Ground solar absorption observations of total column CO, CO$_2$, CH$_4$, and aerosol optical depth from California’s Sequoia Lightning Complex Fire: Emission factors and modified combustion efficiency at large scales

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Abstract. With global wildfires becoming more widespread and severe, tracking their emissions of greenhouse gases and air pollutants is becoming increasingly important. Wildfire emissions have primarily been characterized by in situ laboratory, and field observations at fine scales. While this approach captures the mechanisms relating emissions to combustion phase and fuel properties, their evaluation on large scale plumes has been limited. In this study, we report remote observations of total column trace gases and aerosols in the 2020 wildfire season of smoke plumes from the Sierra Nevada of California with an EM27/SUN solar Fourier transform infrared (FTIR) spectrometer. We derive total column aerosol optical depth (AOD), emission factors (EF) and modified combustion efficiency (MCE) for these fires, and evaluate relationships between them based on combustion phase at large scales. We demonstrate that the EM27/SUN effectively detects changes of CO, CO$_2$ and CH$_4$ in the atmospheric column at ~10 km scales that are attributed to wildfire emissions. These observations are used to derive total column EF$_{CO}$ of 120.5 ± 12.2 and EF$_{CH_4}$ of 4.3 ± 0.8 for a large smoke plume event in mixed combustion phases. These values are consistent with in situ relationships measured in similar temperate coniferous forest wildfires. FTIR derived AOD was compared to a nearby AERONET station and observed ratios of AOD to X$_{CO}$ were consistent with those previously observed from satellites. We also show that co-located X$_{CO}$ observations from the TROPOMI satellite-based instrument are 9.7% higher than our EM27/SUN observations during the wildfire period. Finally, we put wildfire CH$_4$ emissions in context of the California state CH$_4$ budget and estimate that 213.7 ± 49.8 Gg CH$_4$ were emitted by large wildfires in California during 2020, about 13.6% of the total state CH$_4$ emissions in 2019. Our novel application of an EM27/SUN solar spectrometer to quantify wildfire emission ratios at large scales follows predictive relationships that are consistent with in situ studies, offering promise for extensive monitoring from ground networks and satellite remote sensing.

1 Introduction

Wildfires have become deadlier, more destructive, and more frequent globally over the past few years (UNEP, 2022). Particularly, the 2020 wildfire activity season surged with massive wildfires in the Western U.S., Australia, Brazil, and the Arctic. The California 2020 wildfire season was exacerbated by abnormally high temperatures and dry conditions (Jain et al.,
2022; Cho et al., 2022) and emitted ten times more carbon dioxide (CO$_2$) into the atmosphere than the 2000-2019 annual average (California Wildfire Emission Estimates, 2021). Particulate matter 2.5 (PM$_{2.5}$) concentrations in the San Joaquin Valley (SJV), California were found to be four times higher during the 2020 fire season than non-fire periods (Ahangar et al., 2022). The high temperatures and dry conditions, combined with moisture from a tropical storm led to a dry lightning storm event in August, 2020, where lightning-ignited wildfires burned more acres in California than at any other time in recorded history (Morris III and Dennis, 2020). This included the lightning-sparked Castle Fire (part of the Sequoia Lightning Fire (SQF) Complex) that killed 10-14% of the large sequoias in the Sierra Nevada and has become the largest fire in a giant sequoia grove on record at 170,648 acres (Stephensen and Brigham, 2021). Historic fire suppression and land-use changes in this area has led to an increase of wildfires burning at higher intensity and larger areas (Moody 2006; Scholl 2010). Climate change has increased the forest fire activity in the Western U.S. (Zhuang et al., 2021) and will increase the likelihood for wildfires in the Sierra Nevada with greater burned area due to higher daily temperatures (Gutierrez et al., 2021), with implications for air quality and carbon emissions (Navarro et al., 2016).

Wildfires are a major source of air pollutants, including particulate matter (PM), carbon monoxide (CO), and greenhouse gases, primarily carbon dioxide (CO$_2$) and methane (CH$_4$) (Akagi et al., 2011; Wiedinmyer et al., 2011; Andreae, 2019). The high levels of PM and CO released from fires are dangerous to human health and degrade air quality on a local, regional, and global scale (Schneising et al., 2020; Aguilera et al., 2021). CO is an air toxic and is considered an indirect greenhouse gas as it is a major sink for the hydroxyl radical (OH), increasing the abundance of CH$_4$ through photochemical feedbacks (Li et al., 2018) and also produces ozone (O$_3$), a short lived greenhouse gas. CO$_2$ and CH$_4$ are the dominant greenhouse gases and are responsible for most of the current anthropogenic climate change (IPCC, 2014). A majority of carbon emissions from wildfires are of CO$_2$, CO, and CH$_4$ (~95%) while the remainder are carbonaceous aerosols (~5%) (Sommers et al., 2014; Urbanski, 2014). Although emissions from fires are biogenic sources of CO$_2$, they are released rapidly compared to the slow timescales of carbon uptake required to grow vegetation fuels. Increased fire activity increases atmospheric CO$_2$ in the short term, and can locally alter the terrestrial carbon cycle balance by reducing photosynthetic CO$_2$ uptake under high levels of vegetation disturbance (CARB, 2018). While CO$_2$ losses can be estimated as a function of burned area and fuel consumption, emissions of CO, CH$_4$, and aerosols are more difficult to estimate because they vary greatly with fire conditions. As global wildfires become more widespread and severe, tracking emissions of greenhouse gases and air pollutants from smoke will become increasingly important for efforts to track emissions of greenhouse gases and understand the impacts of fire on the atmosphere (Aguilera et al., 2021; Wilmot et al., 2022).

Our understanding of the atmospheric impacts of increasing fire activity relies on accurate observations and process-based estimation of fire emissions that have been developed using in situ measurements (Urbanski, 2014). While several space-based instruments can retrieve and derive emissions of important trace gases globally, observations are limited by spatiotemporal coverage and focus on aerosol burden from smoke plumes with limited attention to trace gases, and a lack of integration of trace gases and aerosols. Ground-based solar spectrometers present a new technique to measure and understand fire emissions at regional scales, and temporally complement satellite observations. Column measurements are insensitive to
the planetary boundary layer growth and are less affected by nearby point sources than in situ measurements, making them a good candidate for regional-scale monitoring (Lindenmaier et al., 2014). The EM27/SUN is a ground-based remote sensing instrument that is relatively portable and robust for field deployments. These instruments are the basis for the ground-based network of FTIR COCCON (COllaborative Carbon Column Observing Network), which complements NDACC (Network for the Detection of Atmospheric Composition Change) and TCCON (Total Column Carbon Observing Network), two high resolution FTIR trace gas monitoring networks (Frey et al., 2019; Wunch et al., 2011; Toon et al., 2009; De Mazière et al., 2018).

Field-based measurements of biomass burning in temperate forests are limited and sparse (Burling et al., 2011; Urbanski, 2014), despite the increase in burning activity in the Western U.S. (Zhuang et al., 2021). The EM27/SUN provides vertically integrated column measurements of CH₄, CO₂, and CO which allows for calculating modified combustion efficiency (MCE) and emission factors (EF) in the total column of smoke plumes downwind of wildfires. MCE values give insight into the relative amounts of flaming and smoldering combustion of the fire. Pure flaming combustion has an MCE of 0.99, while the MCE for smoldering varies from 0.65 to 0.85. A value near 0.90 indicates equal contributions of flaming and smoldering combustion (Akagi et al., 2011). EF are defined as the mass of gas or aerosol emitted per dry biomass consumed and are critical inputs for models to accurately calculate emissions and construct wildfire inventories (Urbanski, 2014). Providing new EFs will help improve regional biomass burning estimates. Past studies have derived atmospheric column-based EFs with respect to CO from wildfires using solar FTIR spectrometers (Kille et al., 2022; Paton-Walsh et al., 2005; Lutsch et al., 2020, 2016; Viatte et al., 2014, 2015). The observed small changes in CO₂ with respect to the large atmospheric background has limited previous FTIR-based studies in their ability to derive EFs with respect to CO₂. This has consequently inhibited the calculation of MCE. Here, we present the first EFs with respect to CO₂ and MCE for wildfires calculated by total-column FTIR.

During part of the 2020 wildfire season, we deployed the EM27/SUN in the SJV downwind of two major wildfires, the Creek Fire and Sequoia Lightning Fire (SQF) Complex, in the Sierra Nevada. We report EF_{CO/CO₂} and EF_{CH₄/CO₂} from the SQF Complex, a mixed conifer forest wildfire in the Sierra Nevada, and follow the wildfire’s combustion phases with MCE values. Furthermore, because ground-based column measurements operate on similar scales as satellites and regional atmospheric models (McKain et al., 2015), we compared EM27/SUN measurements with satellite greenhouse gas observations from TROPOMI collected during the fires. We quantify MCE, EF for CO₂ and CH₄, and AOD enhancements from the SQF using EM27, we compare CO retrievals to TROPOMI, we compare AOD retrieval to an AERONET site, and we put wildfire CH₄ emissions in context of the California state CH₄ budget. Our work demonstrates a novel application of the ground based EM27/SUN solar spectrometers in wildfire monitoring and contributes to the development of techniques for analyzing remotely sensed greenhouse gas measurements.

2 Data Sources and Methods

2.1 EM27/SUN Atmospheric Column Observations
We measured the column-averaged dry mole fractions \( (X_{\text{gas}}) \) of CH\(_4\), CO\(_2\) and CO \( (X_{\text{CH}_4}, X_{\text{CO}_2}, \text{and } X_{\text{CO}}) \) in a location 60 km west of the SQF Complex (Castle and Shotgun fires) and 80 km southwest of the Creek wildfires in the Sierra Nevada, and southeast of major dairy farms in the SJV (Figure 1, panel a). The SQF Complex fires began on Aug. 19 after a dry thunderstorm and lightning event ignited the fires in the Sierra Nevada. By Sept. 12, the SQF Complex had grown to 283 km\(^2\). The Creek fire began on the evening of Sept. 5 and upper-level high winds produced a pyro-cumulus cloud on Sept. 6 that reached an altitude over 15 km (Morris III and Dennis, 2020). Smoke filled the valley and smoky overcast skies remained in large parts of the SJV for the next two weeks as fires kept burning. In total, the SQF Complex consumed 686 km\(^2\) and Creek consumed 1515 km\(^2\), placing both these fires among the top 20 largest California wildfires (Morris III and Dennis, 2020).

The Bruker Optics EM27/SUN solar-viewing Fourier Transform Spectrometer owned by Los Alamos National Laboratory (LANL) collected continuous daytime column measurements in Farmersville, California (36.31, -119.19) from Sept. 8 until Oct. 17, 2020, for a total of 40 days of observations. The EM27/SUN solar spectrometer has been previously used to study emissions from urban and agriculture CH\(_4\) and CO\(_2\) sources (Chen et al., 2016; Viatte et al., 2017; Dietrich et al., 2021; Alberti et al., 2022a; Makarova et al., 2021; Heerah et al., 2021). The recent addition of a CO detector in Bruker’s EM27/SUN Fourier Transform Infrared (FTIR) spectrometer increases the instrument’s utility for measuring combustion sources and as a validation tool for TROPOMI column \( X_{\text{CO}} \) as it covers the same spectral region (Hase et al., 2016). The EM27/SUN uses the sun as the light source which allows it to derive aerosol optical depth (AOD) as demonstrated by Barreto et al. (2020) at the TCCON FTIR and AERONET site at Izaña, Spain. In their study, TCCON spectra were degraded to the same resolution as the EM27/SUN (0.5 cm\(^{-1}\)) and they concluded that EM27/SUN spectra would be able to effectively derive AOD. Following their approach, we derive AOD for the wildfire period from our measurements. Further details of the AOD calculation are found in Section 2.4.

EM27/SUN \( X_{\text{gas}} \) values were retrieved from unaveraged double sided interferograms using the I2S and GFIT (GGG2014 version; https://tccon-wiki.caltech.edu/) retrieval algorithms automated by the EGI processing suite (Hedelius et al., 2016). Surface pressure is required to retrieve dry air columns in GGG and we used Coastal Environmental Systems ZENO weather station to record surface pressure at our field site for retrievals. Retrievals also require atmospheric profiles of temperature, pressure, altitude and water and these profiles were extracted from NCEP/NCAR reanalysis product (Kalnay et al., 1996). We calibrated the EM27/SUN via co-located measurements alongside the IFS125, a high-spectral-resolution FTIR operated by TCCON at the California Institute of Technology (CIT), both before and after the collection periods to determine calibration factors \( (R_{\text{gas}}) \) assuming a linear model forced through the origin for each gas, e.g., \( X_{\text{TCCON}} = X_{\text{EM27}} R_{\text{gas}} \) (Chen et al., 2016; Hedelius et al., 2016). The TCCON network sets the standard as the current state-of-the art ground-based validation system for remote sensing and satellite-based observations of greenhouse gases (Wunch et al., 2011), and TCCON observations are tied to the World Meteorological Organization (WMO) standard greenhouse gas scale. Co-locating the EM27/SUN and TCCON instruments ensures system stability of the EM27/SUN after transportation to field sites. Co-located measurements were performed on Sept. 2–3, 2020 and Oct. 30–Nov. 1, 2020. Results of the correction factors from the co-located measurements are shown in Table A1 of the Appendix. The TCCON instrument also uses the GFIT retrieval algorithm with
the same \textit{a priori} profiles; however, due to different instrument spectral resolutions and averaging kernels, we correct for the differences between the EM27/SUN and TCCON instrument following Hedelius et al., 2016 (Equation A4) to adjust the EM27/SUN retrievals before comparing with TCCON and deriving calibration factors.

Prior to measurements in California, the EM27/SUN was stationed in Fairbanks, Alaska for several months. Given the different settings used with the CamTracker, the solar disk was not centered on the camera and this misalignment was found on Sept. 7. Based on co-located measurements with the CIT TCCON on Sept. 2 and 3, it was determined that the observations within the second detector of $X_{CO}$ were affected on the days prior when camera was misaligned (Sept. 2, 3, 6, and 7). For this reason, we report measurements of $X_{CO}$, $X_{CO2}$ and $X_{CH4}$ beginning on Sept. 8 and use the Oct. 30 – Nov. 1 co-located measurements for calculating correction factors. AOD was derived from micro windows within the first detector, thus calculations of AOD were not affected.

**Figure 1.** a) Satellite imagery captured by NOAA-20 VIIRS of heavy smoke in California on September 12, 2020, highlighting fire and thermal anomalies in red (NASA Worldview; worldview.earthdata.nasa.gov), and with black diamond shape showing the EM27 measurement location and blue diamond shape the AERONET observational site. b) Inset shows more detail of the smoke plume within the SJV from the SQF Complex in the Sierra Nevada, shown by red thermal anomalies at the right of the image. c) Inset of TROPOMI XCO overpass at 2020-09-12 13:54 PDT.
TROPOMI is an instrument launched in late 2017 onboard the European Space Agency’s (ESA) Sentinel-5-Precursor (S5P). The instrument measures Earth radiance spectra in the ultraviolet (UV), NIR and SWIR allowing for measurements of a wide range of atmospheric trace gases and aerosol properties (Veefkind et al., 2012). The satellite has a sun-synchronous orbit with daily global coverage and a spatial resolution of 5.5 x 7 km² for CH₄ and CO operational level 2 (L2) products. The offline (OFFL) CO total column L2 data product filtered for quality assurance values > 0.5 are used in this work as recommended in the product readme file (https://sentinel.esa.int/documents/247904/3541451/Sentinel-5P-Carbon-Monoxide-Level-2-Product-Readme-File, last access: 4 Aug 2022). This selection filters out high solar zenith angles, any corrupted retrievals, and influences from high clouds. The majority of the TROPOMI XCH₄ product was flagged out near the observational site during our measurement period, and hence was not included in this analysis. Following Sha et al., 2021, the TROPOMI CO column densities were converted to XCO (ppb) by using the modeled surface pressure and total column of H₂O to calculate the column of dry air.

We evaluated the agreement between the retrieved XCO from EM27/SUN and TROPOMI overpasses during the measurement period. This allows for a novel evaluation of the TROPOMI sensor under wildfire conditions of high XCO and aerosol loading in the atmosphere. A correction factor was calculated to account for differences in the a priori profile used in the retrieval of XCO in both instruments. We follow the a priori substitution method described in (Sha et al., 2021; Jacobs, 2021) to calculate an additive factor for the EM27/SUN. Due to the possibility of measuring narrow smoke plumes on subgrid spatiotemporal scales, we perform a sensitivity study to determine the best co-location criteria for the EM27/SUN to TROPOMI comparison by varying the maximum radius (5 – 50 km) from the observational site and averaging time (5 – 30 min) for the EM27/SUN measurements around the TROPOMI overpass time. We require a minimum threshold of at least three 1-minute averages within the averaging time aggregations.

2.3 AERONET Data

AERONET (http://aeronet.gsfc.nasa.gov/ accessed on 15 June 2022) is a global network of sun/sky radiometer with over 600 sites operated around the globe. AERONET observations include measurements of aerosol optical depth, microphysical and radiative properties. The stations are frequently calibrated, and they set the standard for aerosol measurements and validation for satellite products. AERONET measures AOD at several spectral windows from 340, 380, 440, 500, 675, 870, 940, 1020 and 1640 nm. The Ångström exponent (AE), describing the wavelength dependence of aerosol optical thickness, is calculated from the spectral AOD. We used the AERONET Level 2.0 version 3 AOD and AE data from the Fresno_2 site (36.78, -119.77) that has been operating in the same location since 2012. This site is located about 90 km away from our EM27/SUN site. Further quality control information can be found in Giles et al., 2019.
2.4 AOD Calculation

To calculate AOD from the EM27/SUN solar measurements, we follow the methods described in Barreto et al. (2020) who found good agreement between AERONET and TCCON FTIR-derived AOD at the high altitude Izaña Observatory in Spain. Their analysis was performed on degraded TCCON FTIR solar spectra (0.5 cm\(^{-1}\)) to assess the capability of lower resolution FTIR EM27/SUN instruments to detect broadband aerosol signal. Ten interferogram scans were co-added to increase the signal to noise ratio of the aerosol retrieval for a total integration time of 1 minute. We calculated AOD from four recommended micro windows with high solar transmission centered at 1020.9, 1238.25, 1558, and 1636 nm and compare to a nearby AERONET site located in Fresno, CA.

We apply the methods further described in Barreto et al. (2020) that are based on the Beer-Lambert-Bougher attenuation law:

\[
V_\lambda = V_{o,\lambda} \cdot d^{-2} \cdot \exp (-m \cdot \tau_\lambda)
\]  

(1)

where \(V_\lambda\) is the measured solar irradiance at wavelength \(\lambda\), \(V_{o,\lambda}\) is the spectral irradiance outside the Earth’s atmosphere at wavelength \(\lambda\), \(d\) is the ratio of mean to actual sun-earth distance, and \(m\) is the optical air mass (Kasten and Young 1989). The \(V_o\) is derived from the Langley method by utilizing the measured solar intensity (\(V\)) versus the optical air mass (\(m\)) and extrapolating to an optical air mass of zero. The total optical depth (\(\tau_\lambda\)) is the sum of the optical depth of Rayleigh scattering (\(\tau_{R,\lambda}\)), gas absorption (\(\tau_{g,\lambda}\)), and aerosols (\(\tau_{a,\lambda}\)):

\[
\tau_\lambda = \tau_{R,\lambda} + \tau_{g,\lambda} + \tau_{a,\lambda}.
\]  

(2)

Barreto et al. (2020) carefully selected and evaluated several FTIR micro windows to minimize the gas absorption, thus \(\tau_{g,\lambda}\) is considered negligible. Rayleigh scattering is calculated following Bodhaine et al. (1999) using the pressure measured at the measurement site by the ZENO weather station. The AOD \(\tau_{a,\lambda}\) can then be calculated by subtracting Rayleigh scattering from the equation below:

\[
\tau_{a,\lambda} = \frac{\ln(V_{o,\lambda} \cdot d^{-2}) - \ln (V_\lambda)}{m} - \tau_{R,\lambda}.
\]  

(3)

A cloud filter is applied to the spectra based on the measured fractional variation in solar intensity (fvsi). We set this quality filter to a maximum of 0.5% variability to ensure minimum cloud interference. The optical air mass range for Langley plot calibrations were performed from 1.5 \(\leq m < 7\) to avoid large errors at smaller air masses and turbidity influence at solar noon. A plot of \(\ln(V_o)\) is found in Appendix B, Figure B1 displaying the calculated \(\ln(V_o)\) over time from September to
November 2020. Mirror degradation and exposure to dust or ash from fires can be observed in a declining \( \ln(\text{Vo}) \) and a sudden jump in \( \ln(\text{Vo}) \) is observed in late October and early November after the mirrors were cleaned, suggesting that debris had diminished the solar intensity measured by the FTIR instrument. Due to the varying \( \ln(\text{Vo}) \), we calculate AOD only for the first week of data collection (Sept. 8 – 15) using the \( \ln(\text{Vo}) \) obtained during the earlier period of September, summarized in Table B1 of Appendix B.

A time series of the FTIR-derived AOD for the four micro windows is shown in Figure B2 of Appendix B where a spectral dependance of the aerosol absorption can be observed in the plot with longer wavelengths recording smaller AOD. Although our FTIR-derived AOD is limited to the spectral range from the FTIR detector (1020.9 – 1636 nm), we used the Ångström exponent to derive FTIR AOD at 500 nm to enable a comparison with other studies shown in Figure 4. A plot of AOD at 1020.9 and 1636 nm with AERONET at 1020 and 1640 nm can be found in the Appendix B, Figure B3.

### 2.5 Estimating Emission Factors and Modified Combustion Efficiency

We demonstrate the capability of ground-based solar column measurements to calculate important variables for fire research including EFs and MCE for determining fire emissions and understanding different combustion phases of wildfires. As a case study, Sept. 12 observations were selected as this day had the highest observed \( X_{\text{CO}} \) and dominant influence from the SQF Complex (Figure 1b). We estimate emission ratios of \( \text{CH}_4 \) and CO (\( \text{ER}_{\text{CH}_4/\text{CO}} \) and \( \text{ER}_{\text{CO/CO}_2} \)) by calculating the slope from a York linear regression of CO and \( \text{CH}_4 \) excess mole fractions (\( \Delta X_{\text{CO}} \) and \( \Delta X_{\text{CH}_4} \)) relative to \( \text{CO}_2 \).

\[
\text{ER}_X = \frac{\Delta X}{\Delta \text{CO}_2} = \frac{X_{\text{Fire}} - X_{\text{Background}}}{\text{CO}_2_{\text{Fire}} - \text{CO}_2_{\text{Background}}}
\]  

(4)

Emission factors (\( \text{EF}_{\text{CH}_4/\text{CO}_2} \) and \( \text{EF}_{\text{CO/CO}_2} \)) were then calculated as shown in equation 5 by multiplying the ER by the molar mass of either CO or \( \text{CH}_4 \) (\( \text{MM}_X \)), divided by the molar mass of carbon (\( \text{MM}_C \)), and total carbon emitted (\( \text{C}_T \)) while assuming 500 ± 50 g C is emitted per kilogram of dry biomass consumed (\( M_{\text{Biomass}} \)) (Akagi et al., 2011; Burling et al., 2010). \( \text{C}_T \) is given by Equation 6, where \( n \) is the number of carbon-containing species measured, \( N_j \) is the number of carbon atoms in species \( j \), and \( \Delta C_j \) is the excess mixing ratio of species \( j \) (Yokelson et al., 1999).

\[
\text{EF}_X = \frac{\text{ER}_X}{\text{C}_T} \cdot \frac{\text{MM}_X}{\text{MM}_C} \cdot M_{\text{Biomass}}
\]  

(5)

\[
\text{C}_T = \sum_{j=1}^{n} N_j \times \frac{\Delta C_j}{\Delta \text{CO}_2}
\]  

(6)

The MCE is commonly used as a relative measure between the smoldering and flaming combustion phases. Smoldering emissions have an MCE from 0.65-0.85, pure flaming emissions have an MCE of 0.99 and emissions near 0.9 have roughly
equal amounts of flaming and smoldering combustion (Akagi et al., 2011). MCE was calculated by dividing excess mole fraction of CO$_2$ ($\Delta$CO$_2$) by the total excess mole fraction of CO and CO$_2$:

$$ MCE = \frac{\Delta$CO$_2}{\Delta$CO + $\Delta$CO$_2$}. $$

Due to averaging kernel differences across the trace gases, an averaging kernel correction is applied to Equations 4 and 7, see Appendix C. The enhancement over background mixing ratios ($\Delta$X$_{\text{gas}}$) for each measurement day was calculated by subtracting the background ($X_{\text{gas, bkdg}}$) determined as the 2nd percentile of daily measured mixing ratios ($X_{\text{gas}}$). A sensitivity test showed that emission ratios did not significantly change if background was calculated using 1st-5th percentiles. The monthly background in September was 411.3 ppm for X$_{\text{CO2}}$, 99.4 ppb for X$_{\text{CO}}$ and 1905.3 ppb for X$_{\text{CH4}}$. The monthly average mixing ratios measured in situ at Mauna Loa for CO$_2$ were 411.5 ± 0.2 ppm and CH$_4$ 1884.7 ± 1 ppb during September 2020 (https://gml.noaa.gov/obop/mlo/).

3 Results

3.1 Observations X$_{\text{CO}}, X_{\text{CO2}},$ and $X_{\text{CH4}}$ from wildfires in the San Joaquin Valley

The first week of trace gas measurements are shown in Figure 2 in addition to the daytime fire radiative power (FRP), an indicator of fire intensity measured by VIIRS Active Fire and Thermal Anomalies product from NOAA-20. Fire-emitted CO can be observed in the timeseries and X$_{\text{CO}}$ is exceptionally high on Sept. 12, reaching mixing ratios 10 times higher than the previous days. A large smoke plume was captured by the NOAA VIIRS satellite on Sept. 12 originating from the SQF Complex and traveling west directly over the measurement site as seen in Figure 1b. Sept. 12 also corresponds to the highest FRP during this record. The next day, Sept. 13, both fires remained active; however, their smoke plumes were transported northward as reflected by a lower X$_{\text{CO}}$ in our observations relative to Sept. 12.

X$_{\text{CO2}}$ and X$_{\text{CH4}}$ were also enhanced on the Sept. 12 smoke event and followed the same trend as X$_{\text{CO}}$ over the course of the day. Over 30 dairy farms are located northwest of the measurement site and they are expected to influence observed X$_{\text{CH4}}$ and X$_{\text{CO2}}$; dairy influence is notable on days with predominantly westerly winds (e.g. Sept. 8 and 11). X$_{\text{CO}},$ X$_{\text{CO2}},$ and X$_{\text{CH4}}$ averaged at 154 ± 78 ppb, 413 ± 1 ppm, and 1938 ± 27 ppb from Sept. 8 to Oct. 17. X$_{\text{CO}}$ and X$_{\text{CO2}}$ peaked on Sept. 12 at 1012.8 ppb and 421.6 ppm, while X$_{\text{CH4}}$ peaked on Sept. 28 at 2050.1 ppm due to dairy farms in the area. The measured X$_{\text{CO}}$ on Sept. 12, 2020, is the highest reported X$_{\text{CO}}$ value in EM27/SUN literature. Retrievals of X$_{\text{gas}}$ using the EM27 in such dense smoke plume has not been reported in previous studies. Using this date as a case study, we calculate total column EF and MCE to study the evolution of the fire over the course of the day further described in Section 3.4. We isolate the Sept. 12 fire smoke plume by taking the X$_{\text{CO}}$ mixing ratios that exceeded the 98th percentile (>335.1 ppb) from all observations over our
measurement period. This period corresponded to mixing ratios recorded after 12:00 pm when $X_{CO}$ and $X_{CO2}$ began to increase considerably.

The time since emission of the observed smoke plume was estimated to be ~1.5 hr. This was calculated by dividing the distance away from the SQF Complex fire (~60 km) by the average wind speed (11.2 ± 0.8 m/s) at the height of the smoke plume (4.1 ± 1.2 km). The height of the plume was determined by taking a mean of the available pixels within the smoke plume of aerosol layer height product from TROPOMI (http://www.tropomi.eu/data-products/aerosol-layer-height). The mean wind speed measured at 4.1 ± 1.2 km came from a 915 MHz Wind Profiler located in Visalia, CA about 20 km west of the observational site (data available at: ftp://ftp1.psl.noaa.gov/psd2/data/realtime/Radar915/).

![Figure 2](https://example.com/fig2.png)

**Figure 2.** Timeseries of daytime total FRP from VIIRS NOAA-20 of Creek fire (red) and SQF Complex (blue) and of 5-minute mean observations from the ground-based EM27/SUN solar-viewing spectrometer during the first week of measurements September 8 – 15, 2020.

### 3.2 Comparison of EM27/SUN and TROPOMI retrievals

In this section, we compare $X_{CO}$ retrieved from ground-based EM27/SUN observations downwind of the Sierra Nevada wildfires to satellite-based $X_{CO}$ retrievals from coincident TROPOMI overpasses. Previous studies of $X_{CO}$ and $X_{CH4}$ comparisons between TROPOMI and EM27/SUN’s have used a TROPOMI soundings between 50 – 100 km from the observational site and used EM27/SUN measurements between 40 mins – 1 hour TROPOMI overpass as a coincident criteria (Sha et al., 2021; Jacobs, 2021; Sagar et al., 2022; Alberti et al., 2022b). Given the spatial and temporal heterogeneity in smoke plumes from wildfires observed in Figure 1 and Figure 2, we perform a sensitivity study of different radii (10, 15, 20, 30, 40,
50 km) from our observational site and time averages (10, 15, 20, 30 mins) to determine adequate criteria for comparison during a wildfire event. An illustration of the sensitivity analysis is shown in Figure D1, Appendix D.

We quantify the sensitivity of different TROPOMI radii and averaging times in comparison with our EM27/SUN data by calculating the mean difference, mean relative difference and R² between the linear regression fits for the measurements. We find that all combinations produce a positive mean bias, meaning that TROPOMI overestimates X_CO compared to the EM27 measurements. TROPOMI pixels within a radius of 5 km averaged with 30-minute aggregations of EM27/SUN gives the lowest mean difference of 10.64 ppb, mean relative difference of 5.5%, and highest correlation coefficient of 0.99, however, only 4 points coincide during the measurement period. To maximize the number of coincidences while maintaining a low bias, we select 15 km as the maximum radius with a 30-minute averaging time. This gives a total of 19 coincident data points and mean difference of 17.2 ppb, mean relative difference of 9.7%, and R² of 0.97. A timeseries of the coinciding data pairs from the EM27/SUN 30-minute average observation period with TROPOMI overpass with a 15 km radii are shown in Figure 3a and the correlations are shown in Figure 3b. Applying these spatial and temporal criteria results in large variance for the largest measured X_CO due to heterogeneity in the smoke plume event. The EM27/SUN displays a larger variance than TROPOMI due to capturing the 30-minute temporal variability in the plume as it was transported above the instrument. We find a strong correlation between CO column averages with an R² of 0.97 and a York linear regression fit of y = 1.36x – 40.15. These results suggest an overestimation of 9.7% X_CO from TROPOMI observations of wildfires.

![Figure 3](https://doi.org/10.5194/acp-2022-671)

*Figure 3.* a) Timeseries of coinciding EM27/SUN 30-minute average observation period with TROPOMI overpass with 15 km radius. b) Correlation between coinciding TROPOMI and EM27/SUN data pairs. The error bars are the standard deviation of the TROPOMI averaged pixels at 15 km and EM27/SUN 30-minute observation.

### 3.3 Aerosol optical depth derived from measured solar intensity

We show a timeseries of AOD at 500 nm derived for the first week of measurements in Figure 4 (Sept. 8 – 15) plotted with AOD at 500 nm from an AERONET station in Fresno (Sept. 4 – 19), about 90 km north of the measurement site (Figure 1). Similar to observations of X_CO, enhancements of AOD are observed through the week with the highest recorded AOD on
Sept. 12. The observational sites were relatively far from each other (~90 km) and although smoke reaching the two sites varied over these spatial scales, the FTIR AOD follows the same inter-day trend as the AOD measured by the AERONET with a peak in AOD on the 12th. Intraday variability between the sites do not seem to follow the same trend. This suggests that the EM27/SUN AOD estimate was also able to qualitatively capture the increase in aerosols in the SJV as fires burned more intensely and smoke from fires moved into the valley due to synoptic conditions. Differences are observed in the AOD timeseries as these two sites were downwind of two different fires in the Sierra Nevada: the Creek Fire was located directly west of Fresno and the SQF Complex composed of the Castle and Shotgun fires was located directly west of the EM27/SUN measurement site. This may be the reason that the peaks observed at the FTIR site are not seen in the Fresno AERONET data. Ahangar et al. (2022) determined that the SJV air quality was mainly impacted during the Sept. 8 – 15 period with Creek and SQF Complex fires responsible for the majority of the smoke within SJV. Although the Creek fire began on Sept. 5, the air quality began to deteriorate a few days after, possibly due to the westerly downslope winds that pushed the smoke east of the Sierra Nevada at the beginning of the fire (Cho et al., 2022). Low AOD from AERONET was observed prior to Sept. 8 with values of 0.50 ± 0.28, illustrating the air quality was cleaner and deteriorated after the activity from the Creek and SQF Complex fires increased (Ahangar et al., 2022).

![Figure 4. FTIR AOD and AERONET AOD at 500 nm. The FTIR AOD at this wavelength was calculated using the Ångström exponent relationship.](https://doi.org/10.5194/acp-2022-671)

We find a strong correlation (R² > 0.94) between the EM27/SUN measured XCO and AOD at 500 nm on most days with slopes ranging from 28.4 to 83.7 ppb CO/AOD (Figure 5). Several studies have shown strong correlation between CO and AOD at 500 and 550 nm from fire events and downwind of polluted sources (Lobert, 2002; Paton-Walsh et al., 2005; McMillan et al., 2008; Kampe and Sokolik, 2007). McMillan et al. (2008) found values for linear regression fits ranging from 44 to 74 from AIRS CO and MODIS AOD observations of fire plumes. Most of our slopes fall within this range and the lower slopes (Sept. 10 and 11) follow a similar linear trend (black line in Figure 5) as observed by McMillan et al. (2008) over a clean region during Alaskan/Canadian fires. The intercepts of the fitted lines reflect different local backgrounds of CO with
Sept. 12 having the largest background of 139 ppb. We find that the AOD on Sept. 12 reached values above 15 indicating extremely high aerosol loading from the smoke plume event transported from the SQF Complex in the Sierra Nevada.

**Figure 5.** Scatterplot correlations of $X_{CO}$ and AOD at 500 nm from the FTIR for each day of the first week Sept. 8 -12. Low smoke days fall along the black line, derived from previous remotely sensed $X_{CO}$/AOD relationships. The teal line corresponds to Sept. 12, the day of highest fire influence in our record.

### 3.4 Emissions factors and Modified Combustion Efficiency

The average MCE for the smoke plume on Sept. 12 was 0.89 ± 0.21, meaning that observations of the smoke plume consisted of a mixture of flaming and smoldering combustion phases (Figure 6). During the flaming phase of a fire, CO$_2$ is produced, and convection is created by high flame temperatures and produces lofting of smoke. High altitude smoke can be transported large distances, corroborated by observations of ash falling from the sky at the measurement site ~60 km away from the fire and clearly observable by satellite imagery (Figure 1b). In contrast to the flaming phase, smoldering fires burn at lower intensity, and incomplete combustion side products like CO, CH$_4$, and organic carbon aerosol are produced. We observed a steady MCE as $X_{CO}$, $X_{CH4}$, and AOD increased, indicating influence of smoldering combustion (Figure 6, a-e). The MCE calculated from total column observations is averaged over the entire vertical plume as it was being transported over the measurement site. The advantage of a plume integrated MCE is that vegetation is burnt differently throughout the fire and the atmospheric column observations can represent the fire as a whole by integrating the smoke plume heterogeneity in the vertical atmospheric column.

Emission ratios of CO and CH$_4$ on Sept. 12 were calculated with respect to CO$_2$. ER$_{CO2}$ was 0.116 and the ER$_{CH4}$ was 0.0073 (Figure 6, f-h), resulting in an EF$_{CO2}$ of 1632.9 ± 163.3 g CO$_2$ per kg biomass combusted, EF$_{CO}$ of 120.5 ± 12.2 g CO per kg biomass combusted, and a EF$_{CH4}$ of 4.3 ± 0.8 g CH$_4$ per kg biomass combusted. We compared findings from our
gas measurements to literature values in temperate coniferous forest studies from the Sierra Nevada and other locations in North America summarized in Table 1 and Figure 7. All the studies listed in Table 1 except for this study were based on aircraft measurements. Most recently, Prichard et al. (2022) compiled emission factors for North American conifer forests and found a fire average for $\text{EF}_{\text{CO}_2}$ of 1629.54 ± 63.43, $\text{EF}_{\text{CO}}$ of 104.01 ± 34.93, and $\text{EF}_{\text{CH}_4}$ of 5.05 ± 2.41. Burling et al. (2011) measured the Turtle Fire in the Sierra Nevada, and we find that our MCE overlaps within error with theirs. Finally, $\text{CH}_4$ emissions reported for more smoldering fires that were characterized by direct $\text{O}_2$/CO measurements for 1999 Big Bar fire (Lueker et al., 2001). Our atmospheric column-based EF fall within the ranges of previous literature, highlighting the ability of the EM27/SUN solar spectrometer observations to be used for deriving important variables for fire research.

**Table 1.** Summary of past airborne studies modified combustion efficiency (MCE) and emission factors (EF, g kg$^{-1}$) relative to CO$_2$ for temperate coniferous forests in North America and Sierra Nevada.

<table>
<thead>
<tr>
<th>Studies</th>
<th>MCE</th>
<th>$\text{EF}_{\text{CO}_2}$</th>
<th>$\text{EF}_{\text{CO}}$</th>
<th>$\text{EF}_{\text{CH}_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>North America</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radke et al., 1991* – Conifer Forest</td>
<td>0.919</td>
<td>1641</td>
<td>93</td>
<td>3.03</td>
</tr>
<tr>
<td>Yokelson et al., 1999* – Southeastern US Pine Forest understory</td>
<td>0.926</td>
<td>1677</td>
<td>86</td>
<td>-</td>
</tr>
<tr>
<td>Yokelson et al., 2011 – Mexico Pine-oak</td>
<td>0.908</td>
<td>1603</td>
<td>103</td>
<td>3.66</td>
</tr>
<tr>
<td>Burling et al., 2011* – Average conifer forests understory burns</td>
<td>0.936 ± 0.024</td>
<td>1668 ± 72</td>
<td>72 ± 26</td>
<td>3.0 ± 2.4</td>
</tr>
<tr>
<td>Urbanski et al., 2013 – Rocky Mts conifer forest fires</td>
<td>0.85 – 0.92</td>
<td>1527 – 1681</td>
<td>89.3 – 173</td>
<td>4.4 – 12.1</td>
</tr>
<tr>
<td>Liu et al., 2017 – Study average</td>
<td>0.912</td>
<td>1454 ± 78</td>
<td>89.3 ± 28.5</td>
<td>4.9 ± 1.5</td>
</tr>
<tr>
<td><strong>Sierra Nevada</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Burling et al., 2011</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turtle Fire* (10-Nov-2009)</td>
<td>0.913</td>
<td>1599</td>
<td>97</td>
<td>5.51</td>
</tr>
<tr>
<td>Shaver Fire* (10-Nov-2009)</td>
<td>0.885</td>
<td>1523</td>
<td>126</td>
<td>7.94</td>
</tr>
<tr>
<td>Yates et al., 2016</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rim fire (26-Aug-13)</td>
<td>0.94</td>
<td>1675 ± 285</td>
<td>92.5 ± 16</td>
<td>4.8 ± 0.8</td>
</tr>
<tr>
<td>Rim fire (29-Aug-13)</td>
<td>0.94</td>
<td>1711 ± 292</td>
<td>69.5 ± 12</td>
<td>4.7 ± 0.8</td>
</tr>
<tr>
<td>Rim fire (10-Sept 13)</td>
<td>0.88</td>
<td>1595 ± 272</td>
<td>138.4 ± 24</td>
<td>7.5 ± 1.3</td>
</tr>
<tr>
<td>Liu et al., 2017</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rim fire (26-Aug-13)</td>
<td>0.923</td>
<td>1478 ± 11</td>
<td>78.7 ± 4</td>
<td>4.43 ± 0.25</td>
</tr>
<tr>
<td>*<em>This study: SQF Complex fire</em> (12-Sept 22)</td>
<td>0.89 ± 0.21</td>
<td>1632.9 ± 163.3</td>
<td>120.5 ± 12.2</td>
<td>4.3 ± 0.8</td>
</tr>
</tbody>
</table>

*Prescribed burns
+ Measurement uncertainties were calculated by propagating the error from the linear regression standard error, $C_T$, and 10% error from $M_{\text{Biomass}}$.
Figure 6. Timeseries of September 12, 2020 of a) MCE and b-e) $\Delta X_{CO}$, $\Delta X_{CO2}$, $\Delta X_{CH4}$, and AOD with shaded grey area representing the SQF Complex fire plume. f-g) Type II linear regression plots of $\Delta CO$ and $\Delta CH4$ against $\Delta CO2$ and h) $\Delta CH4$ against $\Delta CO$ to calculate the slope that represents the ER.
3.5 Enhancement ratios of SJV greenhouse sources

The EM27/SUN’s location enabled us to sample transient fire plumes from local and state wildfires, but was also located near a large cluster of dairy farms, which are a large regional source of CH₄ emissions (Heerah et al., 2021; Marklein et al., 2021). Dairy farms are known to emit significant amounts of CH₄ from the animal’s enteric fermentation and on-farm manure management. Because fires also emit CH₄, we explored whether dairy and fire sources in this region can be disentangled using ratios of the different species measured by the EM27/SUN. Furthermore, our measured XCH₄ enhancement ratios relative to XCO₂ enable us to investigate the contribution of state wildfires to CH₄ emissions in 2020. To constrain the observed enhancements, we compared the enhancement ratios of ΔXCH₄/ΔXCO₂ from September – October 2020 to enhancement ratios collected in September 2018 and 2019 in the same local area that characterize non-fire years. September 2018 and 2019 measurements are further described in the supplemental information. We focused on observation days with statistically significant correlations (n = 26 days) between CH₄ and CO₂ enhancements (R² > 0.5 and p < 0.05) to characterize enhancement ratios of the SJV non-fire years.

Figure 8 shows the ΔXCH₄/ΔXCO₂ enhancement ratios from September 2018, September 2019, and September – October 2020 measurements. We observe a clear influence of dairy farms with larger ΔXCH₄/ΔXCO₂ enhancement ratios of 38.4 ± 21.7 and 30.5 ± 5.0 (ppb/ppm), respectively for September 2018 and 2019, exceeding ΔXCH₄/ΔXCO₂ wildfire smoke periods. During our 2020 observations, ΔXCH₄/ΔXCO₂ reflecting dairy farm influence were found on some days in addition to less steep slopes from smoke influence. This is expected as elevated XCO₂ and lower XCH₄ are emitted from wildfires. The Sept. 12 smoke plume event is highlighted in the figure and has a smaller enhancement ratio of 7.3 (ppb/ppm) than dairy farms. Similar ratios of ΔXCH₄/ΔXCO₂ were found in Hanford, ~50 km west of our observation site, from an aircraft study ranging from 35.9 – 44.4 (ppb/ppm) during a winter campaign (Herrera et al., 2021). Other column-based studies have determined the XCH₄/XCO₂ for urban sources in the Los Angeles City finding ratios for XCH₄/XCO₂ ranging from 6.65 to 9.96 (ppb/ppm) in 2015 (Chen et al., 2016). Wunch et al., 2009 calculated XCH₄/XCO₂ ratio of 11 ± 2 and showed that urban fossil fuel and wildfire XCH₄/XCO₂ ratios

Figure 7. Emission factors (g kg⁻¹) as a function of MCE for temperate coniferous forests in Sierra Nevada wildfires.

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are very similar due to incomplete combustion and ratios are not distinct enough to separate (Wunch et al., 2009). In the vicinity of the measurement site in the SJV, there is a strong influence of dairy farm agriculture and minimal urban emissions away from population centers, thus we are able to separate of $X_{\text{CH}_4}/X_{\text{CO}_2}$ from dairy sources, from fire or possible urban emissions. The CH$_4$/CO$_2$ enhancement ratios observed in this area make it evident that dairy farms operations are the dominant source of CH$_4$ during fire and non-fire periods. Nevertheless, CH$_4$ enhancements during the strong smoke influence periods greatly exceeded CH$_4$ enhancements from local dairy sources. The immense scale of 2020 wildfires, summing to 28% of the states’ CO$_2$ budget for the year (CO2 Inventory Scoping Plan, 2022), in addition our observations of elevated fire-derived CH$_4$, suggest that these fires had a significant effect on the state’s CH$_4$ budget.

Given the importance of reducing CH$_4$ emissions for meeting California’s climate goals, we calculate the amount of CH$_4$ released from the wildfires that burnt in the state in 2020 using estimated CO$_2$ emissions from the state’s wildfire inventory along with emission ratios of CH$_4$/CO$_2$ from our study and the literature on fires in California. The California Air Resources Board (CARB) reported CO$_2$ emissions of 106.7 Tg of CO$_2$ was emitted from 2020 wildfires, with individual CO$_2$ emission estimates from the top 20 wildfires. We use estimated CO$_2$ emissions from the top 20 wildfires to derive CH$_4$ emissions. The total emissions of CH$_4$ are calculated by multiplying the emission or enhancement ratio of wildfire smoke and molecular mass ratios:

$$E_{\text{CH}_4} = \left(ER_{\text{CH}_4} \times \frac{M_{\text{CH}_4}}{M_{\text{CO}_2}}\right)E_{\text{CO}_2}$$  \hspace{1cm} (8)

where $E_{\text{CH}_4}$ is the emissions of CH$_4$ in Gg/yr, $ER_{\text{CH}_4}$ with respect to CO$_2$ in mol/mol, $M_{\text{CH}_4}$ is the molar mass of CH$_4$ and $M_{\text{CO}_2}$ is the molar mass of CO$_2$, and $E_{\text{CO}_2}$ are the fire specific emissions in Gg/yr. ER from fires are dependent on vegetation type; fires in California fell into temperate forest, shrubland or grassland vegetation types (Xu et al., 2022). Based on the generic vegetation classification from the FINN model (https://www.acom.ucar.edu/Data/fire/), we classify the top 20 California wildfires of 2020 into the three types based on the dominant vegetation. The ER for the general vegetation was derived from EFs summarized in Xu et al., 2020 and for the Creek and SQF Complex fires we average the EFs summarized in Table 1 for the Sierra Nevada and derive an ER shown in Table E1, Appendix E. The top 20 wildfires represented 92% of CO$_2$ emissions released from wildfires in 2020 and emitted $213.7 \pm 49.8$ Gg CH$_4$. Figure 9 shows the estimated CH$_4$ emissions from the top 20 largest wildfires of 2020 compared to CARB’s 2019 anthropogenic CH$_4$ inventory emissions, the most recent inventory year available (CH4 Inventory Scoping Plan, 2022).
Figure 8. Correlation plots of $\Delta X_{\text{CH}_4}$ vs $\Delta X_{\text{CO}_2}$ for SJV measurements collected during non-fire years in Sept. 2018 (blue) and 2019 (light blue), and during fire period of Sept. – Oct. 2020 (gray). The Sept. 12 smoke event (red) highlighted with a linear fit through that day’s data clearly shows a distinct $\Delta X_{\text{CH}_4}/\Delta X_{\text{CO}_2}$ relationship from other data.

Figure 9. California CH$_4$ emissions from 2020 calculated for the top 20 wildfires compared to the state’s anthropogenic CH$_4$ emissions from the 2019 inventory (CH4 Inventory Scoping Plan, 2022). The industrial sector also includes oil and gas emissions.
4. Discussion

We made total column measurements of CO$_2$, CO, CH$_4$, and AOD with an EM27/SUN FTIR in the San Joaquin Valley (SJV), California during part of the wildfire season of 2020 from September to October. The emissions of the Creek and SQF Complex fires, two major wildfires burning in the Sierra Nevada, were sampled continuously in the SJV for over a month. We demonstrate that data from the EM27/SUN allows for calculating MCE and EFs in smoke plumes transported from wildfires, especially for high altitude smoke, adding important new estimates for fires in this region. For the Sierra Nevada, only three field-based studies have estimated emission factors in this area despite the increase in wildfires over burns the previous decade (Burling et al., 2011; Yates et al., 2016; Liu et al., 2017). Our emission factor estimates from the September 12 event for CO ($120.5 \pm 12.2$ g kg$^{-1}$ dry biomass burned) and CH$_4$ ($4.3 \pm 0.8$ g kg$^{-1}$ dry biomass burned) are within the range of those reported from the Sierra Nevada conifer forests (Burling et al., 2011; Yates et al., 2016; Liu et al., 2017). Our atmospheric column-based estimates contribute to the limited number of EF for temperate forests and are particularly important given the scale of the fires that occurred in 2020 in California.

Empirically quantified EFs in temperate conifer forests are limited in number and many of the measurements in these regions are from prescribed burning for land management (Burling et al., 2011; Akagi et al., 2011; Urbanski, 2013). Because prescribed burns typically occur during favorable atmospheric conditions, specified fuel, and during non-wildfire seasons, it is possible that prescribed burn EFs may not represent wildfire EFs that burn under different conditions favorable to wildfires (Urbanski, 2013). There is a need for biome-specific EFs to quantify the amount of trace gas or aerosol emitted per kilogram of biomass burned, and these EFs are essential model inputs for estimating total greenhouse gas and aerosol emissions of fires.

Field measurements have also been limited in measuring a smaller fraction of the smoke plume. Airborne measurements are the most common method to estimate EFs from wildfires and involve aircraft equipped with fast response gas analyzers sampling through smoke plumes (e.g. Yokelson et al., 1999; Yates et al., 2016; Iraci et al., 2022). Although highly effective for large and remote wildfires, this method can be costly and logistically complex, limiting the number of fires sampled during a campaign period (Ross et al., 2013). In situ stations downwind of fires are able to provide measurements when aircraft are unable to fly but they oversample in smoldering conditions where the fire burns less vigorously and emissions are released closer to the ground. Aircraft measurements tend to sample lofted fire samples in the flaming phase, resulting in different emissions than a fire in situ measurements (Paton-Walsh et al., 2005). Although much has been learned from these methods, an average sample of the fire plumes is difficult to obtain due to variability in emissions from the fire burning at different stages (Paton-Walsh et al., 2005). Open-path FTIR measurements have allowed for “whole-fire” emission factors (Smith et al., 2014). Total-column measurements can provide a plume-integrated EF and MCE; however, calculating EFs with respect to CO$_2$ in the vertical column has been challenging due to high atmospheric background (Kille et al., 2022; Paton-Walsh et al., 2005; Lutsch et al., 2020, 2016; Viatte et al., 2014, 2015). Portable solar viewing instruments like the EM27/SUN have the advantage of remotely sampling total columns closer to the source and capturing a vertical integration of transported smoke plumes, contributing to the limited number of EFs across biomes and understanding impact on regional smoke influence background.
Simultaneous measurements of ground-based total columns and satellites allow for a spatial and temporal understanding of the fire events. The $X_{\text{CO}}$ enhancement from the 2020 wildfires in the Sierra Nevada was also observed from space and smoke plumes up to ten times higher than the local background are visible in the TROPOMI soundings on the Sept. 12 smoke event. Pairing stationary ground-based column observations with satellites can help in understanding regional wildfires at a greater spatial and temporal scale. Although TROPOMI has daily global coverage with great resolution, daily snapshots are often not enough to understand the behavior of a fire. Conversely, stationary ground-based instruments are limited to observing a point in space. As an instrument with capability of measuring atmospheric columns, the EM27/SUN can help close the gap in the temporal scale of satellite observations. The EM27/SUN measured continuously in the daytime filling in the temporal gaps from the satellite TROPOMI’s single overpass observations. A sensitivity study showed that a smaller radius of 5 or 15 km from TROPOMI observations paired with 30-minute averaging around the overpass time gave better statistical agreement during wildfire events. This strong correlation of $X_{\text{CO}}$ between TROPOMI and the EM27/SUN has been observed before in urban sites (Sagar et al., 2022; Alberti et al., 2022b) and in rural Alaska (Jacobs, 2021). Jacobs (2021) found that wildfire influences in $X_{\text{CO}}$ resulted in high observational variance in EM27/SUN observations and they suggest that this may be due to spatial and temporal variability in the smoke plume measured by TROPOMI and the EM27/SUN. The 9.7% overestimation from TROPOMI found in this study may also be due to averaging of the smoke plume’s heterogeneity within each TROPOMI comparison point. Alternatively, Rowe et al. (2022) found that multiple scattering on aerosols may be responsible for 5-10% increased $X_{\text{CO}}$ observations from TROPOMI in thick smoke plumes.

The air quality index in the SJV was at an all-time high in the hazardous range for weeks during the 2020 wildfire season (Morris III and Dennis, 2020) and AOD at the AERONET site in Fresno increased by three to five times higher than yearly average from 2002-2019 (Cho et al., 2022). FTIR-derived AOD at 500 nm reached extreme highs during the Sept. 12 smoke plume event, and followed the same trend on other days as the trace gas enhancements. The slopes during low smoke and high smoke days were consistent with previous satellite observations by McMillan et al. (2008). Previously, simultaneous measurements of aerosols and trace gases from the same instrument has been limited due to the aerosol burden interfering with retrieval of trace gases. For example, the majority of the TROPOMI $X_{\text{CH}_4}$ product was flagged out completely near the observational site during the Sept 7 – 15 period, and hence was not included in this analysis. The EM27/SUN demonstrated the potential to elucidate trace gas and aerosol relationships even during thick aerosol periods. Similarly, future studies may use simultaneous measurements from TROPOMI $X_{\text{CO}}$ product and AOD to study regional impacts from wildfires (Chen et al., 2021). Scattered diffuse light during high aerosol loading from biomass burning may decrease the reliability of the AOD observations, thus further verification of the FTIR-derived AOD during high aerosol loading is required. Since the nearest AERONET station was relatively far away from our EM27/SUN site, we cannot do a true side-by-side comparison. However, the FTIR derived AOD showed the same baseline pattern as the AERONET site in Fresno, demonstrating the ability of the EM27 to simultaneously measure AOD and trace gases through a thick plume of smoke which can elucidate mechanisms within smoke plumes.
As fires become more frequent with climate change, monitoring trace gases and particulates may become especially challenging in mixed source areas like the San Joaquin Valley where concentrations can become amplified by stagnant conditions in the SJV. Moreover, the fire-added CH$_4$ may hamper evaluation of greenhouse gas emission reduction initiatives at the state and at the global scale by adding unaccounted for CH$_4$ to the atmosphere. Using CARB’s 2020 wildfire emission estimate for CO$_2$, we calculated the CH$_4$ contribution from the top 20 largest fires to be $213.7 \pm 49.8$ Gg CH$_4$, respectively. These wildfires alone emitted 13.6% of the total state CH$_4$ emissions, more than the transportation, electric power, and commercial and residential sectors. While estimated CH$_4$ emissions from wildfires are smaller in magnitude than inventoried emissions from agriculture and industrial sources, this source should be considered in the state’s inventory given its magnitude and large impacts on the atmospheric CH$_4$ during wildfire periods. Additionally, wildfire emitted CH$_4$ may be an important and unaccounted positive feedback to climate change given the effect of increasing temperatures on fire severity.

5. Conclusions

Over the past 50 years, approximately three quarters of the area burned by wildfires in California’s has been in North Coast and Sierra Nevada (Williams et al., 2019), highlighting the importance of studying emission factors from fires in these systems. However, there are surprisingly few observations of emission factors from these fires despite their importance to California’s greenhouse gas budgets and air quality. The ground-based EM27/SUN is a useful instrument for understanding emissions of trace gases and aerosols from wildfires at a regional scales. The portable nature of the EM27/SUN allows for deployment downwind of fires for calculating important variables like EF and MCE. Having alternate techniques to calculate emission factors that are not costly or complex to deploy adds to the small number of emissions required to accurately calculate emissions and construct wildfire inventories. Several studies have demonstrated the utility in FTIR-derived EF for studying whole fire emissions from open path instruments (Paton-Walsh et al., 2014) and vertically integrated measurements (Viatte et al., 2013). Our total column MCE and EF with respect to CO$_2$ are the first to be reported from ground-based FTIR measurements in California.

Wildfire smoke produced overcast skies throughout the Western U.S. during this period, with smoke plumes transported long distances. The EM27 measures a vertically integrated regional signal but is limited spatially compared to observations from satellites. Here we show that a combination of the two can elucidate spatiotemporal variability of wildfire emissions. We find strong agreement between the EM27 and TROPOMI, but TROPOMI overestimates observations by 9.7%. This is consistent with previous studies of EM27 XCO in rural Alaska (Jacobs, 2021) and Idaho wildfires (Rowe et al., 2022). Additionally, our solar spectral measurements were used to derive AOD. We compared to a nearby AERONET site and found AOD values at 1020.9 and 1636 nm that were consistent with AERONET observations. The Ångström exponent was used to calculate FTIR AOD at 500 nm to compare AOD to CO ratios with previous studies. AOD at 500 nm reached extreme levels of up to 15 during the smoke plume event. Good agreements were found of AOD to CO ratios with those observed in McMillian et al., 2008 from MODIS AOD and AIRS CO.
Finally, we find that a significant amount of CH$_4$ was emitted from the top 20 largest wildfires of 2020 in California. Given the importance of CH$_4$ emissions reduction for the state, our study suggests wildfires are an important source of CH$_4$ for California and may delay meeting the state’s ambitious goals of reducing emissions. Atmospheric monitoring of CH$_4$ should account for wildfire periods, as they can significantly affect measured enhancements. Overall, our analysis demonstrates a novel application of the EM27/SUN solar spectrometers and will contribute to the development of techniques for analyzing remotely sensed greenhouse gas measurements from wildfires.
Appendix A: EM27/SUN Correction Factors

The EM27/SUN was co-located with the CIT TCCON for 2-3 days before (Sept. 2 and 3, 2020) and after (Oct. 30, 31 and Nov. 31, 2020) the field measurements. A summary of the correction factors is shown in Table A1. An averaging kernel correction has been applied to the EM27/SUN observations prior to comparison following Hedelius et al. (2016). Due to a camera misalignment on Sept. 2 and 3, X_CO correction factors for those dates are not reported.

Table A1. Summary of correction factors from co-located EM27 measurements with TCCON at Caltech.

<table>
<thead>
<tr>
<th>X_gas</th>
<th>Sept 2 &amp; 3</th>
<th>Oct 30, 31 &amp; Nov 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>X_CH4</td>
<td>0.9986 (0.0002)</td>
<td>0.9976 (0.0001)</td>
</tr>
<tr>
<td>X_CO2</td>
<td>1.0042 (0.0001)</td>
<td>1.0036 (0.0001)</td>
</tr>
<tr>
<td>X_CO</td>
<td>-</td>
<td>0.9737 (0.0028)</td>
</tr>
<tr>
<td>X_H2O</td>
<td>1.0044 (0.0005)</td>
<td>1.0101 (0.0005)</td>
</tr>
</tbody>
</table>

Appendix B: Aerosol Optical Depth

FTIR derived AOD was calculated by following the Langley exponential method where an absolute calibration, ln(Vo), is required.

Figure B1. Absolute calibration for Langley exponential analysis of the EM27/SUN solar spectra over time from September to November 2020. Mirrors became significantly dirtier and dustier over the course of the measurement period. The ln(Vo) increased considerably after instrument mirrors were cleaned after the field campaign ended (black line).
Table B1. Mean values of ln(Vo) from September 14, 19, and 24, 2020 used for deriving AOD.

<table>
<thead>
<tr>
<th>Window</th>
<th>Mean ln(Vo)</th>
<th>sd</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020.9</td>
<td>15.17</td>
<td>0.11</td>
<td>3</td>
</tr>
<tr>
<td>1238.25</td>
<td>16.01</td>
<td>0.09</td>
<td>3</td>
</tr>
<tr>
<td>1558.25</td>
<td>16.34</td>
<td>0.08</td>
<td>3</td>
</tr>
<tr>
<td>1636</td>
<td>16.35</td>
<td>0.08</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure B2. Timeseries of AOD for the four micro windows from September 8 to September 15, 2020.

Figure B3. Timeseries of AOD from FTIR for the 1020.9 (red) and 1636 (blue) nm windows and AERONET (black) located in Fresno, CA ~90 km north of measurement site.
Appendix C: EM27/SUN Sensitivity

The EM27/SUN has different instrument sensitivities defined by the averaging kernels (AK) for each species measured shown below in Figure C1. The difference in sensitivity for the trace gases may introduce a bias in calculated ERs and MCE. Most of the difference is expected to be at the height of the plume where the smoke is concentrated at 4.1 km (~600 hPa). Following the methods of Hedelius et al. (2018), we divide the enhancements of $\Delta X_{\text{CO}_2}$ and $\Delta X_{\text{CO}}$ by the averaging kernel at that smoke plume height:

\[
MCE_{\text{AK corrected}}(\text{SZA}) = \frac{\Delta\text{CO}_2/\text{AK(SZA)}_{\text{CO}_2,600\text{ hPa}}}{\Delta\text{CO}_2/\text{AK(SZA)}_{\text{CO}_2,600\text{ hPa}} + \Delta\text{CO}/\text{AK(SZA)}_{\text{CO},600\text{ hPa}}}
\]  
(Eq. C1)

where $\text{AK}_{600\text{ hPa}}$ is the averaging kernel sensitivity for CO or CO$_2$. The mean relative difference of the correction for the Sept. 12 plume event is -1.1%, thus not applying this correction would overestimate the MCE by 1.1%

Similarly for the ERs, we correct the enhancements prior to fitting the points with a linear regression for the Sept. 12 plume event:

\[
ER_{X,\text{AK corrected}} = \frac{\Delta X/\text{AK(SZA)}_{X,600\text{ hPa}}}{\Delta\text{CO}_2/\text{AK(SZA)}_{\text{CO}_2,600\text{ hPa}}}
\]  
(Eq. C2)

Without applying this correction, $E_{\text{CH}_4}$ would be underestimated by 9.5% and $E_{\text{CO}}$ by 14.2% due to the difference in sensitivity.

Figure C1. Averaging kernel (AK) of EM27/SUN of $X_{\text{CO}}$ and $X_{\text{CO}_2}$ colored by solar zenith angle (SZA).
Appendix D: TROPOMI and EM27/SUN

Figure D1. Results from sensitivity analysis with varying radius away from measurement site for selecting CO enhancements from TROPOMI pixels and varying aggregated times.
### Appendix E: Methane from wildfires

#### Table E1. Emissions of the top 20 of 2020 wildfires. Emission ratios for Sierra Nevada fires (Creek, Castle and North Complex) were derived from EFs compiled in this study. The rest of the ER are derived from literature (Prichard et al., 2020; Xu et al., 2022).

<table>
<thead>
<tr>
<th>Fire Name</th>
<th>General Vegetation</th>
<th>Wildfire Area Burned (acres)</th>
<th>CO₂ (Tg)</th>
<th>ER&lt;sub&gt;CH₄&lt;/sub&gt;</th>
<th>CH₄ (Gg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>August Complex</td>
<td>Temperate evergreen</td>
<td>1,032,700</td>
<td>27.7</td>
<td>0.0055 ± 0.0044</td>
<td>55.4 ± 44.3</td>
</tr>
<tr>
<td>SCU Complex</td>
<td>Grasslands and savanna</td>
<td>396,399</td>
<td>4.6</td>
<td>0.0043 ± 0.0028</td>
<td>7.2 ± 4.7</td>
</tr>
<tr>
<td>Creek</td>
<td>Temperate evergreen</td>
<td>379,882</td>
<td>13.8</td>
<td>0.0084 ± 0.0022</td>
<td>42.2 ± 11</td>
</tr>
<tr>
<td>North Complex</td>
<td>Temperate evergreen</td>
<td>318,777</td>
<td>10.9</td>
<td>0.0084 ± 0.0022</td>
<td>33.3 ± 8.7</td>
</tr>
<tr>
<td>Hennessey</td>
<td>Shrublands</td>
<td>305,352</td>
<td>3.5</td>
<td>0.0033 ± 0.0021</td>
<td>4.2 ± 2.7</td>
</tr>
<tr>
<td>Castle</td>
<td>Temperate evergreen</td>
<td>170,648</td>
<td>6.4</td>
<td>0.0084 ± 0.0022</td>
<td>19.5 ± 5.1</td>
</tr>
<tr>
<td>Slater</td>
<td>Temperate evergreen</td>
<td>157,430</td>
<td>6.7</td>
<td>0.0055 ± 0.0044</td>
<td>13.4 ± 10.7</td>
</tr>
<tr>
<td>Red Salmon Complex</td>
<td>Temperate evergreen</td>
<td>143,836</td>
<td>4.6</td>
<td>0.0055 ± 0.0044</td>
<td>9.2 ± 7.4</td>
</tr>
<tr>
<td>Dolan</td>
<td>Shrublands</td>
<td>124,527</td>
<td>2.1</td>
<td>0.0033 ± 0.0021</td>
<td>2.5 ± 1.6</td>
</tr>
<tr>
<td>Bobcat</td>
<td>Shrublands</td>
<td>115,998</td>
<td>2.5</td>
<td>0.0033 ± 0.0021</td>
<td>3.0 ± 1.9</td>
</tr>
<tr>
<td>CZU Complex</td>
<td>Temperate evergreen</td>
<td>86,553</td>
<td>5.4</td>
<td>0.0055 ± 0.0044</td>
<td>10.8 ± 8.6</td>
</tr>
<tr>
<td>W-5 Cold Springs</td>
<td>Grasslands and savanna</td>
<td>84,817</td>
<td>0.7</td>
<td>0.0043 ± 0.0028</td>
<td>1.1 ± 0.7</td>
</tr>
<tr>
<td>Caldwell</td>
<td>Grasslands and savanna</td>
<td>81,224</td>
<td>0.4</td>
<td>0.0043 ± 0.0028</td>
<td>0.6 ± 0.4</td>
</tr>
<tr>
<td>Glass</td>
<td>Shrublands</td>
<td>67,484</td>
<td>1.9</td>
<td>0.0033 ± 0.0021</td>
<td>2.3 ± 1.4</td>
</tr>
<tr>
<td>Zogg</td>
<td>Shrublands</td>
<td>56,338</td>
<td>0.7</td>
<td>0.0033 ± 0.0021</td>
<td>0.8 ± 0.5</td>
</tr>
<tr>
<td>Wallbridge</td>
<td>Shrublands</td>
<td>55,209</td>
<td>4.1</td>
<td>0.0033 ± 0.0021</td>
<td>4.9 ± 3.1</td>
</tr>
<tr>
<td>River</td>
<td>Shrublands</td>
<td>50,214</td>
<td>0.9</td>
<td>0.0033 ± 0.0021</td>
<td>1.1 ± 0.7</td>
</tr>
<tr>
<td>Loyalton</td>
<td>Grasslands and savanna</td>
<td>46,721</td>
<td>0.7</td>
<td>0.0043 ± 0.0028</td>
<td>1.1 ± 0.7</td>
</tr>
<tr>
<td>Dome</td>
<td>Shrublands</td>
<td>44,211</td>
<td>0.1</td>
<td>0.0033 ± 0.0021</td>
<td>0.1 ± 0.1</td>
</tr>
<tr>
<td>Apple</td>
<td>Shrublands</td>
<td>33,209</td>
<td>0.8</td>
<td>0.0033 ± 0.0021</td>
<td>1.0 ± 0.6</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>213.7 ± 49.8</strong></td>
</tr>
</tbody>
</table>
Data availability: TROPOMI data can be downloaded from https://s5phub.copernicus.eu (last access: 15 July 2022; ESA, 2022); TROPOMI aerosol layer height product can be downloaded from http://www.tropomi.eu/data-products/aerosol-layer-height (last access: 15 July 2022; ESA 2022); Satellite imagery captured by NOAA-20 VIIRS can be downloaded from https://worldview.earthdata.nasa.gov/ (last access: 15 July 2022; NASA 2022); AERONET data can be downloaded from http://aeronet.gsfc.nasa.gov/ (last access: 15 June 2022); Fire radiative power data can be downloaded from https://firms.modaps.eosdis.nasa.gov/ (last access: 15 June 2022), and PSL wind data can be downloaded from ftp://ftp1.psl.noaa.gov/psd2/data/realtime/Radar915/ (last access: 15 June 2022).

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