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The Oxygen to Carbon Dioxide Ratios observed in Emissions from a Wildfire in Northern California

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Abstract. At Trinidad, California we observed elevated CO_2 concentrations and concomitant lowered O_2 levels coincident with forest fires 70 km distant (from 10/8/99 to 10/21/99). The precision of our O_2 data, ± 1 μmol O_2 /mol dry air, revealed the reduction of atmospheric oxygen resulting from the combustion of biomass, and the stoichiometric ratios ($-O_2/CO_2$) of the wildfire emissions. Estimates of daily $-O_2/CO_2$ ratios were obtained by regression of CO_2 against corresponding O_2 data (R^2 0.86 to 0.96). Daily $-O_2/CO_2$ ratios changed from 1.15 to 1.41 on a particularly smoky day that coincided with elevated levels of CH_4 and increased CH_4/CO_2 ratios. The change to a higher ratio during smoky conditions illustrates the association between changing emissions and $-O_2/CO_2$ ratios, possibly due to changing wildfire dynamics.

1. Introduction

Biomass burning is a major source of trace gases and particulates that effect the chemistry and radiative balance of our atmosphere. Fires contribute a significant fraction of the global greenhouse gas emissions of CO_2 and CH_4, with an uncertainty much larger than that of industrial emissions (*Andrea,* 1990; *Crutzen and Andrea,* 1990; *Houghton*, 1999). Biomass burning is also a principal source of reactive gases, (CO, NMHCs and NOx), that account for a significant amount of global tropospheric ozone (O_3) (*Andrea*, 1991; *Yokelson* et al., 1999) and soot and organic aerosols that absorb radiation and effect the global energy balance (*Penner* et al., 1998).

A significant fraction of wildfire emissions are incompletely oxidized products of fuel wood distillation and pyrolysis, including formaldehyde, methanol and oxygenated organic compounds that play a critical role in O_3 production, and hence can significantly impact regional air quality (*Yokelson* et al.,1996; 1999; *Prather and Jacob*, 1997). Emissions depend on the extent of wood pyrolysis as well as combustion dynamics (*Lobert and Warnatz*, 1993; *Yokelson* et al., 1996). In light of the critical role of oxygenated hydrocarbons in atmospheric chemistry it is essential to understand the factors controlling the combustion dynamics responsible for changes in pyrolysis emission products, and to be able to characterize these combustion dynamics over large spatial scales.

The amount of oxygen consumed during biomass burning is a fundamental characteristic of the combustion process. Previously, measurements of O_2 consumption in fires have been made in the heterogeneous region near the combustion source, typically with a precision of 0.5% O_2 mole fraction of air (*Radke* et al., 1991; *Sussot* et al., 1991). Until now, O_2 measurement precision has limited the ability to detect large-scale, or fire-wide, observations of oxygen consumption. Here, we report precise in situ measurements of O_2 and CO_2 in air that could provide a unique tool to help quantify emissions from biomass burning on a fire-wide scale. At a remote measurement facility located on a coastal outcrop at Trinidad Head, CA we continuously monitor atmospheric O_2 and CO_2 variations with measurement precision for O_2 of 1 μmol/mole of dry air (0.0001%) and for CO_2 of 0.1 μmol/mole of dry air. In October 1999 measurements at Trinidad Head included emissions from extensive wildfires in the mountains east of the site. The largest of the fires, (Big Bar complex) was centered 50 km NW of Weaverville CA, 70 km due east of our laboratory. The fire burned in a mostly conifer forest consisting of white, red, and Douglas fir; minor amounts of incense cedar, and sugar, ponderosa, and knobcone pine; and hardwood species including huckleberry oak, chinquapin, live oak, tanoak and madrone (*B. Jones*, pers. com., Six Rivers Natl. Forest). The fires, begun by multiple lightning strikes on August 25, had consumed 41,700 Ha by October 8th. From October 8-21 there were 7 days when our observations were characterized by diurnal variations in CO_2 from ~370 ppm associated with clean marine air to >400 ppm as winds shifted to inland sources. Smoke and haze from the burning fires reduced visibility over a wide area from the fires to offshore, and were clearly visible from space as shown in "SeaWiFS" satellite photos[1]. Back trajectory analyses provided by NOAA[2] verified the transport of air from the fires' location. The absence of large metropolitan areas near the site, the prevailing wind direction, and the local meteorology provided a unique opportunity to analyze the reduction in O_2 accompanying the increased CO_2 levels from the fires burning east of the station.

2. Instrumentation

Air was collected from a 19m tall U.S.C.G. radio tower located on Trinidad Head, 41.05° N, 124.15° W (ground level elevation 120m) at 140 ml min^{-1} with a diaphragm pump (Neuberger NO5T). The air was dried with cold traps of 4°C and then -95°C. The CO_2 concentration of the air was determined with a modified LICOR model 6251 CO_2 analyzer. The O_2 concentration of the air was determined using a Servomex oxygen transducer cell (PM1155B) housed in a temperature and

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[1](seawifs.gsfc.nasa.gov/SEAWIFS/TEACHERS/ATMOSPHERE/China_America_smoke.html).
[2] (http://www.arl.noaa.gov/ready/hysplit4.html).

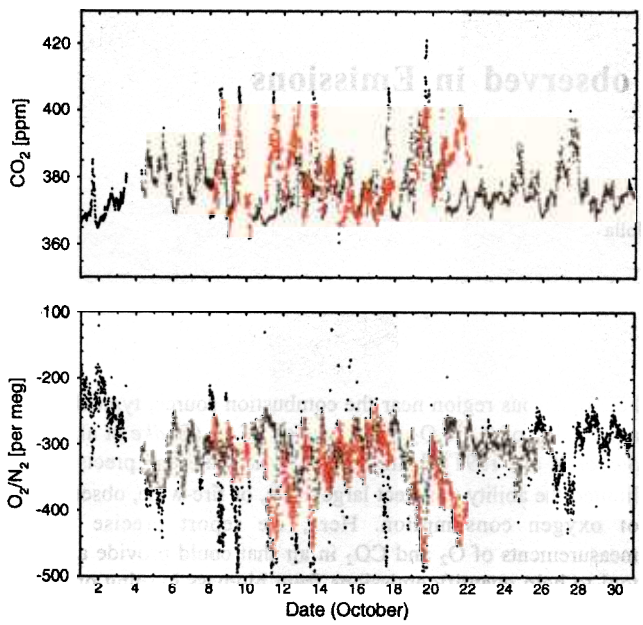

Figure 1. CO_2 and O_2/N_2 ratios observed during October 1999 (red) and Oct. 2000 (black). Elevated CO_2 and reduced O_2/N_2 ratios in 1999 correspond to fires burning 70 km east of the station.

motion stabilized environment. The oxygen sensor utilizes the paramagnetic properties of O_2 by passing the air through a magnetic field to create a pressure gradient, resulting in an electric current that varies linearly with the magnetic susceptibility of the air, primarily due to the concentration of oxygen (see *Manning* et al., 1999). While NO is also a component of the magnetic susceptibility of the air, its concentration is negligible compared to O_2.

Atmospheric O_2 is reported as the difference in the ratio of O_2/N_2 measured against an arbitrary reference, and expressed in per meg units (*Keeling* et al., 1998)[3].

$$\delta(O_2/N_2)\ (\text{per meg}) = [(O_2/N_2)_{sample} / (O_2/N_2)_{reference} - 1] \times 10^6$$

To report paramagnetic analyzer O_2 data as O_2/N_2 ratio, the data have been adjusted for dilution from changes in mole fraction of CO_2 (X_{CO2})[4]

The continuous analyzer at Trinidad Head is calibrated against compressed gases measured at the Scripps Institution of Oceanography, traceable to global O_2 and CO_2 measurement programs (*Keeling* et al., 1998). The instruments' response to the full range of concentration, referred to as the "span", is calibrated daily with high and low span gases. The working gas is analyzed with the span gases, and then compared with the air every 40 minutes. We report 4 minute averages with std. errors typically 2 per meg for O_2 and 0.06 ppm for CO_2. The daily precision of the instruments is given by the reproducibility of the daily working gas analyses, typical std. dev. 0.07 ppm and 4 per meg for CO_2 and O_2, respectively.

[3] In these units, addition of 1 µmol of O_2 to 1 mole of dry air will result in an increase of 1/0.20946 = 4.8 per meg (0.20946 is the mole fraction of O_2 in dry air (X_{O2})).

[4] Changes in concentration of other atmospheric species are too small to have a significant effect on O_2/N_2 ratio. For example, a CO emission value 20% of CO_2 would decrease calculated $-O_2:CO_2$ by only 0.02.

3. Results and Discussion

We compare observations influenced by wildfires to normal, or non-fire conditions observed the following year in Figure 1. An irregular diurnal cycle with elevated CO_2 and reduced O_2 at night is seen, resulting from the land breeze – sea breeze wind pattern at the coastal site. The diurnal cycles may also be influenced to a lesser extent by air-sea exchange of O_2 and CO_2, and by fossil fuel combustion. Regression of the fluctuations of O_2 versus CO_2 yields a fairly consistent ratio of 1.13 ± 0.03, characteristic of respiration processes of land plants and soils (*Severinghaus*, 1995).

During the wildfires, similar diurnal cycles are seen, although the amplitude on most days is somewhat larger than seen the following year. The $-O_2:CO_2$ ratios during the fire were generally higher, and on Oct. 19 were noticeably higher. In all cases, the changes in O_2 and CO_2 were found to be well correlated (R^2 values 0.86-0.96). O_2, X_{CO2} and regressed $-O_2:CO_2$ ratios are shown in Figure 2.

According to elemental fuel analyses, a ratio of about 1.05 would result from combustion of forest biomass if all the carbon were fully oxidized to CO_2[5]. Typically, CO accounts for 10% of the emissions from biomass burning (*Crutzen and Andrea*, 1990; *Hegg* et al., 1990; *Cofer* et al., 1998). Adjusting the full combustion ratio for 10% C emissions as CO results in a ratio of 1.11, indistinguishable from the ratio due to respiration processes. Several of the $-O_2:CO_2$ ratios observed during the fires, summarized in Table 1, are higher than 1.1, even though the background levels (380 ppm) are consistent, suggesting emissions of CO and other compounds more oxidized than the

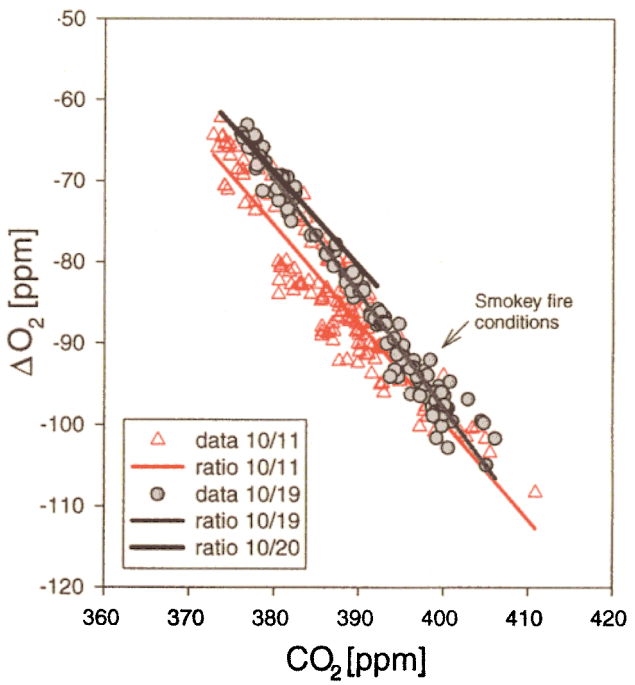

Figure 2. Changes in atmospheric O_2 vs. changes in CO_2 observed on 10/11 and 10/19. O_2 changes expressed in units equivalent to CO_2, i.e. ppm = (per meg / 4.8).

[5] Analysis of selected North Pacific wood fuels by *Tillman* et al., 1981, p.41.

Table 1. Regressions of O_2 (departure from background) vs. X_{CO2} and resulting emission ratios for $-O_2:CO_2$. The fit O_2 concentrations at X_{CO2} = 380 ppm are compared to values for non-fire conditions from 10/2000. 380 ppm was chosen as a typical value for inland air during non-fire conditions (see Figure 1).

Date	$-O_2:CO_2$	Std. Error	R^2	O_2 at 380 ppm CO_2
1999				-73
1999				-75
1999				-71
1999				-69
1999				-70
1999				-69
17 Oct. 2000	1.16	0.014	0.98	-69
18 Oct. 2000	1.11	0.023	0.95	-68
19 Oct. 2000	1.16	0.021	0.96	-67
20 Oct. 2000	1.13	0.023	0.95	-67

fuels contributed to the observed ratios[6]. The highest observed ratio, 1.41, is equivalent to CO release equal to 31% of the CO_2 emitted during combustion (neglecting release of other oxidized compounds and of oxygen from the fuels or water due to pyrolysis). Similar CO emissions have been measured in laboratory studies of smoldering combustion of fuels from pine forest floor (*Yokelson* et al., 1997).

The highest ratio (Oct. 19) coincided with elevated CH_4 measured at Trinidad Head by the Advanced Global Atmospheric Gases program (AGAGE) (*Prinn* et al., 1999). CH_4 emissions are associated with smoldering combustion hence the covariance with $-O_2:CO_2$ ratio suggests enhanced emissions of partially oxidized combustion products. CH_4 levels began to rise on 10/18 as an atmospheric inversion caused severely decreased visibility that interrupted aerial fire fighting. The increased level of smoke and ash fall was noted at the Trinidad Head facility (*Wendy Snible*, pers. com, 1999). On 10/20 the observed $-O_2:CO_2$ ratio and CH_4 levels observed at Trinidad Head reverted to lower values, although CH_4 emissions remained above background levels until 10/24[7]. $CH_4:CO_2$ emissions ratios calculated for 10/19 and 10/20 were 0.33 ± 0.05% and 0.14 ± 0.02% respectively (Figure 3). The CH_4/CO_2 emission ratios observed at Trinidad head were somewhat lower than recent results from wildfire plume measurements (*Yokelson* et al., 1999; *Cofer* et al., 1998).

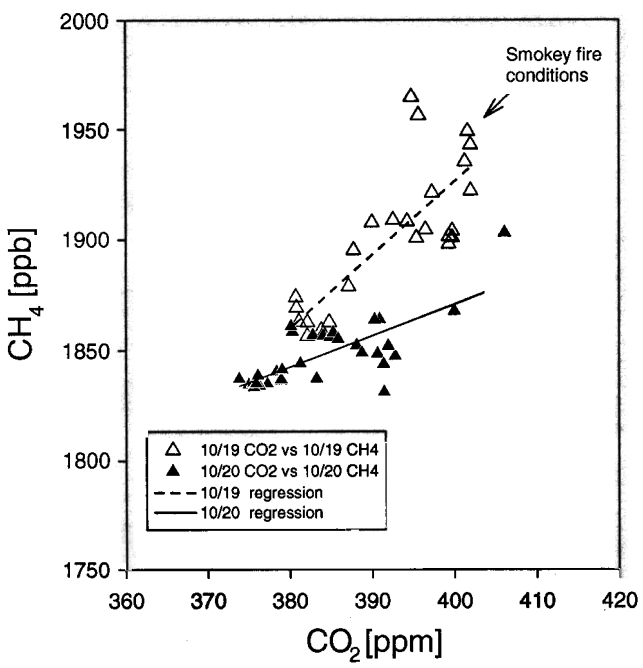

Figure 3. $CH_4:CO_2$ observed during 10/19 and 10/20.

4. Summary

Using continuous, precise measurements of atmospheric O_2 and CO_2 we have shown changes in the consumption of atmospheric oxygen during a large forest fire, and we have demonstrated the feasibility of characterizing far field $-O_2:CO_2$ ratios of biosphere burning emissions. Our measurements indicated that the $-O_2:CO_2$ ratio of the emissions varied from 1.1 to 1.4, with the higher O_2 consumption during observed increases in smoke and ash and elevated CH_4 levels 70km from the fire. Our methods are capable of providing a far field measurement of O_2 consumption resulting from various wildfire processes and of detecting changes in fire dynamics presumably linked to emissions of oxygenated compounds. Future studies will relate the O_2/CO_2 ratios to emissions of other trace gases and particles, providing data to help calibrate physical models of wildfire prediction for emission calculations (*Larini* et al., 1998; *Linn and Harlow*, 1998).

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[6] Examples of partially oxidized compounds that are important emissions from biomass combustion include HCHO, CH_3OH, and HCOOH (*Yokelson* et al., 1996; 1997; 1999).

[7] Due to an incompletely opened reference gas cylinder, we do not have data from 10/18.

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