Airborne measurements and emission estimates of greenhouse gases and other trace constituents from the 2013 California Yosemite Rim wildfire

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ABSTRACT

This paper presents airborne measurements of multiple atmospheric trace constituents including greenhouse gases (such as CO₂, CH₄, O₃) and biomass burning tracers (such as CO, CH₃CN) downwind of an exceptionally large wildfire. In summer 2013, the Rim wildfire, ignited just west of the Yosemite National Park, California, and burned over 250,000 acres of the forest during the 2-month period (17 August to 24 October) before it was extinguished. The Rim wildfire plume was intercepted by flights carried out by the NASA Ames Alpha Jet Atmospheric eXperiment (AJAX) on 29 August and the NASA DC-8, as part of SEAC⁴RS (Studies of Emissions, Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys), on 26 and 27 August during its intense, primary burning period. AJAX revisited the wildfire on 10 September when the conditions were increasingly smoldering, with slower growth. The more extensive payload of the DC-8 helped to bridge key measurements that were not available as part of AJAX (e. g. CO). Data analyses are presented in terms of emission ratios (ER), emission factors (EF) and combustion efficiency and are compared with previous wildfire studies. ERs were 8.0 ppb CH₄ (ppm CO₂)⁻¹ on 26 August, 6.5 ppb CH₄ (ppm CO₂)⁻¹ on 29 August and 18.3 ppb CH₄ (ppm CO₂)⁻¹ on 10 September 2013. The increase in CH₄ ER from 6.5-8.0 ppb CH₄ (ppm CO₂)⁻¹ during the primary burning period to 18.3 ppb CH₄ (ppm CO₂)⁻¹ during the fire's slower growth period likely indicates enhanced CH₄ emissions from increased smoldering combustion relative to flaming combustion. Given the magnitude of the Rim wildfire, the impacts it had on regional air quality and the limited sampling of wildfire emissions in the western United

States to date, this study provides a valuable dataset to support forestry and regional air quality management, including observations of ERs of a wide number of species from the Rim wildfire.

1. INTRODUCTION

Emissions from biomass burning (defined here as the open burning of biomass, including wildfires, prescribed fires and agricultural fires) are an important source of a wide range of trace gases and particles that can impact local, regional and global air quality, climate forcing, biogeochemical cycles and human health (Crutzen and Andreae, 1990; Bein et al., 2008; Pfister et al., 2008; Aurell et al., 2013). Biomass burning emissions are one of the primary causes for the annual variability in growth rates of several trace gases, including carbon dioxide (CO₂) and methane (CH₄) (Langenfelds et al., 2002; Simpson et al., 2006). Because of the importance of these emissions and the projected increases in wildfire activity in many regions due to climate change and fuel management strategies (Fried et al., 2004; Westerling et al., 2006; Yue et al., 2013; Hurteau et al., 2014), measurements of emissions from wildfires are crucial to a better understanding of how biomass burning influences and interacts with the Earth system.

United States (US) temperate biomass burning carbon emissions are relatively small (about 0.5 %) compared to total global emissions (van der Werf et al., 2010). However, such burns have the potential to significantly impact local and regional air quality (Sapkota et al., 2005; Singh et al., 2012). Long range transport of biomass burning emissions can cause air quality standards to be exceeded hundreds and thousands of kilometers downwind of the fire source (Jaffe et al., 2013; Wigder et al., 2013; Real et al., 2007; Sapkota et al., 2005).

In the US, wildland fires can be divided into two categories: prescribed fires and wildfires (Urbanski, 2013). Prescribed fires are ignited by land management programs to reduce wildfire hazards, improve wildlife habitats and increase access (Dale, 2006). The majority of prescribed burns in the western US occur outside of the wildfire season (June-September) (Urbanski, 2013). In the western US, wildfires dominate over prescribed fires, accounting for 85 % of the burned area between 2002-2010 (NIFC, 2015). The majority of wildfires occur when the “Fire Danger” is at high levels and when forest floor moisture is at a minimum (Deeming et al., 1978). Western wildfires typically occur under conditions that result in the consumption of fuels (large dead woody debris, duff, and tree canopy) that are not normally burned in prescribed fires. This could result in different emissions from wildfires compared to prescribed fires as noted by Urbanski (2013).

The extent to which wildfires contribute to atmospheric trace gas budgets is uncertain and varies intra- and inter-seasonally due to the unique and episodic nature of wildfires. Measured trace gas concentrations vary due to degree of dilution and mixing with other air masses, fuel type and condition, meteorological conditions, the fire combustion processes and location and distance from the fire where the data are collected due to chemistry and aging (Jaffe et al., 2013; Trentmann et al., 2003; Reid et al., 2005; Real et al., 2007; Yokelson et al., 2013).

Typically wildfire emissions are expressed as enhancement ratios (ERs) or emission factors (EFs) and modified combustion efficiency ($MCE = \Delta CO_2 / (\Delta CO_2 + \Delta CO)$). ERs are estimated by first calculating the excess mixing ratio of a trace gas, X, compared to its average background value ($\Delta X = X_{plume} - X_{bkgd}$). Figure 1 shows background mixing ratios for a large number of trace constituents measured over the U. S. by the NASA DC-8. Background mixing ratios are determined by using a CO filter (lowest quartile) that removed most pollution influences. ΔX is then divided by the excess mixing ratio of a reference gas (RG), typically carbon monoxide (CO) or CO_2 (Andreae and Merlet, 2001), see Equation 1. The ER is the slope of $\Delta X / \Delta RG$, while forcing the intercept through zero (since the background concentration is typically well known and variability in the plume can affect the intercept if it is not forced) (Yokelson et al., 1999; Akagi et al., 2012). The emission factor, EF, quantifies the amount of trace gas, X, emitted per kilogram of biomass burned and can be calculated using the carbon mass balance technique described by Yokelson et al. (1999). MCE characterizes the relative amounts of flaming and smoldering combustion within a fire. MCE ranges from 0.65-0.99, but is typically near 0.80 for smoldering, while pure flaming combustion has an MCE of 0.99. An overall MCE of 0.90 suggests roughly equal flaming and smoldering combustion (Akagi et al., 2011).

$$ER = \frac{(X_{plume} - X_{bkgd})}{(RG_{plume} - RG_{bkgd})} \quad (1)$$

ERs, EFs and MCE are essential parameters for atmospheric chemical transport models used to understand and predict the impacts of wildfire emissions. However, in the western US, emission estimates rely largely on measurements from prescribed fires, which may not be a suitable proxy for wildfire emissions. There is currently limited information on emissions from wildfires occurring in the western US during the wildfire season (Urbanski, 2013).

86

87 Figure 1. Measured mean U.S. background mixing ratios of selected trace gases as measured by the DC-8
 88 during SEAC⁴RS. Background mixing ratios correspond to the lowest quartile of CO. Mixing ratios are in
 89 units of ppm for CO₂, ppb for CH₄, CO and O₃, and ppt for all other species.

90 This paper presents airborne in situ measurements of greenhouse gases (CO₂, CH₄ and ozone (O₃)),
 91 biomass burning tracers (CO and acetonitrile (CH₃CN)), and other constituents downwind of the
 92 exceptionally large Rim wildfire. The Rim wildfire started from an illegal campfire that burned out of
 93 control on 17 August 2013, about 13 km east of Groveland, California. Over the next several weeks and
 94 months it moved eastward burning a total of 257,134 acres of brush, oaks, and pine conifer stands in
 95 steep, rugged terrain (elevation ranges from <500 to >2000 m above sea level (m.a.s.l)) within the
 96 Stanislaus National Forest and into Yosemite National Park (37.86° N, 120.09° W). Airborne data from four
 97 flights that sampled emissions from the Rim wildfire are discussed. Three flights sampled downwind of the
 98 Rim wildfire during its intense, primary burning period; one by the Alpha Jet Atmospheric eXperiment
 99 (AJAX) on 29 August, and two by the NASA DC-8, as part of the Studies of Emissions and Atmospheric

Composition, Clouds, and Climate Coupling by Regional Surveys (SEAC⁴RS) mission, which sampled mixed smoke from a number of fires throughout the Western US on 26 and 27 August. Another AJAX flight on 10 September sampled emissions from the fire during its increased smoldering, slower growth period.

2. EXPERIMENTAL APPROACH

The two AJAX flights measured in situ CO₂, CH₄ and O₃ mixing ratios. CO₂ and CH₄ were measured using cavity ring-down spectroscopy (Picarro, Inc., model 2301-m), an instrument widely described in the literature (Chen et al., 2010; Tanaka et al., 2012; Karion et al., 2013; Tadić et al., 2014). Raw data was processed by multiplying by the calibration factors, determined from NOAA whole air standards, traceable to the WMO scale, and by application of the water vapor corrections provided by Chen et al. (2010) to calculate the dry mixing ratios of CO₂ and CH₄. Data were also filtered to remove spikes in the data as a result of varying instrument cell cavity pressure and data were averaged and reported at 3 second intervals. The overall uncertainty is determined to be 0.14 ppm for CO₂ and 2.8 ppb for CH₄. O₃ is measured by ultraviolet (UV) absorption (2B Technologies Inc., model 205). Raw data is multiplied by the calibration factors, determined from an O₃ calibration source (2B Technologies, model 306) referenced to the NIST scale. Data is averaged and reported at 10 second intervals with an overall uncertainty of the airborne O₃ measurements estimated at 3.0 ppbv.

SEAC⁴RS was a NASA led airborne mission during summer of 2013 over the continental US (<https://espo.nasa.gov/missions/seac4rs>). Among its many objectives was to investigate the influence of biomass burning emissions, and their interactions with urban pollution, on regional air quality and climate. The main airborne platform for this objective was the NASA DC-8 aircraft equipped with 28 in-situ and remote sensing instruments to measure greenhouse gases, O₃ precursors and oxidation products, reactive nitrogen, and aerosol composition and physical/optical properties, and several unique tracers of pollution with high sensitivity. Toon et al. (2015) present details of the SEAC⁴RS mission, including instrumentation, in an overview paper. The same platform, similarly equipped (Jacob et al., 2010) has been previously used to investigate fire emissions resulting from Boreal fires during ARCTAS (e.g. Singh et al., 2010; Simpson et al., 2011; Hecobian et al., 2011). The DC-8 observations complement those measured from AJAX by filling gaps with additional trace gas species that could not be measured by AJAX. Although the DC-8 sampled many wildfires and agricultural fires, here we will limit our study to the Rim wildfire investigations on 26 and 27 August 2013. The complete data sets are available at <http://www-air.larc.nasa.gov/cgi-bin/ArcView/seac4rs?MERGE=1>. Additional studies of the Rim Fire during the SEAC⁴RS flights are presented by Peterson et al. (2014), Saide et al. (2015) and Forrister et al. (2015). The following references

provide further information on SEAC⁴RS measurements of CO (Sachse et al., 1987), CH₄, C₆H₆, C₇H₈ (Simpson et al., 2011), CO₂ (Vay et al., 2003) CH₃CN, CH₃OH, CH₃COCH₃ (Wisthaler et al., 2002), O₃, NO_x (Weinheimer et al., 1994), PAN (Huey, 2007), NO₃ (Dibb et al., 2003), BC (Moteki and Kondo, 2007), SO₄ and OA (DeCarlo et al., 2006).

SEAC⁴RS flight data were filtered to focus primarily on emissions from the Rim wildfire. Firstly data was segregated by geographical location (37.8-44° N, 102-120° W, altitude <8 km) and secondly filtered based on $\Delta\text{CH}_3\text{CN}$ values ($\Delta\text{CH}_3\text{CN} > 0.2$ ppb). Given that $\Delta\text{CH}_3\text{CN}$ is a preferred tracer of biomass burning as its relative enhancement ($\Delta\text{CH}_3\text{CN}/\Delta\text{CO}$) is nearly independent of combustion efficiency (Singh et al., 2012; Hornbrook et al., 2011), this filter, combined with the geographic filter, selects the data from primarily the Rim wildfire smoke plume. The section of the SEAC⁴RS flight tracks used in this analysis is shown in Figure 7.

3. RESULTS

Within the first few weeks after the Rim fire ignited, fire activity was generally high to extreme (National Fire and Aviation Management Web Applications, FAMWEB, 2014). After 8 September 2013, fire progression remained below 1,500 acres per day as the fire was gradually contained (Inciweb, 2013), with 100 % containment achieved on 24 October 2013. Figure 2 shows the progression and activity of the Rim Fire and timing of the airborne measurement flights.

Figure 2. Time series of total acres burned and 24-hour change in acres burned based from daily fire reports (adapted from <http://inciweb.nwcg.gov/incident/3660/>). Timings of the AJAX and SEAC⁴RS flights are shown as dashed lines.

3.1 INTENSE BURNING (26 – 29 August 2013)

Three flights measured emissions from the Rim wildfire during its intense, primary burning period. The first two flights were on 26 and 27 August 2013 by the NASA DC-8 aircraft followed by an AJAX flight on 29 August 2013. During all three flights, the main smoke plume from the Rim wildfire was transported by southwesterly winds impacting regions to the north and northeast including Lake Tahoe, northern Sierra Nevada mountain communities, and northern Nevada. Some smoke detrained at lower altitudes and settled into near-by valleys, as shown in Figure 3. Air quality maps reported highly elevated values of particulate matter (PM 2.5) to the north and northeast of the fire (AirNow, 2013), see Figure S1.

Figure 3. Photograph of the main smoke plume and low altitude smoke plume (valley haze) in Bear Valley (38.367° N, 120.170° W) taken in-flight on 29 August 2013.

The extent and progression of the smoke plume was analyzed using the California State University Mobile Atmospheric Profiling System (CSU-MAPS) (Clements and Oliphant, 2014). The mobile profiling system is mounted on a truck and includes a scanning Doppler Lidar (Halo Photonics, Ltd., Streamline 75) and

166 radiosonde system (GRAW Radiosondes GmbH & Co. KG, model GS-E). On 29 August 2013, the CSU-MAPS
167 was operated from Donnell Vista (38.342° N, 119.925° W, elevation 1921 m.a.s.l), just north of the main
168 fire exclusion zone and within 0.5 km of the AJAX flight path.

169 The Lidar provided information on the dynamics and progression of the Rim wildfire plume. Three distinct
170 layers were observed in the attenuated backscatter coefficient and vertical velocities (shown in Figure 4).
171 The local convective boundary layer extended from the surface to 3000 m.a.s.l (also evident in radiosonde
172 data, see Figure S2) and was rich in smoke from the Rim wildfire. The 3000 to 4000 m.a.s.l layer was also
173 rich in smoke, likely representing smoke injected to greater heights caused by overshooting of the fire
174 plume beyond the depth of the convective boundary layer. Above 4000 m.a.s.l the dry, free-troposphere is
175 devoid of backscatter.

176 The flights targeting the Rim wildfire plume on 26, 27 and 29 August 2013 all took place in the afternoon,
177 at a time when the concentrated plume within the boundary layer was starting to dissipate. During the
178 time of the AJAX flight the boundary layer smoke plume was less dense than an hour prior, and smoke is
179 at all levels below 4000 m.a.s.l (see vertical line in Figure 4 for timing of the AJAX flight).

180
181 Figure 4. Lidar profiles of a) attenuated backscatter coefficient ($\text{m}^{-1} \text{sr}^{-1}$) and b) vertical velocity (m s^{-1})
182 taken at Donnell Vista, CA (38.342° N, 119.925° W) on 29 August 2013. The black vertical line represents
183 the time that the AJAX flight sampled the main smoke plume from the Rim wildfire (Local time = UTC – 7
184 hours). Height is meters above sea level (m.a.s.l).

185

186 Figure 5. Time series plots of CO_2 , CH_4 , O_3 and altitude from the AJAX flight on 29 August 2013 (Local time
187 = UTC – 7 hours). Trace gas enhancements from background values (ΔCO_2 , ΔCH_4 , ΔO_3) are plotted as red
188 dashed lines. Black dashed lines represent the region used to define background trace gas values.

189 For each flight, trace gas enhancements (e.g. ΔCO_2 , ΔCH_4 , ΔO_3) were calculated based on subtracting the
190 average background value for each species from the measured mixing ratios (e.g. $\Delta X = X - X_{\text{bkgd}}$). For
191 AJAX data the background is defined as an upwind section of the flight. For example, on 29 August 2013
192 background is calculated from the average mixing ratios observed in transects above the smoke plume;
193 see Figure 5 (background average CO_2 : 393.48 ± 0.38 ppm, CH_4 : 1845 ± 5 ppb, O_3 : 49 ± 8 ppb). To estimate
194 sensitivity associated with determining background mixing ratios, the time period used to calculate the
195 background was altered resulting in negligible effects (within the 1σ deviation), providing realistic time
196 periods are used. For SEAC⁴RS data the background was calculated from the average backgrounds shown
197 in Figure 1.

198 Large deviations from background values were observed in-flight for many trace gas species. For example,
199 notable values of ΔCO_2 , ΔCH_4 and ΔO_3 during the 29 August 2013 AJAX flight occur in four instances (see
200 Figure 5): Within the San Joaquin Valley (SVJ) boundary layer (< 2000 m.a.s.l. at 21:30 UTC, located upwind
201 of the wildfire), the main smoke plume encounter (22:16 UTC, 4400 m.a.s.l.), sampling above the foothills
202 upwind of the wildfire (22:25 UTC, 3100 m.a.s.l.) and sampling the smoke-filled valley haze (22:37 UTC,
203 2100-3700 m.a.s.l.). ΔCO_2 in the SVJ boundary layer is depleted compared background, consistent with

uptake by the biosphere. In contrast, ΔCH_4 within the SJV boundary layer is enhanced due to local, surface-based sources in the region. Above the Sierra Nevada foothills upwind (southwest) of the fire ΔCO_2 is slightly depleted and ΔCH_4 significantly depleted, consistent with biospheric uptake and limited local CH_4 emissions in this region. Large enhancements were observed when sampling the main smoke plume (maximum ΔCO_2 : 41.14 ppm, maximum ΔCH_4 : 312 ppb, maximum ΔO_3 : 105 ppb, mean altitude: 4.4 km a.s.l) and within the smoke-filled valley haze (maximum ΔCO_2 : 13.29 ppm, maximum ΔCH_4 : 140 ppb, maximum ΔO_3 : 38 ppb, mean altitude: 2.4 km a.s.l).

While sampling the Rim wildfire smoke plume, AJAX is limited to sampling only the top of the plume (~ 4.4 km), as the aircraft cannot descend to deep within the plume. When AJAX overflowed the Lidar (which observed smoke to 4 km a.s.l), AJAX reported CO_2 , CH_4 and O_3 mixing ratios at 4.4 km a.s.l close to background values, consistent with the Lidar observations that the smoke was not impacting higher altitudes over the measurement site. The main Rim wildfire plume captured by AJAX was located ~6 km to the SE from the Lidar site at 4.4 km. Variation in plume height between the two sites is likely given the complex local topography and the changing plume dynamics. The Lidar data confirms that when AJAX samples the top of the smoke plume it is sampling smoke which has overshoot the boundary layer and is not sampling the boundary layer itself.

AJAX observed large enhancements in ΔO_3 at the top of the Rim wildfire plume on 29 August 2013 (maximum ΔO_3 : 105 ppb). Enhanced O_3 was not reported at near-by surface sites (e.g. Yosemite national park (Turtleback Dome, CA) and Reno/Sparks (NV)), even though these surface sites were impacted by the wildfire plume, indicated by high $\text{PM}_{2.5}$ levels (see Figure S1). ΔO_3 observations from a nearby valley (valley haze, Figure 5) confirm less ΔO_3 within the valley boundary layer (and further from the main fire activity (maximum ΔO_3 : 38 ppb)). Previous studies of O_3 formation within wildfire plumes show varying rates of production, from O_3 depletion to substantial amounts (e.g. Bein et al. 2008; Pfister et al. 2008; Jaffe and Widger 2012; Singh et al. 2012). In this case, AJAX data shows significant O_3 formation within the upper layers of the Rim wildfire smoke plume.

The estimated age of the smoke plume (time since emission) can be calculated by dividing the distance of the smoke downwind of the fire by the average wind speed at the altitude the smoke is sampled; see Equation 2 (Agaki et al., 2013). We estimate the AJAX measurements of the main plume were ~1.2 hours downwind of the Rim wildfire (~50 km from the center of the Rim wildfire, average wind speed at 4 km a.s.l was 11.8 m/s). Previous work has reported an immediate decrease in O_3 at the source of the fire due to rapid reaction of background O_3 with high levels of NO within the fire plume (Evans et al., 1974; Agaki

et al., 2013). O₃ levels can rebound within the plume rapidly, as little as 0.5 hours after downwind (Agaki et al., 2013), with a peak in O₃ being reached within ~1 hour (Packham and Vines, 1978). AJAX O₃ measurements occur within the window of rapid O₃ formation and support evidence presented in prior work.

$$\text{Time since emission} = \text{sample distance from source (m)} / \text{average wind speed } \left(\frac{\text{m}}{\text{s}}\right) \quad (2)$$

Comparing the main plume of the Rim wildfire with the smoke-filled valley haze highlights the markedly different conditions at each location. The main smoke plume overshoot the top of the boundary layer and at 4.4 km a.s.l encountered an average wind speed of 14.7 m/s and direction of ~197°, whereas low-altitude smoke, at 2.1 km a.s.l within the boundary layer at Bear Valley (38.367° N, 120.170° W) encounters an the average wind speed of 5.2 m/s and direction of ~239°. The main plume and valley haze also differ in their compositions; for example ER's were 2.0 ppb O₃ (ppm CO₂)⁻¹ and 6.7 ppb CH₄ (ppm CO₂)⁻¹ within the main smoke plume, compared to 2.7 ppb O₃ (ppm CO₂)⁻¹ and 8.7 ppb CH₄ (ppm CO₂)⁻¹ within the valley haze. Although ER's for ΔO₃ and ΔCH₄ (relative to ΔCO₂) are higher within the valley, the overall, absolute values of ΔO₃, ΔCH₄ and ΔCO₂ are less within the valley haze compared to the main plume. Differences in smoke constituents within the two locations may be because smoke sampled within the valley is within the boundary layer. Lidar observations indicate that the boundary layer contains a more concentrated plume than what overshoots the top of the boundary layer and is sampled as the main plume by the AJAX flight (see Figure 4). Smoke within the valley may also be more aged with respect to the main plume as wind speeds within the valley are reduced compared to aloft, meaning dispersion will be slower, or the valley haze may be more representative of more smoldering combustion (with minimal plume rise) as opposed to more flaming combustion (and convective plume).

The two SEAC⁴RS flights provide additional context to AJAX data by measuring multiple tracers of biomass burning emissions (e.g. CO, CH₃CN) and chemically reactive species involved in O₃ formation including both PAN (peroxyacetyl nitrate) and NO_x (NO and NO₂). Figure 6 shows the complex relationships between ΔCH₃CN and the ERs (relative to ΔCO) of key species involved in O₃ formation. Fresh wildfire plumes (indicated by higher ΔCH₃CN mixing ratios) contain negligible enhancements of ΔO₃ and ΔPAN and higher levels of ΔNO_x. As plumes age the moderate-high levels of ΔNO_x are depleted in association with O₃ and PAN formation. The average ERs observed by SEAC⁴RS are 0.01 for ΔO₃/ΔCO (ppb/ppb), 2.6 for ΔPAN/ΔCO (ppt/ppb) and 3.8 for ΔNO_x/ΔCO (ppt/ppb), and are similar to values reported by Singh et al. (2012). The enhancements represent some aging of the plume from the fit-curves shown in Figure 6.

265 Previous studies have reported that O_3 production within wildfire plumes can occur over a range of time
 266 intervals, with O_3 production being more rapid in warmer environments, for example Hobbs et al. (2003)
 267 observed ΔO_3 of 98 ppb in less than 30 minutes of aging in South African biomass burning plumes.
 268 SEAC⁴RS flights sampled fresh Rim wildfire emissions on 26 August 2013 and aged emissions on 27 August
 269 2013. SEAC⁴RS observed elevated ΔO_3 close to the source (maximum ΔO_3 of 100 ppb) which remained
 270 elevated ($\Delta O_3 > 40$ ppb) to ~100 km downwind (estimated age: 3.6 hours, average altitude ~4 km a.s.l,
 271 average wind speed: 7.6 m/s); see Figure 7. AJAX and SEAC⁴RS flights observed similar O_3 emissions from
 272 the Rim wildfire on different days during the intense, primary burning period, with both flights supporting
 273 the concept of rapid O_3 formation within the Rim wildfire plume.

274
 275 Figure 6. Evolution of key constituents in the Rim wildfire plume during 0-2 day transport time measured
 276 by SEAC⁴RS. Y-axis represents the ratio of $\Delta NO_x/\Delta CO$ (red), $\Delta PAN/\Delta CO$ (blue) and $\Delta O_3/\Delta CO$ (black) and X-
 277 axis shows mixing ratio of CH_3CN (a fire tracer) as an indicator of air mass age from wildfire emissions
 278 measured during SEAC⁴RS (Diskin et al., 2002; Huey et al., 2004; Weinheimer et al., 1994).

Figure 7. Flight paths of: SEAC⁴RS 26/27 August 2013 (37.8-44° N, 102-120° W, altitude <8 km) and AJAX 29 August 2013, data points are colored by ΔO_3 (delta O_3). Co-plotted with MODIS Terra satellite image from 26 August 2013 in GoogleTM Earth.

3.2. INCREASED SMOLDERING (10 September 2013)

During the second AJAX flight on 10 September 2013 the Rim wildfire was 80 % contained and had burned 250,000 acres. The previous night, easterly downslope winds brought smoke from the Rim wildfire to the San Joaquin Valley (SJV). A morning inversion over SJV kept smoke impacts high for the region. Air quality maps report elevated PM 2.5 in a large dispersed area surrounding the fire (AirNow, 2013), see Figure S3. As the day progressed, vertical mixing within the convective boundary layer improved air quality.

The second AJAX flight took place between 14:00 – 16:00 local time (21:00 – 23:00 UTC). The aircraft flew a descending profile over Castle airport, in the SJV, then proceeded to twice circumnavigate the Rim wildfire, sampling an outer and an inner circle. Sharp increases in ΔCO_2 and ΔCH_4 were observed within the SJV boundary layer and within the Rim wildfire smoke encounters, as seen in Figure 8 (O_3 data collection was unsuccessful for this flight).

On 10 September 2013, ΔCH_4 and ΔCO_2 were enhanced within the SJV boundary layer. Smoke from the Rim wildfire influenced the boundary layer and outweighed the effects of biosphere uptake, resulting in increasing ΔCO_2 (in contrast to 29 August 2013). ΔCO_2 values within the SJV boundary layer were a similar

order of magnitude to those observed within the smoke plume (see Figure 8). The maximum ΔCO_2 within the SJV boundary layer (<1 km.a.s.l) is 8.36 ppm, compared to maximum ΔCO_2 within the outer circle smoke encounter of 5.90 ppm, and 9.91 ppm within the inner circle. Maximum ΔCH_4 values for the entire flight were observed within the SJV boundary layer, suggesting that local, surface-based sources were present in addition to the Rim wildfire emissions. Maximum ΔCH_4 within the SJV boundary layer is 334 ppb; within the outer circle smoke encounter it is 119 ppb and 159 ppb within the inner circle smoke plume encounter.

Figure 8. Time series of CO_2 (top), CH_4 (middle) and altitude (bottom) from AJAX flight on 10 September 2013 (local time = UTC – 7 hours). Trace gas enhancements from background values (ΔCO_2 , ΔCH_4) are plotted as red dashed lines. Black dashed lines indicate the region used to define background trace gas values.

3.3 EMISSION MEASUREMENTS

The ER for ΔCH_4 relative to ΔCO_2 is used to compare all four flights (Figure 9). The SEAC⁴RS data has been separated by day of flight. The 26 August 2013 SEAC⁴RS flight and both AJAX flights show strong correlations within the Rim wildfire smoke plumes ($R^2 = 0.84\text{--}0.97$), as all three flights flew within close vicinity of the Rim wildfire, sampling very fresh emissions (within a few hours). The SEAC⁴RS flight on 27

August is less well correlated ($r^2 = 0.33$); this flight sampled aged smoke from the Rim wildfire (up to ~2.3 days old). Dilution as the smoke plume ages as well as the presence of other wildfires impact the emission ratios within aged plumes, reducing the $\Delta\text{CH}_4/\Delta\text{CO}_2$ correlation. Calculated fresh plume CH_4 ER's were 6.5-8.0 ppb CH_4 (ppm CO_2)⁻¹ during the intense, primary burning period (flights on 26 and 29 August 2013). The good agreement between CH_4 ER's during the period between 26 and 29 August 2013 is likely due to a similarity in fire conditions and fuels burned on these days, as well as the proximity of the flights to the emission source. During the increased smoldering period of the Rim wildfire (AJAX flight on 10 September 2013), the CH_4 ER increased to an average of 18.3 ppb CH_4 (ppm CO_2)⁻¹, in close proximity to the emission source. CH_4 ER in the aged smoke was slightly less compared to the fresh plume at 5.7 ppb CH_4 (ppm CO_2)⁻¹ on 27 August 2013.

The change in CH_4 ER within the fresh plume from 6.5-8.0 ppb CH_4 (ppm CO_2)⁻¹ to 18.3 ppb CH_4 (ppm CO_2)⁻¹ implies a change in fire conditions, indicating an increase in smoldering combustion relative to flaming combustion and changes in fuel/materials involved. During the more active fire stages (prior to 5 September 2013) the major fuels involved were categorized by the United States Department of Agriculture (USDA) as fuel model 5 (brush (2 feet)) consisting of brush, oaks and pines, in the later stage of the fire. On 10 September 2013, the major fuels involved were categorized by USDA fuel model 9 (hardwood litter) consisting of pine, fir, conifer stands mixed with patches of brush and open grasses (FAM WEB, 2014). Smoldering combustion is less efficient than flaming combustion, producing more CH_4 per unit mass of fuel consumed than flaming combustion, which would increase the $\Delta\text{CH}_4/\Delta\text{CO}_2$ ratio (Yokelson et al., 2008). This finding is in good agreement with the reported activity of the Rim wildfire shown in Figure 2. The CH_4 ER's reported in this study are in good agreement with those reported by Urbanski (2013) from four wildfire-season fires in mixed conifer forests of the northern Rocky Mountains (USA), who reported CH_4 ER values of 7.4 - 22.0 ppb CH_4 (ppm CO_2)⁻¹.

Figure 9. Relationship between CH₄ and CO₂ enhancements from the Rim wildfire plume measured during flights on 26 August (black) and 27 August (blue, aged smoke), 29 August (green) and 10 September (red) 2013.

3.4 BREIF COMPARISON WITH OTHER STUDIES

Emission factors, EF's, are typically calculated using the carbon mass balance approach (Yokelson et al., 1999) (see Equation 2). The mass fraction of carbon in the fuel, F_c , is assumed to be 500 g kg⁻¹ (reported to be accurate to 10 % (Susott et al., 1996; Yokelson et al., 1999)); MM_x is the molar mass of species, x , ($MM = 12$ for carbon); and ΔC_i is the excess mass carbon in each species, which is calculated using ER's. The total carbon emitted from the fire is estimated using only ΔCO_2 , ΔCO and ΔCH_4 , resulting in an overestimation of EF by ~5 % (Yokelson et al., 1999). EF's for the Rim wildfire were calculated from the SEAC⁴RS flights on 26 and 27 August 2013 for a range of long-lived compounds (See Table 1).

$$EF_x = F_c \times \frac{MM_x}{12} \times \frac{\Delta x}{\Delta C_{CO_2} + \Delta C_{CO} + \Delta C_{CH_4}} \quad (2)$$

Given that CO was not measured during AJAX flights, we use the SEAC⁴RS data to calculate estimated emission factors. The similarity of ERs observed during the primary, intense burning period imply a similarity in fire conditions (see Figure 9). Hence, we assume MCE to be the same on these days and use the median MCE calculated from SEAC⁴RS flight data to calculate EFs for measured CO₂ and CH₄ during the AJAX flight on 29 August 2013. For 10 September 2013 we use MCE of 0.88, reported by Urbanski (2014) to estimate EFs for CO₂ and CH₄ (see Table 1). EFs and MCE calculated for the Rim wildfire compare well to previous studies as shown in Table 1. There are a wide number of variables which alter fire EFs including fire combustion stage, fuel type and condition, meteorological conditions and distance of sample from fire source. Table 1 highlights some of the variety of EFs measured over North America during different measurement campaigns, as well as the complexity in analyzing fire EFs. For example, CH₄ EFs from the Rim wildfire during the primary, intense burning period agree closely with previously reported values from Boreal wildfires (Simpson et al., 2011) and Rocky Mountain wildfires (Urbanski et al., 2013). During the increased smoldering, slower growth period of the Rim wildfire, CH₄ EFs are elevated but not to the same extent as the CH₄ EFs reported from Californian wildfires during ARCTAS-CA. In all cases, Rim wildfire CH₄ EFs are increased relative to those from prescribed fires reported by Burling et al. (2011). Table 1. MCE, ER and EF ($\pm$ 1-sigma uncertainty) of selected species relative to CO from the Rim wildfire compared to previous studies.

	Rim Fire			ARCTAS-CA California biomass burning plumes ^a	ARCTAS Boreal forest fires Simpson et al. (2011)	Rocky Mountains conifer forest fires Urbanski et al. (2013) ^e	Temperate forest fires Akagi et al. (2013) ^f	Prescribed conifer forest understory fires Burling et al. (2011) ^f
	26 Aug-13 Intense	29-Aug-13 Intense	10-Sep-13 Smoldering					
MCE	0.94 ^b	0.94 ^c	0.88 ^d	0.90	0.89	0.85-0.92	0.93	0.94
EF _{CO}	92.5 $\pm$ 16	69.5 $\pm$ 12	138.4 $\pm$ 24	164.1 $\pm$ 28	113 $\pm$ 72	89.3 - 173	79 $\pm$ 19	72 $\pm$ 26
EF _{CO₂}	1675 $\pm$ 285	1711 $\pm$ 292	1595 $\pm$ 272	1572 $\pm$ 268	1616 $\pm$ 180	1527 - 1681	1675 $\pm$ 42	1668 $\pm$ 72
EF _{CH₄}	4.8 $\pm$ 0.8	4.7 $\pm$ 0.8	7.5 $\pm$ 1.3	13.0 $\pm$ 2.2	4.7 $\pm$ 2.9	4.4 - 12.1	2.7 $\pm$ 1.8	3.0 $\pm$ 2.4
EF _{CH₃CN}	0.14 $\pm$ 0.03	-	-	0.31 $\pm$ 0.07	0.30 $\pm$ 0.06	-	0.03 $\pm$ -	-
EF _{C₃H₆O}	0.56 $\pm$ 0.1	-	-	0.85 $\pm$ 0.2	0.37 $\pm$ 0.1	-	0.65 $\pm$ 0.3	-
EF _{CH₃OH}	1.6 $\pm$ 0.4	-	-	1.9 $\pm$ 0.4	1.2 $\pm$ 0.3	-	1.2 $\pm$ 0.5	1.1 $\pm$ 1.0
EF _{C₆H₆}	0.40 $\pm$ 0.07	-	-	0.63 $\pm$ 0.1	0.55 $\pm$ 0.11	-	0.28 $\pm$ 0.4	-
EF _{C₇H₈}	0.26 $\pm$ 0.05	-	-	0.25 $\pm$ 0.04	0.24 $\pm$ 0.06	-	0.20 $\pm$ 0.3	-

^a Data from Californian wildfires observed during ARCTAS-CA DC-8 study calculated based on archived data. (<http://www-air.larc.nasa.gov/cgi-bin/ArcView/arctas>).

^b Median MCE from SEAC⁴RS observations.

^c MCE assumed to be the same as that observed during the SEAC⁴RS flights on 26, 27 August 2013.

374 ^d MCE assumed to be 0.88, as reported for wildfires in northwest US conifer forests fires (Urbanski, 2014).

375 ^e Urbanski et al. (2013) data shows range of values (minimum – maximum).

376 ^f Akagi et al (2013) and Burling et al. (2011) data reported are average airborne EF's.

377 DISCUSSION AND SUMMARY

378 Emissions from the Rim wildfire were sampled by two airborne platforms during the fire's intense, primary
379 burning period (flights on 26, 27 and 29 August 2013) and increased smoldering, slower growth period
380 (flight on 10 September 2013). Trace gases showed considerable variability, with notable deviations from
381 background levels observed within the SJV boundary layer and within the Rim wildfire smoke plume.

382 During the primary burning period, Lidar data shows the vertical extent and progression of the Rim
383 wildfire plume. Emissions from the Rim wildfire were sampled by flights during the afternoon when Lidar
384 data shows that the main, concentrated plume has started to dissipate and mix to higher elevations.
385 During three flights (26, 27 and 29 August 2013), the main smoke plume was transported
386 north/northeastwards. Airborne measurements show large deviations from background levels in many
387 trace gas species when sampling emissions from the Rim wildfire.

388 The three flights during the primary burning period all support the concept of rapid O₃ formation resulting
389 from the Rim wildfire, with ΔO₃ up to 100 ppb (26 August 2012) and 105 ppb (29 August 2013) observed
390 within the upper layers of the smoke plume, within close proximity to the Rim wildfire source. The high
391 ΔO₃ measured aloft were not observed at surface sites in downwind regions impacted by the plume. The
392 AJAX flight observed much higher ΔO₃ in the main plume (aloft) than in a local smoke-filled valley, perhaps
393 indicating that boundary layer measurements of ΔO₃ in smoke affected regions may be more applicable
394 for determining impacts of wildfires on local regions than measurements from the main smoke plume,
395 which can overshoot the boundary layer and be transported large distances as observed in the SEAC⁴RS
396 flights on 26/27 August 2013.

397 The AJAX flight on 10 September 2013 occurred during the Rim wildfire increased smoldering period.
398 Meteorological conditions were markedly different to previous flights. The previous overnight down-slope
399 easterly winds brought the Rim wildfire smoke plume into California's SJV, and daytime stagnant
400 conditions on 10 September 2013 kept smoke impacts high in the region. ΔCO₂ values within the SJV
401 boundary layer were similar in magnitude to those observed within the smoke plume, and ΔCH₄ values
402 were much higher as a result of combined Rim wildfire smoke influence and local CH₄ emissions.

403 In the fresh smoke plume, there was a strong correlation between ΔCH₄ and ΔCO₂. Emission ratios were
404 8.0 ppb CH₄ (ppm CO₂)⁻¹ on 26 August, 6.5 ppb CH₄ (ppm CO₂)⁻¹ on 29 August, and 18.3 ppb CH₄ (ppm CO₂)⁻¹

¹ on 10 September 2013. The increase in CH₄ ER from 6.5-8.0 ppb CH₄ (ppm CO₂)⁻¹ during the 26 and 29 August 2013 period to 18.3 ppb CH₄ (ppm CO₂)⁻¹ on 10 September 2013 likely indicates enhanced CH₄ emissions from increased smoldering combustion relative to flaming combustion on 10 September 2013 and a difference in fire fuel types. The wide range in CH₄ ER in fresh plumes from the Rim Fire on the different flight days represents the unique and variable nature of a wildfire plume during the fire's lifetime and progression.

Characterization of wildfire emissions is crucial for understanding atmospheric trace gas budgets and variability. The quality of these characterizations depends on accurate observations associated with fuel type, meteorological conditions and fire combustion burn cycle. Observations are key in validating forward model predictions of trace gas emissions (including greenhouse gases), transport, chemistry, and plume injection heights associated with the wildfires. This study provides a set of wildfire ERs and EFs taken close to the emission source of an extremely large wildfire during a prolonged drought. These observations coupled with wildfire emission inventories, estimates of fossil fuel emissions and background concentrations could be used to determine contributions of the Rim wildfire emissions to trace gas budgets by the use of inverse modeling.

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