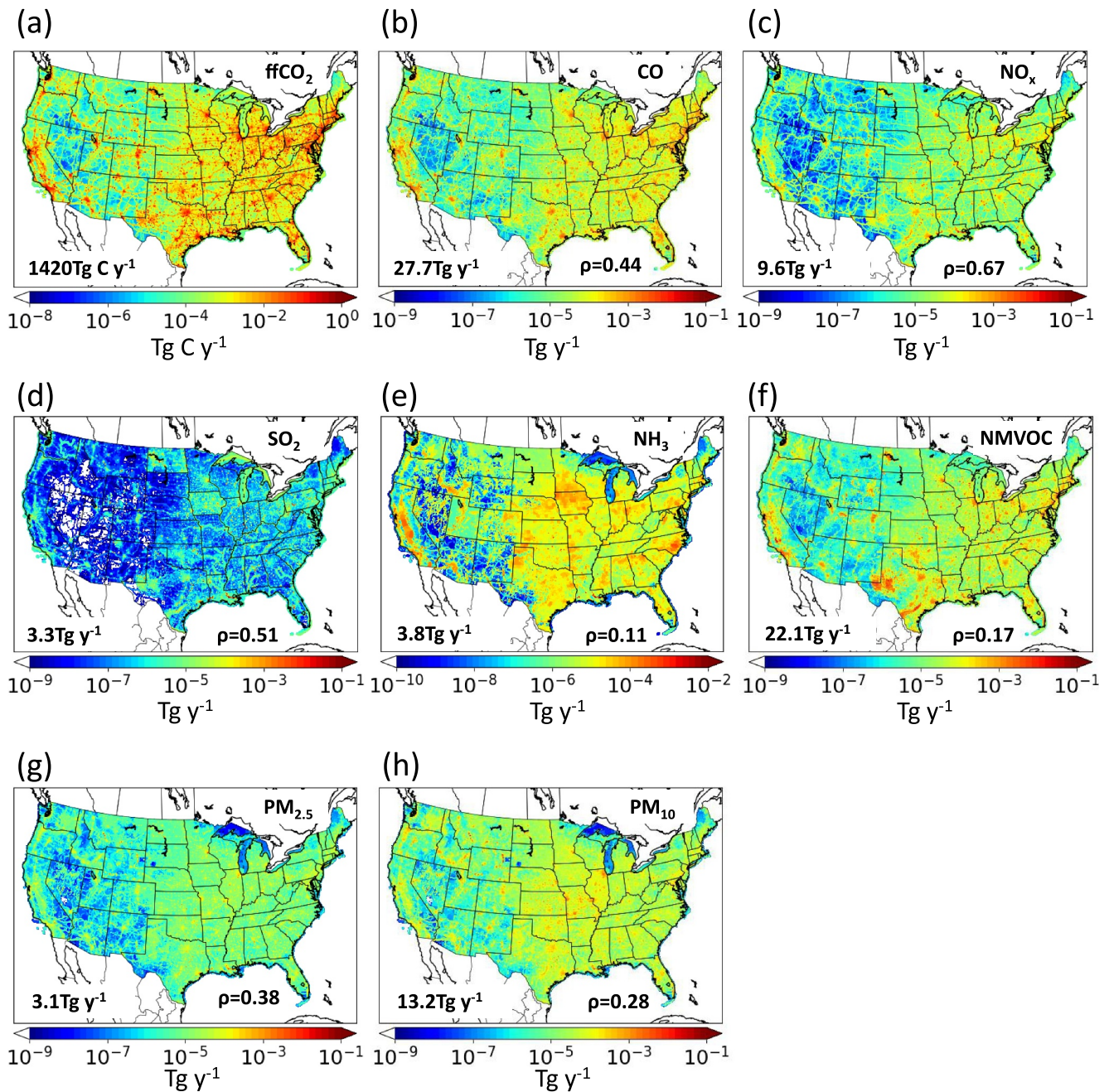


Figure 4. GRA²PES 2017 ffCO₂ (a), CO (b), NO_x (c), SO₂ (d), NH₃ (e), NMVOC (f), PM_{2.5} (g), and PM₁₀ (h) national emission maps. CONUS totals are shown in the bottom left of each panel. The spatial Pearson correlation coefficient (ρ) between each AQ species and ffCO₂ is shown in the bottom right, which is calculated at the grid-level.

combustion byproduct, SO₂, also has high degree of correlation with ffCO₂ emissions at $\rho = 0.51$ (Figure 4d), which is largely from EGUs, industrial sources, and transportation. NH₃ is largely from agricultural practices, such as livestock and use of fertilizer (Cao et al., 2022), and has the lowest degree of spatial correlation with ffCO₂ ($\rho = 0.11$; Figure 4e). Anthropogenic NMVOCs have a large contribution from non-combustion sources, including oil and gas infrastructure, VCPs, and nonroad engines (Francoeur et al., 2021; McDonald, de Gouw, et al., 2018), and thus have low degree of correlation with ffCO₂ emissions ($\rho = 0.17$; Figure 4f). Lastly, PM_{2.5} (Figure 4g) and PM₁₀ (Figure 4h) are at moderate ($\rho = 0.38$) and low ($\rho = 0.28$) degree of correlation with ffCO₂, respectively, because of contributions from anthropogenic dust, which is not a combustion source.

3.2. FLEXPART-WRF Modeling of ffCO₂

In Section 3.1, we compared GRA²PES against publicly available inventories to get a first order estimate of ffCO₂ uncertainty, which at the urban scale varies −49% to +87%. Here, we utilize Los Angeles as a case study city for assessing GRA²PES with measurements of radiocarbon (¹⁴C) during the SUNVEx 2021 field campaign. Figure S10 in Supporting Information S1 shows the ffCO₂ emissions in Southern California with emission totals in the lower left corner of each panel. The three national-scale inventories (Figures S10a–S10c in Supporting Information S1) have higher spatial resolutions, and more clearly represent the road network and large point sources than the three global inventories (Figures S10d–S10f in Supporting Information S1). The average of ffCO₂ emissions across the six inventories is 50.5 Tg C yr^{−1} for the domain shown, close to the GRA²PES estimate of 51 Tg C yr^{−1}. Compared to other urban areas, the range of ffCO₂ emission estimates for Southern California tends to be smaller (−23% to +23%) than across all urban areas (−49% to +87%) shown in Figure S6 in Supporting Information S1.

Figure 5 shows the FLEXPART-WRF modeling results, where GRA²PES is evaluated with ¹⁴C-derived ffCO₂ observations (panel a). Each marker represents the GRA²PES emissions times the FLEXPART-WRF footprints, which result in modeled ffCO₂ mole fraction convolutions with units of μmol/mol, and can be compared directly with atmospheric observations. The average footprints from the three measurement sites are shown in Figure S11a in Supporting Information S1, and in total there were 73 samples. Since emissions at locations upwind from and close to the observation sites (Figure S11a in Supporting Information S1) can more effectively contribute to the mole fractions at the measurement sites, the footprint values are the highest at these locations. We fit the data points shown in Figure 5a with an orthogonal distance regression with intercept forced to zero, because both the modeled ffCO₂ mole fractions and ¹⁴C-derived ffCO₂ observations represent enhancement above background values. The regression slope is 0.81 ± 0.09 (Figure 5a), which suggests a $19\% \pm 9\%$ underestimate of modeled ffCO₂ mole fractions using GRA²PES relative to the atmospheric observations. The reasons for the differences could include uncertainties in footprints caused by model transport errors, uncertainties in the emissions inventory related to magnitude and spatial-temporal disaggregation methods, and to minor extent, model resolution and uncertainties in observation-derived ffCO₂. With respect to meteorology, Yu et al. (2023) simulated FIVE NO_x (i.e., the transportation emissions in GRA²PES) using the same WRF configuration used in this study. While the model was able to reproduce spatial patterns of NO₂ observed by the spaceborne TROPOspheric Monitoring Instrument (TROPOMI), there was a slight displacement of the plume center to the northeast of downtown Los Angeles, which suggests some model transport errors. The WRF simulated NO₂ columns were about 20% higher than the satellite observed values, an absolute bias similar to that in GRA²PES ffCO₂ versus radiocarbon measurements.

To get observationally-constrained ffCO₂ emissions in Los Angeles and Orange counties, we performed a 3DVar inversion with once-a-day observations from the three ground sites. While the spatial and temporal coverage of ¹⁴C-derived ffCO₂ observations are limited, our inversion with ¹⁴C-derived ffCO₂ in an urban area is novel and demonstrates the value of ¹⁴C measurements. For all three measurement sites (USC, Fullerton, and Pasadena), the inversion increased the agreement between model and observations, illustrated by increased R^2 (Figure S12 in Supporting Information S1) and reduced mean bias (Figures S13a–S13c in Supporting Information S1). In addition to reduced absolute values of the mean bias after the inversion, the model-observation bias also shows a more centered distribution with smaller standard deviation from the mean bias (Figure S13d in Supporting Information S1). The emissions adjustment resulted from the inversion is visualized in Figure S11b in Supporting Information S1, which shows the posterior/prior ffCO₂ emissions scaling ratios. In general, due to high emission sensitivities in locations upwind from and close to the observation sites (Figure S11a in Supporting Information S1), the emissions adjustments at these locations tend to be stronger. One interesting finding is that the emissions from two large refineries in the Los Angeles area are adjusted downwards from the inversion (Figure S11b in Supporting Information S1), even though these emissions are provided at the facility-level from the GHGRP. These findings further demonstrate the challenges in quantifying industrial sector emissions, including at the facility level, utilizing bottom-up methodologies.

To test the influence of emissions magnitude and spatial patterns, we multiply ffCO₂ emissions from each inventory with the footprints and get ffCO₂ mole fraction convolutions, which are then evaluated with the ¹⁴C-derived ffCO₂ observations (Figure 5b). Since 2017 is the only common year across the six inventories (GRA²PES, ACES, Vulcan, CEDS, ODIAC, CAMS), we choose to use the 2017 annual average emissions across

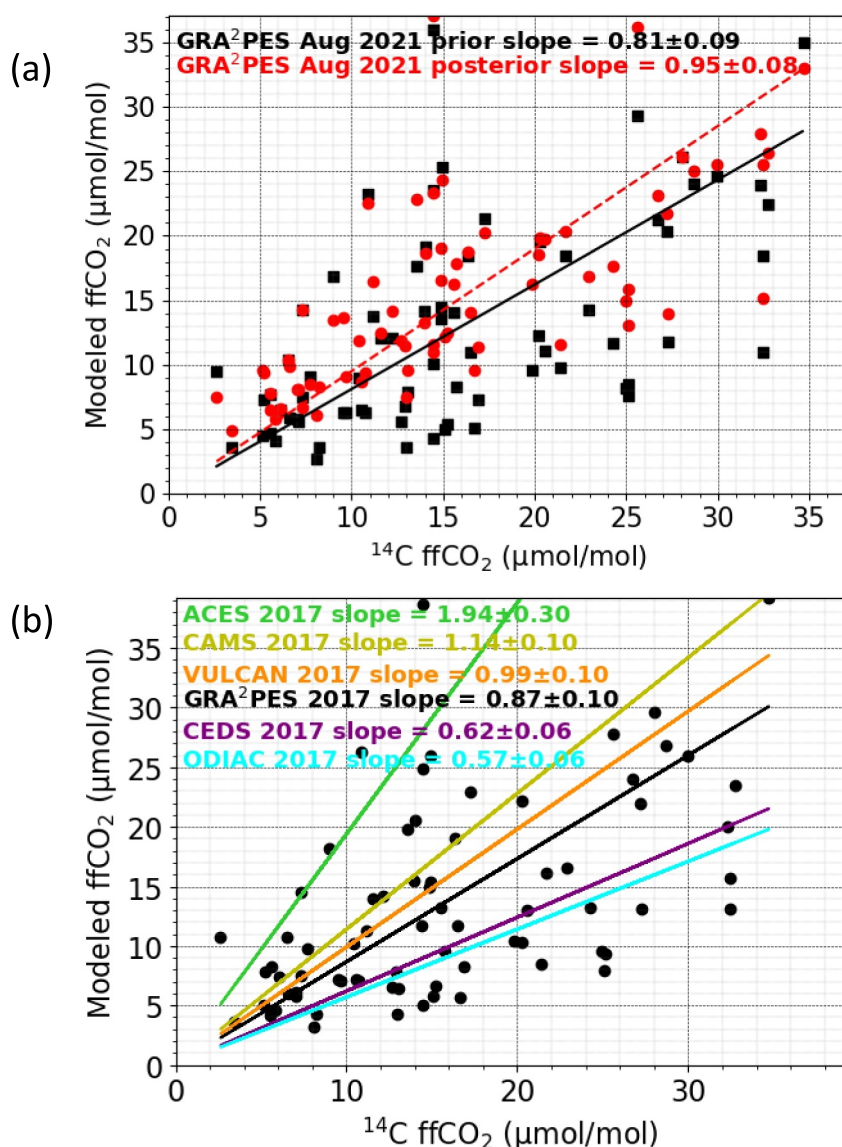


Figure 5. (a) Modeled ffCO_2 (convolution of GRA²PES ffCO_2 emissions) versus ^{14}C -derived ffCO_2 observations. Black line represents convolution of August 2021 GRA²PES prior emissions and red line represents convolution of GRA²PES posterior emissions from a 3DVar inversion. Slopes calculated utilizing an orthogonal distance regression, and uncertainty bars represent the 95% confidence interval. (b) Same as panel (a), except convolutions are shown for calendar year 2017 across six publicly available inventories.

all the inventories for comparison. Additionally, not all of the inventories provide hourly data. Here, we apply day of week and diurnal profiles extracted from GRA²PES (Figure S7 in Supporting Information S1) to the other five inventories shown in Figure S10 in Supporting Information S1. We note that this mismatch in years is unlikely to significantly affect the model inter-comparison as the convolutions of GRA²PES August 2021 (slope = 0.81 ± 0.09 , Figure 5a) and GRA²PES Annual 2017 (slope = 0.87 ± 0.10 , Figure 5b) emissions are within 6% of one another. By contrast, the spread in convolutions across all the inventories is far larger (slope = 0.57 to 1.94 , Figure 5b). On the upper bound is ACES (slope = 1.94 ± 0.30), the lower bound are ODIAC (slope = 0.57 ± 0.06) and CEDS (slope = 0.62 ± 0.06), and in the center are CAMS (slope = 1.14 ± 0.10), Vulcan (slope = 0.99 ± 0.10), and GRA²PES (slope = 0.87 ± 0.10). Though the Southern California ffCO_2 emission estimates vary by a factor of 1.6 across inventories (Figure S10 in Supporting Information S1: 39 Tg C yr^{-1} to 62 Tg C yr^{-1}), the convolutions differ by a factor of ~ 3.4 (Figure 5b). This suggests that in addition to magnitude

differences in area total emissions, approaches to downscaling emissions further drive uncertainties across ffCO_2 inventories.

3.3. Deriving LA Area Emissions With AQ/ ffCO_2 Ratios

AQ/CO tracer-tracer ratios have commonly been used to evaluate AQ inventories (Borbon et al., 2013; McDonald, de Gouw, et al., 2018). However, scaling these observed ratios to CO emissions requires accurate knowledge of both CO surface emissions and atmospheric CO production via oxidation of anthropogenic and biogenic NMVOCs. Additionally, AQ/CO ratios can also be hard to determine because of uncertain definitions of background CO, as was the case in August 2021 when very high CO values were observed due to wildfires. CO emissions are also becoming more uncertain due to the effectiveness of three-way catalytic converters reducing transportation emissions (McDonald et al., 2013). Though there are uncertainties in ffCO_2 inventories, including over Southern California ($\pm 23\%$), the uncertainties in CO are potentially larger. McDonald, McKeen, et al. (2018) found factor of ~ 2 differences in mobile source CO emissions between FIVE and NEI 2011/13 inventories, which is the dominant anthropogenic source of CO. Given these challenges for using AQ/CO tracer-tracer ratios with uncertain CO emissions inventory, using AQ/ ffCO_2 tracer-tracer ratios and ffCO_2 emissions to infer AQ emissions can be a valid alternative. In the foreseeable future, the advantages of using AQ/ ffCO_2 ratios over AQ/CO ratios will remain. Zero-emission vehicles (ZEVs) are gradually replacing diesel and gasoline internal combustion engine vehicles. Utilizing GRA²PES, under a full 100% ZEV adoption rate, anthropogenic CO₂ emissions in the Los Angeles basin will be halved, NO_x emissions will be reduced by $\sim 65\%$, and VOC emissions will be reduced by $\sim 10\%$ (Zhu et al., 2025). By contrast, the poorer correlation of AQ/CO ratios is due to 2–3 order of magnitude reductions in CO emissions due to the advent of three-way catalytic converters on automobiles (McDonald et al., 2013; Warneke et al., 2012). Hence, we do not expect ffCO_2 emissions to disappear as drastically as they have had for CO, since buildings and industry will still remain important sources of ffCO_2 emissions. An advantage of GRA²PES is that it contains both CO₂ and AQ species, so it can be utilized to infer AQ emissions if ffCO_2 emissions and AQ/ ffCO_2 ratios are well-constrained. To evaluate the latter, we compare GRA²PES footprint-weighted AQ/ ffCO_2 emission ratios with observed AQ/ ffCO_2 ratios at the Pasadena ground site for several hydrocarbons, NO_y, and CO (Figure 6a). Evaluating across the observed species, GRA²PES AQ/ ffCO_2 ratios have a NMB of +4% and R^2 value of 0.90 calculated in logarithmic space (Figure 6a). The correlation is calculated in logarithmic space because atmospheric concentrations of hydrocarbons and trace gases vary by multiple orders of magnitude. The inventory-observation differences of GRA²PES AQ/ ffCO_2 is consistent with past analyses of VOC/CO (McDonald, de Gouw, et al., 2018) and NO_x/CO (Kim et al., 2016) ratios in the Los Angeles basin with previously developed inventories utilized in GRA²PES. In particular, SUNVEx observations of ffCO_2 and associated AQ tracers suggest that GRA²PES estimates of ethyne, toluene, and CO are in strong agreement with the observations (Figure 6a).

Figure 6b shows the top-down AQ emissions flux (black markers) for the same species over Los Angeles and Orange counties. The top-down AQ flux is estimated by first performing a 3D variational inversion on the GRA²PES ffCO_2 emissions prior (black line in Figure 5a) and multiplying the optimized ffCO_2 emissions (red line in Figure 5a) with atmospherically measured AQ/ ffCO_2 ratios as described in Section 2.3. Because the observed and GRA²PES prior AQ/ ffCO_2 are generally consistent with one another (Figure 6a), the statistics for the AQ flux are similar (Figure 6b). The added value of the bottom-up GRA²PES is the sectoral emissions detail, which are shown as stacked bars (mobile, residential and commercial, industry, power, and non-combustion) and can be shown by individual species. For example, CO and NO_y are both dominated by combustion sources where CO is almost entirely from mobile sources and NO_y is distributed between mobile sources (67%) and industry (30%). Similarly, benzene is emitted by both mobile sources (44%) and industry (51%). In general, mobile source and industry contributions can be found across most of the species shown in Figure 6, whereas unique markers of the power and residential and commercial sectors are harder to find. The exception is NO_y where there are minor contributions from the power (1%) and residential and commercial (3%) sectors. Another key aspect of Figure 6b is that a significant fraction of AQ species is emitted from non-combustion sources, including VCPs and cooking, and must be taken into account when simulating air quality (Coggon et al., 2021; Qin et al., 2021). The AQ species most strongly influenced by fossil fuel combustion are NO_y (99.9%), CO (99.7%), ethyne (99.5%), ethene (98.3%), pentanes (96.4%), benzene (96.0%), and propene (89.6%). Reductions of emissions in some sectors like mobile sources can simultaneously lower NO_y, CO, and NMVOCs (e.g., pentanes, ethene, propene, ethyne,

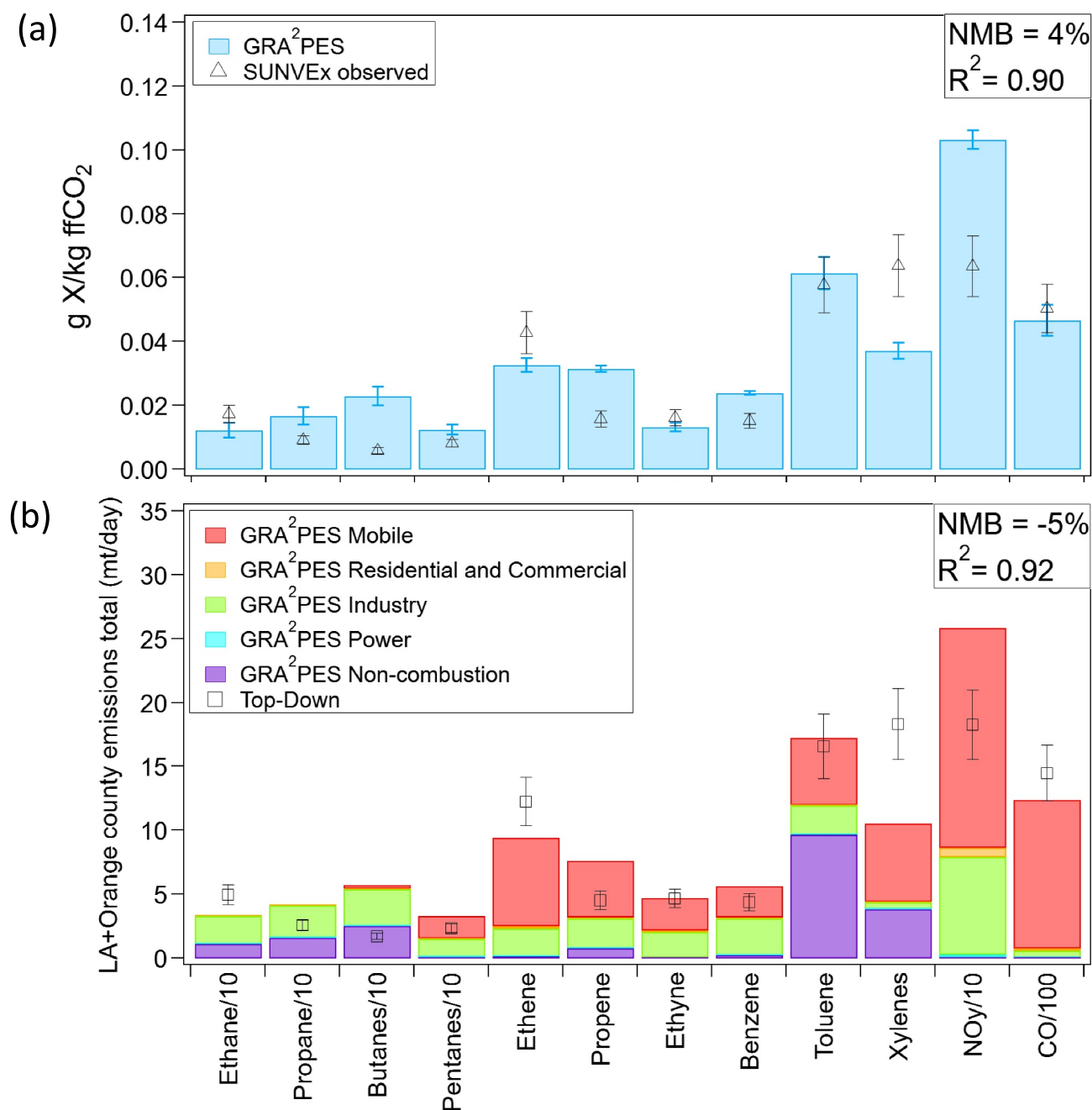


Figure 6. (a) Selected GRA²PES AQ species to total ffCO_2 ratios compared with SUNVEx observed ratios; (b) Comparing AQ species emission totals in the LA and Orange county between sector-specific GRA²PES and the top-down estimates using SUNVEx observed ratios and 3DVar posterior ffCO_2 emissions. The error bars are 95% CI. The R^2 value is in log-space.

benzene, toluene, and xylenes). Understanding source contributions for air toxics (e.g., benzene), as well as $\text{PM}_{2.5}$ and ozone precursors (VOCs and NO_x), along with ffCO_2 in a self-consistent inventory system such as GRA²PES can help estimate AQ impacts.

Due to the scarce availability of the ^{14}C -based ffCO_2 as well as AQ species measurements, such analyses are only conducted for the Los Angeles area, which might not be representative of other cities and rural areas with different apportionments of emission sources. Even though, the outcomes from this case study might be unique to Los Angeles, the methods can be extended to other areas with available observations. We note that similar measurements were made during the Atmospheric Emissions and Reactions Observed from Megacities

to Marine Areas (AEROMMA, <https://csl.noaa.gov/projects/aeromma/>) field campaign in the summer of 2023, and our analytical methods will be extended to other major US cities (Chicago, New York City, and Indianapolis) in future work.

4. Conclusions

In this study, we have developed a new self-consistent ffCO_2 and AQ emissions inventory for CONUS. We find NO_x emissions to be the most highly spatially correlated AQ species with ffCO_2 ($\rho = 0.67$; Figure 4c), and potentially a useful covariate species to distinguish fossil and non-fossil CO_2 (Goldberg et al., 2019; Miyazaki & Bowman, 2023). Nationally, the GRA^2PES inventory is within 1.4% of an ensemble mean of seven global and regional inventories and the range of differences for each inventory from the ensemble mean is -10.0% to $+5.7\%$. At the state and urban levels, GRA^2PES is within 1.5% NMB ($R^2 = 0.98$) and 11.5% NMB ($R^2 = 0.97$), respectively, of the ensemble average. This is also within the ensemble range of publicly available inventories at the state (NMB = -9.8% to $+5.6\%$, $R^2 = 0.93$ to 0.99) and urban (NMB = -27.8% to $+15.8\%$, $R^2 = 0.92$ to 0.98) scales. The increased differences amongst inventories at state and urban levels highlights significant uncertainties associated with down-scaling emissions from national to sub-national scales.

Given the significant range of sub-national estimates in ffCO_2 emissions, we also evaluate GRA^2PES with atmospheric observations in Los Angeles. The modeled ffCO_2 concentrations using GRA^2PES emissions are lower than the ^{14}C -derived ffCO_2 observations by $19\% \pm 9\%$. We also modeled ffCO_2 mole fractions with five other publicly available inventories (ACES, Vulcan, CEDS, ODIAC, CAMS), which differ with the ffCO_2 observations by -43% to $+94\%$. In addition to assessing ffCO_2 , we demonstrate a method by which to assess AQ inventories using GRA^2PES . We assimilate ^{14}C -derived ffCO_2 observations through a 3DVar system and estimate a GRA^2PES -posterior ffCO_2 flux. Using ambient measured AQ/ ffCO_2 ratios, we are able to estimate a top-down AQ flux. Overall, GRA^2PES AQ/ ffCO_2 ratios compare reasonably with the observed ratios (NMB = $+4\%$, $\log R^2 = 0.90$) and top-down derived fluxes (NMB = -5% , $\log R^2 = 0.92$). At the urban scale, the AQ species most strongly influenced by fossil fuel combustion are NO_y , CO, ethyne, ethene, pentanes, benzene, and propene. We also show that NMVOC emissions have a significant non-combustion source of emissions, which needs to be taken into account in GHG-AQ studies. In the future, our analysis can be replicated to assess GRA^2PES continentally, using measurements from the AEROMMA airborne field campaign, which flew over New York City, Chicago, and Los Angeles in the summer of 2023.

These results motivate a few future research directions. One is to provide more robust uncertainty estimates of GRA^2PES at finer spatial scales. Better uncertainty quantification can enhance emissions inversion systems that typically rely on simple and uniform estimates of prior uncertainty, which is a critical component of the cost functions in Bayesian inversions. Second, the wide multitude of species provided by GRA^2PES (94 in total) with sectoral detail (17 in total) can enhance multi-species approaches for sectoral attribution and sector-based emissions inversions. Lastly, integrating ffCO_2 and AQ emissions with high sectoral and species detail also assists with modeling and assessing potential air quality impacts from combustion sources.

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Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

GRA^2PES emissions processing scripts are publicly available here: <https://csl.noaa.gov/groups/csl4/gra2pes/datasets/>. GRA^2PES emissions products are publicly available from the NIST server: <https://doi.org/10.18434/mds2-3520>.

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