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Trace Gas Emissions from Specific Biomass Fire-types

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Abstract

The Land-Use Change and Forestry chapter of the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* recognizes biomass fires as an important source of greenhouse gases and other trace gases. The guidelines also suggest that it may be appropriate to use different trace gas emission factors for different types of fires. However, currently, a single set of "default" emission factors is given which is intended for application to all on-site biomass burning. We have been using a simple, preliminary classification scheme for tropical fire-types and a straightforward model for predicting emission factors as a function of fire-type for estimating emissions from biomass burning (Ward et al 1992). Use of this system results in a CH_4 emission factor ($EFCH_4$) from primary forest deforestation burns which is four times larger than $EFCH_4$ from savanna fires *per unit mass of fuel*. In general, adjusting emission factors for fire-type should improve trace gas inventories; even when only rudimentary knowledge is available regarding the distribution of fire-types occurring in a region. In this paper, the use of this system (and related systems) is referenced, described, or developed for a number of atmospherically significant, biomass fire emissions. This approach could be used by national level experts, together with the best information on the fire-types occurring in their countries, to develop more accurate alternatives to the IPCC default values.

Introduction

Fires transform biomass into many different products. Trace gases and aerosols are injected into the atmosphere while charcoal and tar remain on site. Large quantities of ash also result; of which a significant fraction is usually redistributed by wind or rain (Raison et al 1985). The combustion processes leading to these products have been discussed elsewhere (Yokelson et al 1996b; Yokelson et al 1997a). A summary is given here. Initial heating of unburned fuel releases the more volatile components by distillation and produces oxygenated organic compounds by depolymermization and bond breaking. The residual solid is known as low temperature char and has high aliphatic content. Continued temperature increase releases hydrocarbon gases resulting in high temperature char (with high aromatic content). Glowing combustion on the surface of char releases CO_2 and CO and other gases. A small fraction of the gases, especially the higher molecular weight compounds, may recondense into "tar." A somewhat larger fraction of the gases escape into the atmosphere without being oxidized in flames and are known as smoldering products. Normally, most of the initially produced gases undergo further oxidation in flames resulting in CO_2, H_2O, NO, SO_2 and other flaming products. Aerosols are made by a variety of less well-understood processes. The residual, on-site, solid

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products are primarily found as char, which is enriched in carbon, or as ash, which is high in inorganic content. The relative production of the flaming and smoldering compounds is affected by many variables (Ward et al 1996). Fine, dry, or loosely packed fuels tend to be consumed by flaming combustion while large, wet or densely packed fuels tend to be consumed by smoldering combustion. Other variables affecting the mix of flaming and smoldering include weather (such as wind, rain, temperature, and RH) or the burning (slashing and ignition) techniques (Seavoy 1973; Kunstadter et al 1978; Kauffman and Uhl 1990).

Several useful parameters have been developed which indicate the relative amount of flaming and smoldering combustion in a fire. These parameters are computed from fire-integrated measurements of the emissions as discussed by Ward and Radke (1993). These parameters and their definitions include:

1. Combustion efficiency (CE) which is defined as the fraction of fuel carbon burned released as CO_2.
2. Modified combustion efficiency (MCE) defined as $(\Delta CO_2/(\Delta CO_2 + \Delta CO))$.
3. CO/CO_2 ratio defined as $\Delta CO/\ \Delta CO_2$.

In these definitions, "Δ" refers to the measured fire production of a gas above background levels. CE requires the most data to compute while MCE and CO/CO_2 require the measurement of only two gases. MCE has the further advantage that it is highly correlated with CE (Ward and Radke 1993). The methodology used to measure carbonaceous products varies among studies and the mathematical form of MCE is not identical to the CO/CO_2 ratio. However, the important point is that proper use of any of these parameters can illustrate the different fire-integrated combustion characteristics that result from different fire-types. Flaming combustion has high CE, even higher MCE, and a low CO/CO_2 ratio. Smoldering combustion has lower CE and MCE than flaming, but a higher CO/CO_2 ratio. Thus, the fire-integrated CE, MCE, or CO/CO_2 ratio is a useful index of the relative amount of flaming and smoldering that occurred over the course of the whole fire. Further, production of emissions other than CO_2 is often found to be highly correlated with these parameters. For example, see Figure 1 or the equation for the emission factor for CO as a function of CE in Ward et al (1992).

A series of extensive field measurements of fuel types, combustion efficiency, and other fire variables, by several workers, in tropical ecosystems in Brazil and Africa suggested a working, preliminary classification scheme for tropical fire-types (Ward et al 1992; 1996; Shea et al 1996). Typical fires during the peak of the burning season in savannas, partially-treed savannas, or cerrado were found to burn with a CE of 0.93 - 0.94 (MCE 0.94 - 0.95). In contrast, deforestation burns in primary moist forest burned with an average CE of 0.86 (MCE 0.89). In comparison to primary forest, fires in second-growth forest (smaller fuels than primary) burned with a higher average CE of 0.89 (MCE 0.91). Pastures, which often have large fuel elements left over from pre-existing forests, burned, on average, with an intermediate CE of 0.92 (MCE 0.934). The absolute values of CE obtained in an experiment (such as that described above) depend partly on the number of components measured and the measurement time (Hurst et al 1994). For differentiation of fire-types, the important result is that different parameter values are obtained for different fire-types within any consistent approach.

Our concept of a fire-type recognizes that the emissions (per unit area and time) for a land-cover type depends on the fire CE and also on the biomass density (Whitmore 1984), combustion factor (CF, the fraction of biomass exposed to fire that burns), and fire frequency (Shea et al 1996). In summary, land-cover types with low biomass density, such as grasslands, normally feature fires with high CE (~0.94), high CF (~1.0), and shorter (1-4 yr) "fire return intervals" (Kauffman et al 1994). Land-cover types with high biomass density, such as primary moist forest, typically feature fires with lower CE (~0.86), and lower CF (0.3-0.5). Intermediate values for CE and CF are appropriate for pastures and secondary forests. Within a land-cover type, the combustion factors are normally higher for the finer fuels (Fearnside et al 1993; Ward et al 1992; Shea et al 1996).

The premise of this paper is that emissions estimates, in general, and national greenhouse gas inventories, in particular, can be significantly improved by estimating the appropriate fire-types involved and then coupling that information to fire-type-specific emission factors.

Fire-Type Specific Emission Factors

This paper is not intended to be a complete review, or even a list, of all previous emissions measurements. The purpose is to describe the methodology for modeling emissions by fire-type and to refer the reader to the data needed to successfully apply this model.

Hydrocarbons. Figure 1 shows $EFCH_4$ (grams CH_4 per kilogram of dry fuel) *vs.* CE. Each data point represents integrated data from a field fire. The points are divided into two groups; one from forest and one from grassland ecosystems. A line is fit to the data for each group, which is then a "best-fit" model for $EFCH_4$ as a function of CE for that group of ecosystems. The vertical lines represent the average CE observed in Ward et al (1992) for two of the fire types. For example, cerrado fires (solid lines) typically burned with a fire-integrated CE of 0.94 and produced about 2 g CH_4/kg, while fires in primary forests (dashed lines) burned with lower CE and produced about 8 g CH_4/kg.

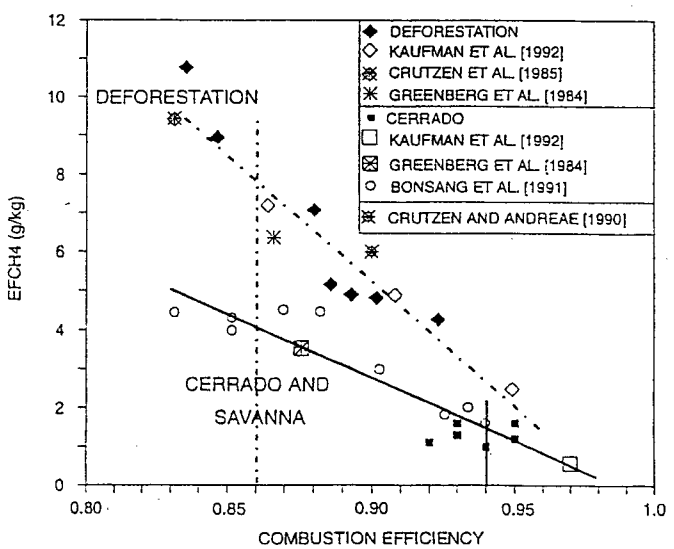

Figure 1. Methane production versus combustion efficiency shown for fires in grass-dominated and forested ecosystems (Ward et al. 1992).

The EF for non-methane hydrocarbons (NMHC's) can also be modeled as a function of CE or MCE. However, in Hao et al (1996), NMHC emissions were found to correlate better with CH_4 emissions and so *emission ratios* (ER) in the form NMHC/CH_4 are presented. Thus, NMHC EF's can be estimated by first determining the appropriate EFCH_4 and then applying the appropriate ER. In fact, much of the biomass burning literature presents emissions measurements as emission ratios to CO or CO_2 (Lobert et al 1991). Data in this form can be readily used in a fire-type specific model by first scaling CO and CO_2 appropriately and then applying the reported ER. The two step process will not generally give exactly the same result as the CE model, but should be preferred to ignoring fire-type. (In the special case of a very high CE fire for which very little data was obtained at high CE the two step process may be preferred. This is because a linear fit effectively weights the low CE points.) Finally, large amounts of terpenes may also be emitted in some fires (Yokelson et al 1996a; work in progress).

Oxygenated organic compounds (OVOC). Organic acids, alcohols, and aldehydes are not primarily created by the same process that produces CH_4 (Yokelson et al 1996b; 1997a). OVOC emission factors do not correlate well with CH_4 or MCE in most studies (Talbot et al 1988). However, in our open-path spectroscopic measurements, we obtain emission factors for OVOC which are 10 - 1000 times higher than other studies and *are* well-correlated with MCE. This is shown in Figure 2 for acetic acid where a single line is fit to spectroscopic measurements from grass, brush, and coniferous fuels. More study will be required to determine if fuel-specific slopes are appropriate.

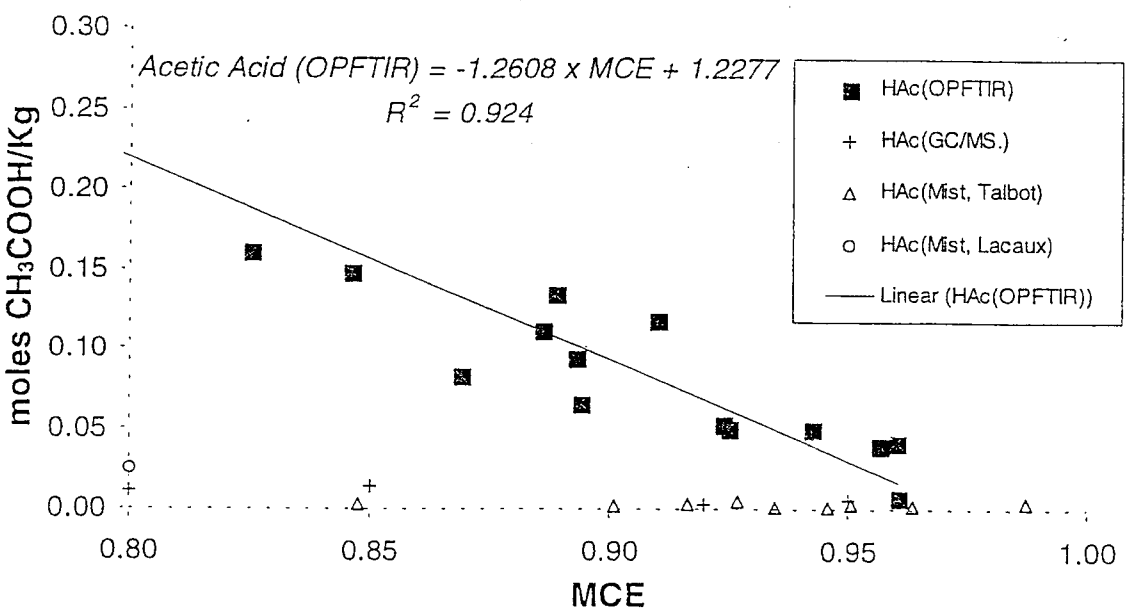

Figure 2. The line is fit to the open-path Fourier transform infrared spectrometer measurements of the Acetic acid emission factors for grass, brush, and coniferous fuels (Yokelson et al 1996b; 1997a). The EF is in moles/kg (MM CH_3COOH = 60 grams per mole).

Nitrogen compounds. Plots of EF *vs.* CE for N compounds often show poor correlation due to large variation in fuel N. One solution is to normalize EF to fuel N, but fuel N is not always measured. We have developed another alternative which can effectively normalize key N emissions without requiring fuel N data as explained next (Yokelson et al 1996b). Several studies have quantified ammonia (from smoldering) and NO_x (from flaming) for fires primarily consuming aboveground biomass. Hurst et al (1994) measured the percentage of fuel nitrogen released as the sum "NH_3+NO_x" from Australian savanna fires and obtained 44%. Yokelson et al (1996b) obtained 54% for this quantity in laboratory studies of coniferous fuels. In both these studies, HCN, N_2O, and other compounds were minor products accounting for less than 1 % of fuel N. Many studies report that about 10 percent of fuel N remains in the ash (e.g. Hurst et al 1994; Crutzen and Andreae 1990). Finally, Kuhlbusch et al (1991) report that N_2 will account for 36 ± 13% of fuel N on average. The above observations can be combined with measurements of NH_3/NO_x from a variety of studies and the major nitrogen emissions (except for N_2) can then all be estimated within a single model. This approach is illustrated in Figure 3. NH_3 and NO_x are estimated as follows: 1. Fuel N can be measured or extensive tables of C, N, and H content in tropical fuels are available (Sussot et al 1996), 2. The approximation is made that 50% of the fuel N is released as NH_3 or NO_x, and 3. the ratio NH_3/NO_x (for the estimated fire MCE) is given by the equation in Figure 3.

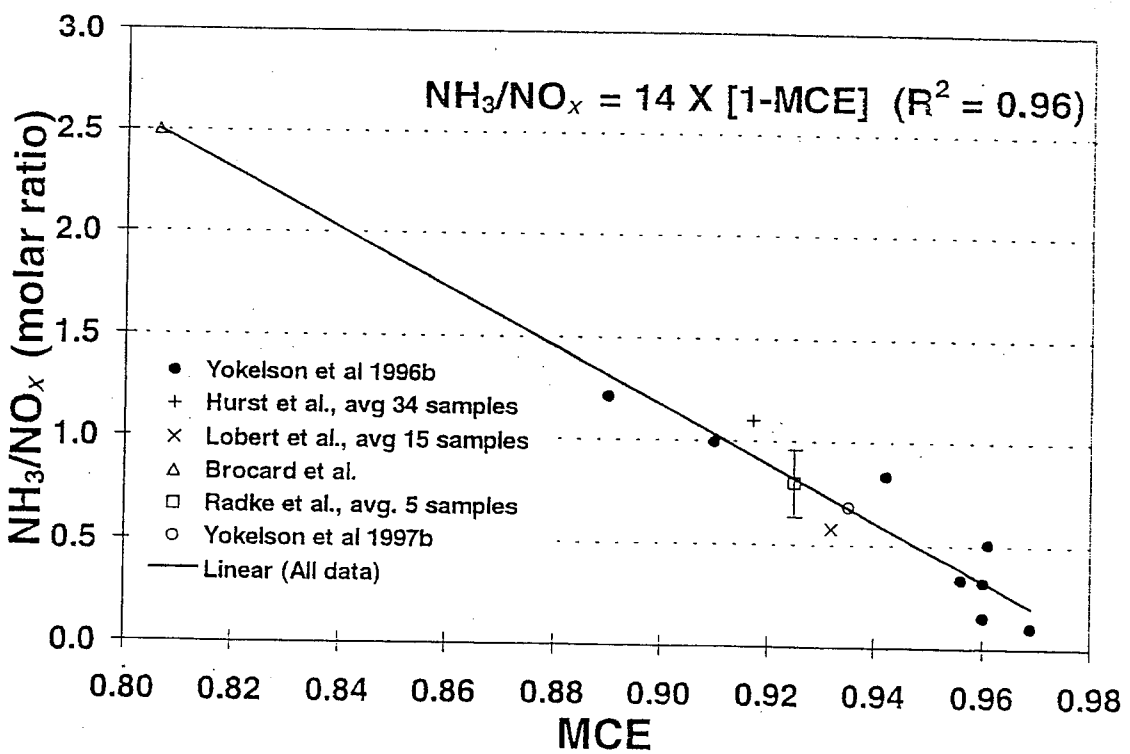

Figure 3. The data for NH_3/NO_x as a function of MCE, a linear fit to the data, and an equation to predict emissions are shown.

Hydrogen and Sulfur Compounds. The bulk of the fuel H can be accounted for fairly easily in the trace gas emissions. H_2O is the major flaming combustion product with the "combustion water" accounting for some 90% of fuel H (Yokelson et al unpublished work). H_2 is a major H-containing product of smoldering combustion (Crutzen et al 1979; Cofer et al 1988; 1990; Ward et al 1992) and substantial quantities of hydrogen are also contained in the OVOC and hydrocarbons. It has been more difficult to account for fuel S in the emissions. Qualitatively SO_2 is identified with flaming (Yokelson et al 1996b) and OCS with smoldering (Crutzen et al 1979; 1985; Ward et al 1982; Yokelson et al 1997a).

Aerosols. The chemical composition and the initial production and growth mechanisms for aerosol emissions from biomass fires are still poorly characterized. Qualitatively, PM2.5 usually accounts for *ca.* 1% of the fuel carbon which is much less than the ~ 20 % soot yields sometimes reported from open fires in fossil fuels. (Biomass fire particulate also has much lower PAH content than particulate from fossil fuel combustion.) Some equations have been derived from ground-based measurements to predict EFPM2.5 as a function of CE:

(1)EFPM2.5 (g/kg) $\cong$ 88 X [1-CE] $\qquad r^2 = 0.56$

Equation 1 was determined from studies of savanna fires in Africa (Ward et al 1996).

(2)EFPM2.5 (g/kg) $\cong$ 70 X [1-CE] $\qquad r^2 = 0.59$

Equation (2) fits data from fires in the cerrado, and secondary and primary forest of Brazil (Ward et al 1992). Finally, equation (3) relates the observed particulate concentration to the excess CO concentration and has been verified downwind of biomass fires in both the tropics and temperate regions (Babbitt et al 1995).

(3) [PM2.5] (μg/m3) $\cong$ 100 X [CO] ppm

Flaming combustion is found to contribute strongly to black aerosol which may absorb significant amounts of solar radiation while smoldering combustion contributes strongly to a white, more reflective (higher albedo) aerosol (Susott et al 1991; Yokelson et al 1997a). Glowing combustion does not release visible aerosol, but the emissions contain NH_3 which is a precursor for secondary aerosol formation in the plume (Yokelson et al 1997a).

Belowground biomass. Globally, it has been estimated that over two-thirds of the carbon in forest ecosystems is contained in soils and peat deposits (Dixon et al 1994) and that carbon contained in soils represents a larger carbon pool than carbon in aboveground biomass (Woodwell et al 1978). Land-use change and global warming may cause more of this carbon to be exposed to fire (Kasischke et al 1995; Keane et al 1997). Organic soils and "litter" differ from aboveground fuels in that they burn almost exclusively by smoldering combustion. The general picture of emissions from soils can be predicted by referring to the "low CE" portion of the EF plots. However soils develop under many different physical, chemical, and fire regimes and from a large variety of biological and

geological precursors. These factors may explain why our soil fire emissions database is apparently not well-described by simple relationships. For instance, in organic soils the HCN/NH_3 ratio varies about two orders of magnitude. HCN production is evidently higher in drier soils and actually dominated ammonia production by a factor of five for a fire in dry North Carolina bog soil (Yokelson et al 1997a). Finally, we measured the tar yield from smoldering peat at slightly over 1%. However, the tar was enriched in N by a factor of 6 or 7 over the parent peat, suggesting that the tar may account for a significant portion of fuel N in soils. Table 1 presents the major emissions we detected from burning organic soils (Yokelson et al 1997a).

Table 1. Average of all emission data for smoldering organic soils. Adapted from Yokelson et al. 1997a.

compound name	formula	100 X moles compound / total moles C detected		Approx.[1] g/kg
carbon dioxide	CO_2	78.82	(3.593)[2]	1445
carbon monoxide	CO	17.10	(3.634)	200
methane	CH_4	1.220	(0.440)	8.13
ammonia	NH_3	0.932	(0.767)	6.60
acetic acid	CH_3COOH	0.306	(0.145)	7.65
hydrogen cyanide	HCN	0.292	(0.166)	3.29
methanol	CH_3OH	0.281	(0.100)	3.75
propene	C_3H_6	0.149	(0.027)	2.61
ethene	C_2H_4	0.140	(0.040)	1.63
formaldehyde	HCHO	0.132	(0.096)	1.65
phenol	C_6H_6O	0.107	(0.122)	4.19
formic acid	HCOOH	0.073	(0.060)	1.40
2-hydroxyethanal	$C_2H_4O_2$	0.032	(0.031)	0.80
carbonyl sulfide	OCS	0.021	(0.038)	0.53
ethyne	C_2H_2	0.013	(0.007)	0.14

[1]Calculated assuming fuel is 50% carbon.
[2]The value of one standard deviation is given in parentheses.

Secondary product formation. Most of the initial emissions from fires (except for CO_2 and CH_4) are too reactive to become well mixed in the global troposphere (Prather et al 1994). Photochemical processes transform the initial plume constituents into new products on the time scale of hours to months (Finlayson-Pitts and Pitts 1986). Of these secondary products, O_3 has attracted the most attention because of its importance as a pollutant, oxidant, and an indirect greenhouse gas. O_3 formation in biomass burning plumes has been the focus of major, international, collaborative measurement and modeling efforts which are only very briefly summarized here (Talbot et al 1996; Singh et al 1996; Fishman et al 1996; Yokelson et al 1997c). Fires initially cause a large reduction in the O_3 levels in entrained background air by reaction with NO and perhaps terpenes. Under the right conditions, O_3 can then increase to high levels in the plume over a period of weeks as discussed in detail elsewhere (Crutzen and Carmichael 1993; Thompson et al

1996). The model of Chatfield et al (1996) indicated that O_3 formation was "NO_x limited." This suggests that a high N:C ratio of the fuel coupled with a high fire CE may increase the O_3 formation potential of fires. These same fire-types may also have relatively large potential to contribute to acid rain and deposition. However, it is not yet possible to make a simple assignment of emission factors for secondary products from specific fire-types.

Conclusions

It is well established that different types of fires can produce significantly different emissions. Coupling this information with measurements of fire-types and amounts should improve regional-global emissions estimates. Future improvements will result from researching seasonal trends in fire-types and amount burned and from measurement of specific emission factors for more compounds and fires. Finally, detailed understanding of the influence of fires on the atmosphere will require integrated study of the post-emission transport and transformation of the trace gases and aerosols.

Literature Cited

Babbitt, R. E., D. E. Ward, R. A. Susott, W. M. Hao, and S. P. Baker. 1995. Smoke from western wildfires, 1994, Paper presented at the 1994 Meeting of the Interior West Fire Council, Cour D'Alene, Idaho.

Bonsang, B., G. Lambert, and C. Boissard. 1991. Light hydrocarbon emissions from African savanna burning. *In*: J. S. Levine (editor). Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications. MIT Press. Cambridge, Mass, USA. pp. 155-161.

Brocard, D., C. Lacaux, and J-P Lacaux. 1996. Emissions from the combustion of biofuels in western Africa. *In*: J. S. Levine (editor). Biomass Burning and Global Change. MIT Press. Cambridge, MA, pp 350-360.

Chatfield, R. B., J. A. Vastano, H. B. Singh, and G. Sachse. 1996. A general model of how fire emissions and chemistry produce African/oceanic plumes (O3, CO, PAN, Smoke) seen in Trace-A. *Journal of Geophysical Research*, 101: 24279-24306.

Cofer, W. R. III, J. S. Levine, E. L. Winstead, P. J. LeBel, A. M. Koller, Jr., and C. R. Hinkle. 1990. Trace gas emissions from burning Florida wetlands. *Journal of. Geophysical Research*, 95: 1865-1870.

Cofer, W. R. III, J. S. Levine, P. J. Riggan, D. I. Sebacher, E. L. Winstead, E. F. Shaw, Jr., J. A. Brass, and V. G. Ambrosia. 1988. Trace gas emissions from a mid-latitude prescribed chaparral fire. *Journal of. Geophysical Research*, 93: 1653-1658.

Crutzen, P. J., L. E. Heidt, J. P. Krasnec, W. H. Pollock, and W. Seiler. 1979. Biomass burning as a source of atmospheric gases CO, H_2, N_2O, NO, CH_3Cl and COS. *Nature*, 282: 253-256.

Crutzen, P. J., A. C. Delany, J. Greenberg, P. Haagenson, I. Heidt, R. Lueb, W. Pollock, W. Seiler, A. Wartburg, and P. Zimmerman. 1985. Tropospheric chemical composition measurements in Brazil during the dry season. *Journal of Atmospheric Chemistry*, 2: 233-256.