**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "**The tropical forest and fire emissions experiment: laboratory fire measurements and synthesis of campaign data**" *by* **R. J. Yokelson et al.**
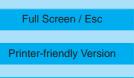
R. J. Yokelson et al.

Received and published: 28 May 2008

2. Anonymous Referee #3

Received and published: 26 April 2008

Referee 2.1. Overview: This is a good paper and topic for ACP, and deals with a critical; namely comparison of lab with field measurements with the ultimate derivation of a "fire averaged" emission factor much higher than those derived from spot measurements. This is a difficult problem and the work does not end with this paper. Am worried about the extrapolations performed within, but discussion and debate needs to start somewhere. But it is a great study to add to the scientific knowledge base and as a whole is pretty executed. I have revealed myself to the lead author, and I agree with

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

the previously posted reviewer in all aspects. To reduce repetition, I will go directly to two major comments.

Most importantly, the authors fail to acknowledge in their paper that this is an issue that has been considered for over 15 years in various ways. While the issue has not before been tackled as directly or as well as this manuscript findings previous findings need to be considered. I say this not simply to increase the number of citations in the paper (including my own), but they bare real relevance to the issue at hand. To begin, the authors are encouraged to read the two review papers by Reid et al., [2005], in particular the sections on smoke evolution, mass growth and emission. In there the authors will find several key references. For example, Guild et al., (1998) showed that for pasture fires in Brazil (important topic for this paper being reviewed here), the authors found that a significant amount of smoke production is not from the grass, but from lingering fallen trees from the original clear cut. They clearly point out the nature of the problem discussed in the current manuscript. Comparing Guild with Yokelson, the issue of large woody fuel (much bigger than what was in the burn chamber), shows an even more compelling reason why fire averaged emission factors are so important.

Response 2.1. This comment actually raises a few issues. First, we now refer to several papers describing previous work right after we mention the importance of tropical forests at the beginning of the introduction. Our citations include some of the earliest papers we know of to stress the long-term interest of the community in these topics:

Page 4223, Line 11

"Numerous studies have measured the emissions from forest vegetation and deforestation fires in the tropics including e.g.: Rasmussen and Khalil (1988), Crutzen et al., (1985), and Ferek et al., (1998)."

We also slightly modified the sentence that follows in the introduction (lines 11-15) so it highlights what was new about the TROFFEE campaign by pointing out that it applied new instrumentation to these topics. The revised sentence now also clues the reader

that an overview of TROFFEE is in Yokelson et al., 2007a – a paper which contains exhaustive references to past work.

New sentence:

"The Tropical Forest and Fire Emissions Experiment (TROFFEE) used new instrumentation to quantify the emissions from tropical deforestation fires and tropical vegetation in laboratory experiments (October 2003) and airborne and ground based field campaigns during the 2004 Amazonian dry season (see Yokelson et al., 2007a for an overview)."

Also, as noted above in the response to the other Referee, this paper is already attempting two main tasks: (1) present and integrate the lab results with 4 other papers mostly on field results and (2) describe the new findings from the overall TROFFEE campaign. The paper would be too long if we also included a comprehensive literature review. Indeed, Referee Holzinger would like to see the paper shortened where possible. However, the Referee is correct that much earlier work is both useful and critical. Thus, we added the references as shown above and we also assure the Referee that the companion papers exhaustively cite the literature. We keep this paper to reasonable length and preserve the flow by referring the reader to the companion papers for more details. For example the entire companion paper by Christian et al., (2007) is on the topic of emissions from "lingering fallen trees" as is now specified in the revised introduction; and the work of Guild et al and numerous other similar studies are cited there-in. We refer to this paper repeatedly and rely heavily on its results in our synthesis section. Finally, we modified the abstract to mention logs specifically.

Referee 2.2. Along a similar thread, the authors must be very mindful of the differences between a "fire lab" fire and a "real fire." As the authors are as I am sure so keenly aware, combustion is a true chemical reaction process with extraordinarily complex reaction sets. Real fires have different temperatures, ventilations and concentrations. Big fires make up the bulk of emissions (Kaufman et al., 1998), and the chemistry

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

of such fires is different from small fires, as is fuel makeup and heterogeneity. Thus, while I truly believe that there is much to be learned from lab fires, simple comparison between lab and field data is not in the slightest way straightforward.

Response 2.2. Since we have access to the largest combustion simulation facility in the world, extensive experience observing field fires, and a commitment to correctly simulating field fires; we have actually been pretty successful in building lab fires with fine fuels (i.e. grasses) that had emissions very similar to field fires in fine fuels. Obviously, as we point out on numerous occasions throughout the text, we did not burn a variety of large-diameter tropical hardwoods in our lab and this is a serious limitation. Also, no-one really knows how many small fires there are. In any case we used the field results almost exclusively to derive our recommended emission factors. We use the lab data in the recommendations only when no field data was measured (2 out of $\sim$50 species). Even then, we used the lab data only after applying a transfer function to normalize it to the field results.

Referee 2.3. In Section 2.1, the authors go to great lengths to impress upon the reader all of the advantages of a burn lab. How about equal coverage of all of the reasons why burn lab data is problematic?

Response 2.3. We think that the reorganization of the text detailed in response 1.2 will address this comment also. In particular, we eliminated the word "advantage" and simply give reasons why lab fires are "worthwhile."

Referee 2.4. Regarding references on particle condensation/secondary production, as I stated in my first review, the reference to the material in Reid et al., 1998 is incorrect should be 40% (pg 4242 l3). Particle mass growth is probably on the order of 15-40%. This is inline with the papers discussed in Reid et al., 2005. On one occasion for a very intense fire during SCAR-C a data point said 80%, as described in Martins et al., 1996; Hobbs et al., 1996. Thus, while it is possible for it to happen, more likely values are probably half this.

Response 2.4. We had read the Reid et al reviews in detail and cite them now. However, we relied mainly on the original, detailed Reid et al., 1998 paper, which we also studied thoroughly. This was the most extensive study that we knew of that measured particle mass changes between young and old smoke as opposed to particle volume changes, which can be partly due to coagulation. The page range for the Reid et al 1998 article we cited is 32059-32080. Clearly the results for post-emission mass growth are variable and uncertain as shown by Reid et al., (1998).

In Reid et al, 1998, at the bottom of column 1 on page 32071, we find the following text discussing post-emission growth:

"The slope of the '(aerosol to CO)' regression for young smoke is 156 ± 16 ug m^{-3} ppmv^{1} with an r^{2} value of 0.79 (Figure 6a). Figure 6b shows a similar regression but for aerosol mass and CO data collected in the convective boundary layer in regional hazes. The slope of the aerosol mass/CO regression drops to 145 ± 23 ug m^{-3} ppmv^{-1}, with a regression coefficient (r^{2}) value of 0.72. This implies that the mass of the aerosol decreases by 7% during aging, although this number is not statistically significant.

Figure 6a shows that the regression for the young smoke is heavily weighted by one extreme data point (at a CO concentration of 17 ppmv) collected in Maraba. This data point comes from the largest fire studied. As discussed by Ferek et al [this issue], for large fires such as this, the particle-to-CO emission ratio can be several times greater than normal. If this one data point is removed, the slope of the aerosol mass-CO regression falls by almost a factor of 2, to 80 ± 12 ug m^{-3} ppmv^{-1}, and the r^{2} value remains high at 0.64. This slope is similar to the value of 81 ug m^{-3} ppmv^{-1} for fresh smoke in TRACE A derived by Anderson et al. [1996a]. Utilization of this value for young smoke implies that the aerosol mass in evolving smoke plumes increases by roughly a factor of 1.8 during evolution over a period of 1 to 3 days."

The above text was the basis for our statement that Reid et al 1998 measured a PM/CO growth factor of 1.8. However, the same article does go on to say that (indirect) recep-

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

tor modeling (Table 8) implies aerosol growth of 17 $\pm$ 6 to 62 $\pm$ 8%. In addition, the abstract for this article gives 20-40 percent for the growth factor as the Referee states above. However, continuing to illustrate the variability, this same paper goes on to state on page 32075 that Babbit et al (1997) observed a factor of two growth in the post-emission PM/CO ratio. The Referee mentions above a case of 80% growth, which is close to the 1.8 we used. The abstract of the SCAR-B overview paper cited by the Referee mentions particles increasing by 60% in radius to a mean radius of 0.15 microns in aging smoke in Brazil. This is a volume growth of 400%, but some of that is due to coagulation. In work in progress, using an aerosol mass spectrometer on aging fire plumes in the Yucatan, our preliminary result is that PM/CO increased by a factor of two in 1.4 h of aging and then may have doubled again in another hour or so of aging. However, the Yucatan regional haze is not "enriched" in PM/CO, but then again it is a small land-area that is continuously refreshed by clean marine air. The excellent review article written by Reid et al (ACP 5, 799-825), which is now cited in the revised text mentions several cases of extreme particle size growth. This includes "blue moon" events due to aged forest fire plumes with average particle diameters close to 0.7 microns! Hobbs et al 1996 are cited as observing volume mean diameters (VMD) increase from 0.25 to 0.38 in two hours and Reid et al 1999a are cited as observing VMD increase from 0.12 to 0.18 after emission. The latter two diameter increases correspond to volume increases by factors of 3.5 and 3.4, respectively. Those factors are a minimum since aged particles are more spherical. The review states that "numerous" other examples of size growth are in the literature. However, all these size increases can be partly due to coagulation.

Given the uncertainty and variability in observed growth factors, it is appropriate to revise our text so that it does not imply that a growth factor of 1.8 results from a definitive, highly certain measurement of a quantity with low variability about the mean. For purposes of our discussion, we simply need a reasonable, clearly stated value as sample input for a template calculation. And our description of the calculation needs to be clear enough for a reader to redo the calculation using any different growth factor value they

desire in our template.

In the original and revised text we spared the reader all the details given above, which are more suited for a review article on the topic. In the new text we now state that the amount of growth is highly uncertain (0-400%), cite the original and review articles by Reid et al, cite our work in progress in Mexico, and we then select a factor of 1.8 as a hypothetical value to illustrate the implications of a factor that size. We could select many other values and redo/revise more extensively. However, the key point for the atmospheric science community is not the value selected, but that a very small fractional gas-particle conversion corresponds to a huge increase in the amount of PM. This is very significant and may not be common knowledge.

Section 3.3 has been lightly revised throughout to address the above issues as well as the other Referee's concerns about the scope and clarity of the discussion. The new text follows:

3.3 Characteristics of biogenic and pyrogenic sources: Amazon to global

In the TROFFEE experiment our focus was improved measurements of the pyrogenic and biogenic emissions from the Amazon basin. In this section we show how the new information improves our understanding of tropical tropospheric chemistry at various scales.

3.3.1 Impact of major trace gas and particle sources in the Amazon basin.

We start at the local scale noting that Karl et al. (2007a) measured average isoprene emissions from pristine tropical forest of $\sim$400 $\pm$ 130 g/ha day. This can be compared to the affect of burning a hectare of tropical forest (which typically requires less than one day) assuming a fuel consumption of $\sim$120 $\pm$ 40 Mg/ha (Christian et al., 2007) and our primary deforestation EF for isoprene from Table 4 (0.42 $\pm$ 0.13 g/kg). The burned hectare releases a pulse of $\sim$50000 $\pm$ 23000 g of isoprene, which is $>$ 120 days of production by an unburned hectare. However, only a small percentage of the Amazon

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

basin burns every year ($\sim$2.5%) so we expect the emissions from plants to dominate the annual basin-wide isoprene budget. Explicitly, assuming four million km^2 of tropical forest in the Amazon basin (Yokelson et al., 2007a) implies an annual biogenic isoprene source of $\sim$58 $\pm$ 19 Tg. (The uncertainty quoted in the biogenic source does not include the uncertainty in forest area in this and the following estimates.) Approximately 2.0 $\pm$ 0.5 million ha of the Amazon are subjected to primary deforestation fires annually (http://www.obt.inpe.br/prodes/), which suggests that these fires consume about 2.4 $\pm$ 1.0 $\times$ 10^{11} kg/yr of fuel. Kauffman et al., (1998) calculated that pasture fires in the Amazon basin consume roughly the same amount of biomass as primary deforestation fires. We combine the fuel consumption for these fire types with the EF for isoprene for these fire types from Table 4 and obtain an annual pyrogenic isoprene source of 0.28 $\pm$ 0.16 Tg ($\sim$0.5% of biogenic source).

Analogous basin-wide annual estimates can be made for other individual NMOC emitted by both sources. For instance, the methanol to isoprene emission ratio for tropical forests was measured at 14% in Costa Rica (Karl et al., 2004) and 4% during TROF-FEE (Karl et al., 2007b). Taking an average value of 9 $\pm$ 5% then implies an annual methanol source of $\sim$5.3 $\pm$ 3.4 Tg from intact Amazonian forest. Using the fuel consumption estimates above and the EF for methanol from Table 4 yields an annual Amazon-basin pyrogenic source of methanol of $\sim$2.1 $\pm$ 1.1 Tg. In this case the fire source is about 40% of the plant source on an annual basis and the two sources would be comparable during the dry season.

Significant biogenic emissions of acetaldehyde, acetone, and monoterpenes have also been quantified from tropical forest. Taken together, Karl et al. (2004) and Karl et al (2007a) imply that the sum of quantified non-isoprene emissions from tropical forest equals about 35 $\pm$ 9% of isoprene. Increasing our estimate of isoprene emissions (58 Tg) by 35% implies emissions of 79 $\pm$ 33 Tg/yr of "known" NMOC from the Amazon basin. Using the sum of measured pyrogenic NMOC from Table 4 ($\sim$26 or $\sim$48 g/kg for deforestation or pasture fires, respectively) yields a pyrogenic source of known NMOC

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

from the Amazon basin of $\sim$18 $\pm$ 11 Tg/yr. The pyrogenic NMOC are about one-quarter of the biogenic NMOC in this case. Next, we note that the total mass of NMOC emitted by fires is actually about twice the measured mass of NMOC (see Sect 2.4.) and the ratio of total/known, non-isoprene NMOC for plants could be similar (Goldstein and Galbally, 2007). If we double both the pyrogenic NMOC and the non-isoprene biogenic NMOC, we estimate the annual Amazonian pyrogenic and biogenic total NMOC at about 35 $\pm$ 20 and 99 $\pm$ 53 Tg, respectively.

Biomass burning emissions are extremely reactive and the post-emission transformations depend partially on the speciation of the initial emissions, which is now better known as a result of TROFFEE. An important secondary process is O_3 formation and Trentmann et al., (2005) showed that the details of the initial NMOC mix strongly influenced the modeled rate of O_3 formation for a savanna fire plume. Therefore, use of the new TROFFEE EFNMOC could improve the modeled O_3 formation for deforestation fire emissions.

Another important post-emission process is secondary aerosol formation. The post-emission mass growth factor for pyrogenic fine mode aerosol is probably highly variable and currently very uncertain with estimates ranging from 0-400% (Reid et al., 1998, 2005; Yokelson et al., work in progress). Here, for illustrative purposes, we assume that the 8 $\pm$ 5 Tg of PM2.5 initially emitted by Amazonian fires annually (Table 4) increases in mass by a factor of 1.8 during the first 1-3 days after emission due to secondary processes involving mostly co-emitted pyrogenic trace gases. If we also assume that the co-emitted inorganic, pyrogenic species such as NO_x, NH_3, and SO_2 (Table 4) were 100% converted to aerosol nitrate, ammonium, and sulfate; then about 2.4 Tg of the total regional mass growth in PM2.5 ($\sim$6.4 Tg) would be due to these species. Thus, the inorganic species would account for $\sim$38% of the mass growth and about 62% (4 Tg) would be due to co-emitted pyrogenic NMOC. This implies that less than $\sim$11% of the co-emitted pyrogenic NMOC (35 Tg) would have oxidized and/or condensed on the fine particles (during 1-3 days) since we are ignoring changes in NMOC mass during

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

oxidation. It's also likely that some of the secondary organic aerosol (SOA) would have come from the biogenic NMOC, which are more abundant regionally although less concentrated in initial plumes. A biogenic component to the Amazonian, moderately-aged, dry-season, fine-mode aerosol was not observed (or ruled out) by Echalar et al. (1998) even though they clearly measured a large biogenic contribution to the coarse-mode, dry-season aerosol (diameter > 2 microns). They also observed large biogenic components to both modes in the wet season. In any case, our total assumed regional PM2.5 mass growth (6.4 Tg) is equivalent to only ~7.5% of our estimated total mass of NMOC emitted during the Amazonian dry-season by pyrogenic and biogenic sources together (assuming dry season equals one-half annual for biogenics). The estimated organic part of the regional mass growth (4 Tg) is less than 5% of the total regional NMOC. Thus, over the time scale of several days, 5% represents a rough upper limit on the percentage conversion via SOA for regional NMOC. This upper limit is consistent with the lower end of estimates of the fraction of biogenic emissions converted to PM by secondary processes, which range from ~3 to ~66% (Andreae and Crutzen, 1997; Goldstein and Galbally, 2007). Clearly the percent conversion for individual NMOC varies greatly and more measurements are needed to support a rigorous overall accounting.

In light of the above budgets, it seems unlikely that 66% of the Amazonian biogenic NMOC condense on the Amazonian pyrogenic fine particles within 1-3 days of aging as might be inferred from Goldstein and Galbally (2007). A percentage conversion that high would represent a mass growth factor of > 8.2. No Amazonian field measurements support a growth factor this large at this time to our knowledge. Conversely, if 66% of biogenic NMOC did convert to secondary organic aerosol, then tropical forest regions would be producing well over ten times more fine particle mass than is currently included in conventional inventories of primary aerosol.

Further, the amount of regional SOA formation is constrained somewhat by source apportionment studies of the total aerosol mass in the Amazon dry season. Artaxo et

al., (1998) made airborne measurements of aerosol characteristics in approximately the same regional haze investigated by Reid et al., (1998) during SCAR B. They observed an average regional value for total aerosol of 107 ug/m^3 of which 78% was in the fine mode. These authors also performed source apportionment for the total aerosol mass and obtained a ratio for the biogenic/pyrogenic components of 34.6%. Guyon et al., (2004) measured the average ratio for the biogenic/pyrogenic component of total aerosol mass as 35.5% in a tower-based study conducted during the Amazonian dry season. We can couple this with a rough estimate of the total pyrogenic, regional, dry-season, aerosol mass by multiplying our annual, regional, primary, pyrogenic PM10 (10 Tg, Table 4) by 1.8 to obtain 18 Tg. If the biogenic component is 35% of 18 Tg, that implies a regional, dry-season, biogenic total aerosol mass of 6.3 Tg. This last value is $\sim$12% of the regional, dry-season, biogenic NMOC production of $\sim$50 Tg. Thus, 12% would be a large overestimate of the percentage conversion by SOA as we are ignoring a large biogenic component to the primary total aerosol mass and mass changes during oxidation. In summary, only $\sim$ 5% of the regional NMOC seem to be converted to aerosol within the Amazonian boundary layer on the time scale of 1-3 days. However, a larger percentage could convert to SOA on longer times-scales and/or outside of the Amazonian boundary layer. This could involve NMOC with lifetimes greater than several days and/or NMOC with shorter lifetimes that experience rapid transport to the free troposphere (Heald et al., 2005; Andreae et al., 2001).

3.3.2 New global estimates of biogenic and pyrogenic NMOC

Next we roughly characterize the total NMOC emissions from fires and plants at the global scale. We start by deriving a best estimate of global isoprene emissions from vegetation of 600 (range 500-750) Tg/yr using the MEGAN model (Guenther et al., 2006). Using the same assumptions as above for both non-isoprene and unknown NMOC suggests a global biogenic NMOC source of $\sim$ 1000 Tg/yr (range 770-1400 Tg/yr).

Our global, pyrogenic, NMOC estimate is derived in some detail. Coupling the sum of

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

our EFNMOC for deforestation fires (Table 4) with an estimate of biomass consumption in global deforestation fires (1330 Tg/yr, Andreae and Merlet, 2001 (uncertainty not provided, but large)) implies that global deforestation fires produce over 34 Tg/yr of identified NMOC. We are not considering the higher emissions from pasture maintenance fires in our global estimate. Our estimate does include the 12% increase we applied to our airborne EF for primary deforestation fires to account for residual smoldering combustion. Since we only measured about one-half the NMOC on a mass basis (Sect. 2.4), then the total annual NMOC from global deforestation fires should be about 69 Tg/yr. This estimate and an analogous estimate for each main type of biomass burning listed by Andreae and Merlet (2001) are shown in Table 5. In Table 5, we have shown the biomass consumption by each type of burning, the total NMOC currently quantified for that type of burning, and we assume that real total NMOC are twice the measured total NMOC. This last assumption is conservative since the instrumentation required to measure half the NMOC was only available for tropical forest fires (in this work). In fact, for the category of biomass burning that produces the most global NMOC (cooking fires) only FTIR was available. The real conversion from measured to total NMOC for cooking fires could be closer to three. Also, as part of TROFFEE, Christian et al., (2007) reported a sum of NMOC measured by FTIR from burning dung (an important cooking fuel in China and India) that was 32% higher than the value we use (for wood cooking fires) in Table 5. The last column of Table 5 shows our estimate of total annual NMOC by type of fire and a conservative global sum of 466 Tg/yr. For reasons given just above, the real global sum is probably over 500 Tg/yr. Its worth noting that this global pyrogenic NMOC estimate is much larger than the $\sim$ 100 Tg/yr estimated earlier by Andreae and Merlet (2001). There are sound reasons for this increase. Mainly: (1) subsequent development of methods (FTIR, PTR-MS, and GC-PTR-MS) to quantify the previously poorly-characterized emissions of reactive OVOC, that account for $\sim$80% of the NMOC in biomass burning smoke, (2) deployment of the new instrumentation on previously undersampled burning types such as cooking fires, charcoal kilns, agricultural waste, etc., and (3) the capability of PTR-MS to estimate

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

the unknown NMOC.

In light of our updated estimate, biomass burning is easily the second largest source of global NMOC behind plants ($\sim$1000 Tg/yr, see above) and well ahead of anthropogenic sources (142 Tg "C as NMOC"/yr, Middleton, 1995). Biomass burning has already long been recognized as the largest global source of primary fine carbonaceous particles (50-190 Tg/yr, diameter $<$ 1 micron, Kreidenweis et al., 1999 (see their Table 4.1)). In addition, the $\sim$500 Tg/yr of NMOC from biomass burning should probably be added to the $\sim$1000 Tg/yr of NMOC from vegetation as major global sources of secondary organic aerosol.

Finally, it is a fair approximation to assume that biogenic NMOC emissions are given off in diffuse manner according to a predictable daily cycle that should be fairly straight forward to implement in local-global models. On the other hand, fire emissions are produced in concentrated pulses and undergo significant initial processing in an altered chemical regime whose best depiction in local-global models is still unknown (Trentmann et al., 2005).

Full Revised Introduction:

1. Introduction

Biomass burning and biogenic emissions are the two largest sources of volatile organic compounds (VOC) and fine particulate carbon in the global troposphere. Tropical forests produce about one-third of the global biogenic emissions and tropical deforestation fires account for $>$15% of the global biomass burning (Andreae and Merlet, 2001; Kreidenweis et al., 1999; Guenther et al., 2006). Numerous studies have measured the emissions from forest vegetation and deforestation fires in the tropics including e.g.: Rasmussen and Khalil (1988), Crutzen et al., (1985), and Ferek et al., (1998). The Tropical Forest and Fire Emissions Experiment (TROFFEE) used new instrumentation to quantify the emissions from tropical deforestation fires and tropical vegetation in laboratory experiments (October 2003) and airborne and ground based

field campaigns during the 2004 Amazonian dry season (see Yokelson et al., 2007a for an overview). Four previously published TROFFEE papers focused on: (1) a detailed campaign overview and the airborne measurements of the emissions from fires (Yokelson et al., 2007a), (2) ground-based measurements of the emissions from smoldering logs (Christian et al., 2007), (3) airborne and ground-based measurements of biogenic emissions (Karl et al., 2007a), and (4) intercomparison of the instrumentation used in both the lab and field (Karl et al., 2007b). This paper completes the series by presenting the lab-fire emission factors and demonstrating how the different elements of the TROFFEE campaign can be synthesized to improve our understanding of the tropical troposphere.

Field measurements can probe the actual fires that are of global significance and they have obvious priority in developing recommended emission factors, but measurements of lab fires can also be useful. The TROFFEE lab experiment was conducted for a number of reasons - both general and specific. In general, it is often possible to quantify more species from lab fires because smoke concentrations tend to be higher and it is easier to deploy more extensive instrumentation. Also, in the lab, one can capture and probe all the smoke from a whole fire, while the vast majority of the smoke from field fires must go unsampled. In the field, the possibility exists for over estimating the relative importance of strongly lofted flaming emissions from airborne platforms; or under estimating their importance from ground based platforms. Measuring the elemental composition of the fuel that actually burned is easier for laboratory fires, which then facilitates mass-balance studies that account for the fate of various elements in the fuel. A very serious disadvantage of laboratory fire simulations is the possibility that the lab fire emissions are different from fire emissions produced in the field. This is especially critical for tropical forest fuels as it is impractical to burn a diverse suite of large diameter tropical logs in the lab.

Reasons for carrying out our laboratory component that were specific to TROFFEE included: (1) Determine the proton-transfer reaction mass spectrometry (PTR-MS) sam-

pling protocol for the field campaign (by identifying the significant mass/charge (m/z) ratios observed by PTR-MS in smoke). (2) Employ techniques in addition to those used in the field including particle collection on filters, ash analyses, open-path Fourier transform infrared spectroscopy (FTIR), and gas chromatography coupled to PTR-MS (GC/PTR-MS). (3) Intercompare PTR-MS with open-path FTIR and GC/PTR-MS. The intercomparison showed good agreement in most cases, but also revealed important biomass burning emissions that are difficult to measure by FTIR (due to interference by water lines) or PTR-MS (due to low proton affinity or sampling losses). (4) Use GC/PTR-MS and FTIR to measure the fractional contribution for fire-emitted species that appear at the same m/z in the PTR-MS (Karl et al., 2007a). (5) Measure the emissions from burning sugar cane, which are important, but not accessible in our field study.

The laboratory experiment involved measuring the emissions from 32 fires that burned tropical forest fuels and a few other fuels (e.g. sugar cane, pine needles, and savanna grass). In this paper we present and discuss: (1) a partial accounting of the fate of the nitrogen, chlorine, and potassium in the biomass fuel in our lab fires, (2) a synthesis of the lab, ground, and airborne EF to derive recommended EF for primary tropical deforestation fires and tropical pasture maintenance fires, (3) new estimates of the vegetative and fire emissions of NMOC at the Amazon-basin and global scale with comments on the significance of the new information, and (4) excess emission ratios and emission factors for sugar cane fires.