

Emission factors for open and domestic biomass burning for use in atmospheric models

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Received: 19 September 2010 – Published in Atmos. Chem. Phys. Discuss.: 12 November 2010

Revised: 14 April 2011 – Accepted: 15 April 2011 – Published: 3 May 2011

Abstract. Biomass burning (BB) is the second largest source of trace gases and the largest source of primary fine carbonaceous particles in the global troposphere. Many recent BB studies have provided new emission factor (EF) measurements. This is especially true for non-methane organic compounds (NMOC), which influence secondary organic aerosol (SOA) and ozone formation. New EF should improve regional to global BB emissions estimates and therefore, the input for atmospheric models. In this work we present an up-to-date, comprehensive tabulation of EF for known pyrogenic species based on measurements made in smoke that has cooled to ambient temperature, but not yet undergone significant photochemical processing. All EFs are converted to one standard form (g compound emitted per kg dry biomass burned) using the carbon mass balance method and they are categorized into 14 fuel or vegetation types. Biomass burning terminology is defined to promote consistency. We compile a large number of measurements of biomass consumption per unit area for important fire types and summarize several recent estimates of global biomass consumption by the major types of biomass burning. Post emission processes are discussed to provide a context for the emission factor concept within overall atmospheric chemistry and also highlight the potential for rapid changes relative to the scale of some models or remote sensing products. Recent work

shows that individual biomass fires emit significantly more gas-phase NMOC than previously thought and that including additional NMOC can improve photochemical model performance. A detailed global estimate suggests that BB emits at least 400 Tg yr⁻¹ of gas-phase NMOC, which is almost 3 times larger than most previous estimates. Selected recent results (e.g. measurements of HONO and the BB tracers HCN and CH₃CN) are highlighted and key areas requiring future research are briefly discussed.

1 Introduction

Biomass burning (BB) can be broadly defined as open or quasi-open combustion of any non-fossilized vegetative or organic fuel. Examples range from open fires in forests, savannas, crop residues, semi-fossilized peatlands, etc. to bio-fuel burning (e.g. cooking fires, dung burning, charcoal or brick making, etc.). Savanna fires, domestic and industrial biofuel use, tropical forest fires, extratropical (mostly boreal) forest fires, and crop residue burning are thought to account for the most global biomass consumption (in the order given). Overall, BB is the largest source of primary fine carbonaceous particles and the second largest source of trace gases in the global atmosphere (Bond et al., 2004; Andreae and Merlet, 2001; Forster et al., 2007; Guenther et al., 2006).



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Particles emitted and formed in BB plumes have major direct and indirect effects on climate (Hobbs et al., 1997; Rosenfeld, 1999) and contribute to dense continental-scale haze layers that occupy much of the tropical boundary layer (and sometimes large parts of the boreal boundary layer) during the dry season (Andreae et al., 1988; Reid et al., 1998; Wofsy et al., 1992; Eck et al., 2003). A multipart review by Reid et al. (2005a, b) focused on the physical and optical properties of biomass burning particles and their impacts. These topics have been the subject of much ongoing research (e.g. Andreae et al., 2004; Ramanathan and Carmichael, 2008; Grieshop et al., 2009).

The trace gases emitted by biomass burning have a significant influence on the atmosphere, which includes a major contribution to the formation of global tropospheric ozone (O_3), an important greenhouse gas (Sudo and Akimoto, 2007). The O_3 formed can also affect air quality: e.g. Pfister et al. (2007) show that BB emissions from California wildfires in 2007 increased downwind ozone concentrations in rural regions. Trace gases from BB can contribute to the secondary formation of aerosol particles (Reid et al., 1998; Alvarado and Prinn, 2009; Yokelson et al., 2009). The effect of BB trace gases on the oxidizing power of the troposphere is an important, complex issue. The hydroxyl radical (OH) is a key oxidant in the global troposphere and is mostly produced in the tropics, which is also where ~ 70 – 80% of BB is thought to occur (Crutzen and Andreae, 1990; van der Werf et al., 2010). The carbon monoxide (CO) and NMOC produced by BB are continually removed via reaction with OH while photolysis of some of the oxygenated NMOC and the O_3 formed in BB plumes can be an OH source (Crutzen and Andreae, 1990; Singh et al., 1995). Coupled with this picture are large tropical biogenic emissions of isoprene, which has a complex oxidation scheme that is still under investigation, but results in some OH regeneration and significant CO production (Lelieveld et al., 2008; Paulot et al., 2009; Archibald et al., 2010; Peeters et al., 2009)

Among the earliest studies to point out the importance of biomass burning on the global scale are the seminal work of Crutzen et al. (1979) and Seiler and Crutzen (1980). Major field campaigns in the 1980's and 1990's resulted in a boom in BB related publications. These are well summarized in a number of review and compilation papers, such as Haywood and Boucher (2000), Andreae and Merlet (2001), Simoneit (2002), Lemieux et al. (2004), and Reid et al. (2005a, b). The work of Andreae and Merlet (2001), in particular, continues to have widespread use in the atmospheric modeling community. For example, the emission factors (EF or EFs, the grams of a compound emitted per kg of dry biomass burned) reported therein can be combined with databases that provide estimates of global biomass consumption such as Global Fire Emissions Database (GFED, van der Werf et al., 2006, 2010) and Fire Locating and Modeling of Burning Emissions (FLAMBE, Reid et al., 2009), to produce emission estimates for atmospheric models. De-

spite the continued utility of previous reviews, a large number of studies have been carried out since ~ 2000 that benefited from advances in instrumentation and the understanding of BB plume chemistry. The results of these studies have not been conveniently compiled in one work. Thus, to aid in the assessment of biomass burning impacts in model simulations, we present an updated compilation with the following rationale:

1. In recent years, the ability has been developed to quantify a wide range of emitted species that were previously unmeasured and thus, often ignored in modeling applications.
2. The effect of rapid plume chemistry on measured emission ratios is better understood. This has led to recognition of the need to compare or combine data from smoke samples of a similar well-defined age in a standardized way. Our compilation of "initial" EF is based on measurements made in smoke that has cooled to ambient temperature, but not yet undergone significant photochemical processing.
3. Many of the studies compiled in this work sampled smoke meeting the "freshness" criteria above and measured a wide range of species from a large number of fires. Studies that are more comprehensive and of fresher smoke may better represent the true regional initial emissions. These EF measurements need to be compiled for convenient use in atmospheric models to promote improved modeling results and assessments.
4. With computational capacity increasing and to promote a wide variety of applications, the link between the fire emissions and the fire type needs to be available at a high level of detail, but still allow straightforward implementation of less detailed schemes. The difference between fire types is small for the EF of some species, but can be quite large for others.
5. Methods need to be developed for dealing with the abundant, but as yet unidentified NMOC, which strongly impact plume chemistry.
6. The calculation of emission rates requires emission factors to be linked to estimates of biomass consumption. Thus we also compile a large number of measurements of biomass consumption per unit burned area for major fire types and several estimates of global biomass consumption by the main fire types.
7. The emission factor tables will be updated when warranted and available at: <http://bai.acd.ucar.edu/Data/fire/>.

In this paper we assess the literature on BB emission factors to address the above issues. We organized the available data into 14 different categories based on the type of fuel

burned and then analyzed each study considering the different properties of the sampled fires (e.g. amount of flaming and smoldering), the attributes of the measuring platforms, instrument sensitivity, and the number of fires sampled. We carefully selected measurements in smoke roughly 5–20 min old, after immediate condensational processes on smoke particles yet prior to most of the photochemistry that can alter the composition of a plume. The age of the smoke sample is important, since current photochemical plume models and larger-scale global atmospheric chemistry models (GACMs) use the emissions as direct inputs before chemical changes occur. Despite the difficulty of modeling rapid changes occurring after emission, initial emission measurements obtained in fresh smoke, as described above, may provide the only clearly defined point in smoke evolution for a bottom-up approach. We also briefly discuss measurements in aged smoke separately to summarize our knowledge of post-emission chemistry, which is both complex and so variable that a single EF for an advanced smoke age would be highly uncertain for most species emitted by BB. This work presents a comprehensive effort tying together recent measurements of emission factors, fuel loadings, plume chemistry, and global BB estimates for the main types of biomass fires to facilitate improved understanding of regional/global tropospheric chemistry.

2 Methods and results

2.1 Terminology and the scope of this compilation

2.1.1 Emission ratios, emission factors and combustion efficiency

An excess mixing ratio (EMR) is defined as the mixing ratio of species X in smoke minus its mixing ratio in background air. The EMR of X is often denoted by “ ΔX ,” where the measured value reflects the degree of plume dilution and the instrument response time (Andreae et al., 1988; Yokelson et al., 1999). As a standardization measure, ΔX is often divided by an EMR of a fairly non-reactive co-emitted smoke tracer (ΔY), such as CO or CO₂; this molar ratio is defined as the normalized excess mixing ratio (NEMR), which can be measured anywhere within a plume. A special case of the NEMR is the “emission ratio” (ER); the molar ratio between two emitted compounds (also written as $\Delta X/\Delta Y$), which should be reserved for emission measurements taken at the source (fresh smoke). The NEMR is highly variable for reactive gases and some aerosol species downwind from fires, and is dependent on the details of the post-emission processing (see Sect. 3.5). Thus for a reactive compound, a NEMR measured downwind may not be equal to the emission ratio even though it is expressed in similar fashion. A simpler alternative term sometimes used to refer to downwind NEMR is the “enhancement ratio” (Lefer et al., 1994),

but since it would have the same abbreviation as “emission ratio” and some species are “depleted” downwind, we do not use this term in this work.

We use ERs to derive EFs in units of grams of X emitted per kilogram of dry biomass burned using the carbon mass balance method (Ward and Radke, 1993) with explicit equations shown elsewhere (e.g. Yokelson et al., 1999). The method assumes that all burned carbon is volatilized or contained in the emitted aerosol and that all major carbon-containing species have been measured. The inability to detect all carbon species can inflate emission factors by 1–2% when using the carbon mass balance method (Andreae and Merlet, 2001). The carbon content in the fuel must also be measured or estimated. In this study we assume a 50% carbon content by mass (dry weight) when a measured value is not available. Except for organic soils and dung, the carbon content of biomass normally ranges between 45 and 55% (Susott et al., 1996; Yokelson et al., 1997; McMeeking et al., 2009). EF scale linearly in proportion to the assumed fuel carbon fraction. Our calculation of EF from charcoal kilns (in units of g X per kg charcoal made) reflects the changing carbon content during the kiln lifetime, as detailed by Bertschi et al. (2003a) and briefly discussed in Sect. 2.3.9.

Combustion efficiency (CE) – the fraction of fuel carbon converted to carbon as CO₂ – can be estimated from measured emission ratios with the detailed equation given elsewhere (e.g. Sinha et al., 2003). The CE at any point in time during a fire, or for the fire as a whole, depends strongly on the relative contribution of flaming and smoldering combustion, with a higher CE indicating more flaming (Ward and Radke, 1993; Yokelson et al., 1996). Flaming combustion involves rapid reaction of O₂ with gases evolved from the solid biomass fuel and is common in foliage or dry, small diameter aboveground biomass. Flaming combustion converts the C, H, N, and S in the fuel into highly oxidized gases such as CO₂, H₂O, NO_x, and SO₂, respectively, and produces most of the black (or elemental) carbon particles. As a fire progresses, smoldering combustion tends to play a more dominant role via both surface oxidation (also known as “glowing” or gasification) and pyrolysis (mostly the thermal breakdown of solid fuel into gases and particles), often affecting large-diameter aboveground biomass and belowground biomass. Smoldering produces most of the CO, CH₄, NMOC, and primary organic aerosol. Smoldering and flaming frequently occur simultaneously during a fire, and distinct combustion phases may not occur. Flaming (~1400 K) and glowing (~800–1000 K) are the two heat sources driving pyrolysis and fuel temperatures can range from unheated to that of a nearby heat source. The widely used term “fire temperature” is based on the amount of 4-micron radiation emitted by a geographic area containing a fire and may not reflect the relative amount of flaming and smoldering (Kaufman et al., 1998). We also note that smoldering is not caused by a deficiency of O₂; rather chemisorption of O₂ on char is exothermic and helps drive glowing combustion (Yokelson

et al., 1996). Depletion of O₂ was measured at only a few percent or less within intense, open fires and O₂ levels may not have a large effect on the gas-phase species emitted by fires (Susott et al., 1991). Large natural variability in fuel geometry, growth stage, moisture, windspeed, etc. causes large natural variability in the relative amount of biomass consumption by flaming and smoldering combustion; even within a single fire type category. This, coupled with variation in fuel chemistry, leads to a large range in the naturally occurring EF for most species for any fire type as discussed more below.

The combustion efficiency, as stated above, can be useful in indicating the relative abundance of flaming and smoldering combustion. Since CE is hard to measure, the modified combustion efficiency (MCE), which is defined as $\Delta\text{CO}_2/(\Delta\text{CO}_2 + \Delta\text{CO})$, is commonly reported as an estimate of CE accurate within a few percent (Ferek et al., 1998). Pure flaming has an MCE near 0.99 while the MCE of smoldering varies over a larger range (~ 0.65 – 0.85), but is most often near 0.8. Thus an overall fire-integrated MCE near 0.9 suggests roughly equal amounts of biomass consumption by flaming and smoldering. Since both CE and MCE indicate the relative amount of flaming and smoldering combustion, both parameters often correlate reasonably well with EF (Fig. 4.3 in Ward and Radke, 1993; Fig. 3 in Yokelson et al., 2003). For example, in Fig. 3 of Yokelson et al. (2003) airborne measurements of EF(CH₄) for individual fires range from $\sim 0.5 \text{ g kg}^{-1}$ to $\sim 3.5 \text{ g kg}^{-1}$ (a factor of 7) with decreasing MCE. Additional variation in EF and MCE would result from considering the unlofted emissions from residual smoldering combustion (RSC) (see, e.g., Bertschi et al., 2003b; Christian et al., 2007; Yokelson et al., 2008). In general, the MCE dependence of “EF(X)” for a fire type allows calculation of a specific EF(X) for any known MCE. However, we do not yet have good data on how regional average MCE may evolve with time over the course of the biomass burning season for the major types of burning. Thus, in this work we only report average EF for each fire type and (where possible) a very rough estimate of the expected naturally occurring range in the average EF appropriate for a typical group of fires. The calculation of these values is described in detail in Sect. 2.3.

2.1.2 NMOC, OVOC, and NMHC

Non-methane hydrocarbons (NMHC) are defined as organic compounds excluding methane (CH₄) that contain only C and H; examples include alkanes, alkenes, alkynes, aromatics, and terpenes. Oxygenated volatile organic compounds (OVOC) contain C, H, and O; examples include alcohols, aldehydes, ketones, and organic acids. NMHC and OVOC together account for nearly all the gas-phase non-methane organic compounds (NMOC) emitted by fires. The distinction is important when discussing the role of NMOCs in post-emission chemistry. All of the organic compounds are impor-

tant in secondary processes such as ozone and aerosol formation, but the OVOC are more abundant (60–80% of NMOC on a molar basis, Yokelson et al., 2008), and the OVOC and NMHC tend to have different atmospheric chemistry (Singh et al., 1995; Finlayson-Pitts and Pitts, 2000). It is also important to note that only on the order of 50% (by mass) of the observed gas-phase NMOC can be assigned to specific compounds (Christian et al., 2003; Karl et al., 2007). The remaining unidentified species are mostly high molecular weight NMOC. The unidentified species evidently play a large role in plume chemistry (Sect. 3.4, Trentmann et al., 2005; Alvarado and Prinn, 2009). We discuss NMOC in detail and estimate total global NMOC considering the large percentage of compounds that remain unidentified in Sect. 3.4.

2.1.3 Common terminology used in computing regional/global emission estimates

We briefly define common terms used in quantifying biomass for emission estimates. Biomass is described as primarily live (phytomass) or dead (necromass) plant material and can be discussed as total aboveground biomass (TAGB) – referring to the litter layer and everything above – or total belowground biomass (TBGB), referring to duff, peat, organic soils, and roots (Seiler and Crutzen, 1980). Both terms are normally expressed on a dry weight basis. Fuel moisture can be calculated as (wet weight-dry weight)/dry weight, and along with fuel geometry affects what biomass is likely to burn. The term “fuel” in the forestry literature refers to only that portion of the total available biomass that normally burns under specified fire conditions (Nearby et al., 2005). Thus, “fuel” and “biomass” are not equivalent terms in forestry, although they are sometimes used interchangeably by atmospheric chemists. Both fuel and biomass *loading* are typically expressed as the mass of fuel or biomass per unit area on a dry weight basis. A combustion factor is the fraction of biomass exposed to a fire that was actually consumed or volatilized. The biomass loading is often multiplied by a combustion factor to derive an estimate of how much biomass was consumed, otherwise known as the biomass consumption (per unit area). An estimate of the total combusted biomass can be obtained given biomass consumption per unit area and an estimate of the area burned. Measurements of biomass consumption per unit area burned have been published and we compile these values for several main fire types (e.g. savanna, boreal and tropical forest) in Sect. 2.4.

2.1.4 Sampling considerations and study selection criteria for this compilation

Smoke contains numerous species with atmospheric lifetimes ranging from micro-seconds to years. Other than a few continuously regenerated intermediates, current technology can only measure atmospheric species that are abundant and

stable enough to have lifetimes of a few minutes or longer. In practice this means that measurements show the effects of aging for some detected species unless samples are taken within 10s of meters above lab fires or within 1–2 km of fires in the field. Under these conditions, smoke typically has CO concentrations in the range 5–1500 ppmv in the lab or on the ground, and 2–30 ppmv in airborne studies. Figure 3 in Christian et al. (2003) or Figs. 2–4 in Yokelson et al. (2008) show that field samples meeting the above “freshness criteria” can often return similar emission factors for trace gases when compared to lab studies at the same MCE. Laboratory fires sometimes tend to burn with a different average MCE than fires in similar fuels burning in the natural environment, but this can be accounted for as described in Yokelson et al. (2008).

For particles and semi-volatile organic compounds (SVOC) the picture is less clear. Particulate matter (PM, solid or liquid particles suspended in air) is directly emitted from fires, but can also be formed through secondary processes that may involve SVOC. The lab EF(PM) vs. MCE can be quite consistent with low-level airborne measurements of EF(PM) vs. MCE (e.g., Fig. 5 of Yokelson et al., 2008). On the other hand, Babbitt et al. (1996) compared EF(PM_{2.5}) (particles with aerodynamic diameter <2.5 microns) measured from 30 m towers above Brazilian fires to EF(PM_{2.5}) measured using identical gravimetric methods from an aircraft flying over the same fires. Except for the lowest MCE fire (perhaps the coolest smoke) the ground-based EF(PM_{2.5}) were only about one-half those measured from the air, while the agreement for volatile trace gases vs. MCE from both platforms was excellent. In order to prevent highly sensitive particle instruments from saturating, some lab BB studies employ rapid dilution with room temperature air. This could possibly differ from the dilution/cooling regime associated with injection of emissions into the atmosphere during some real fires. Thus, for now, we favored the data from low-level airborne smoke samples (taken after any rapid initial cooling, but before most of the photochemistry) to derive our “initial emissions” of particles (and SVOC if available). Our compilation does include lab-measured EF for two scenarios: (1) when the fuel burns entirely by smoldering combustion in the natural environment (e.g. peat, duff), and (2) when the fuel burns by both flaming and smoldering, but the authors took special care to realistically replicate the natural fuel complex and they report data for compounds not yet measured in the field. For example, the lab study of Goode et al. (1999) was the first to use FTIR on grass fires, but none of the results are included because they are superseded by the FTIR-based field study of savanna fires by Yokelson et al. (2003). On the other hand, we include the lab study of Christian et al. (2003), which carefully replicated savanna fires and also features the only proton-transfer mass spectrometer (PTR-MS) measurements of the emissions from this fire type. Finally, we point out that a lot of important work has characterized particle emissions from lab fires recently

(e.g. Chen et al., 2006; Engling et al., 2006; Hopkins et al., 2007; Mazzoleni et al., 2007; Chakrabarty et al., 2010), but did not report the results as EF. Thus, it was not always clear how to incorporate these results into initial particle characteristics for models that would be analogous to the trace gas and particle EF we report.

Another important consideration for field studies is that smoldering combustion can produce unlofted smoke with low MCE that is not amenable to airborne sampling. Ground-based sampling can measure these sometimes substantial emissions, but realistic estimates of the biomass consumption contributing to the two different types of smoke are needed to properly weight the ground-based and airborne measurements (Christian et al., 2007).

In order to present a compilation that is as up to date as possible, we include some EF values from papers under review and a few preliminary EF values that are believed to be “final” from papers on the verge of submission. These values are clearly indicated in the Supplement Tables and the reader using these values should locate the forthcoming publications, check for updates, and cite those publications directly. In general we encourage the reader to examine and cite the original work that we compile and also consider modifying our averaging schemes to better suit their specific needs.

2.2 Fire-type categories

2.2.1 Vegetation

We organize the selected EF for landscape-scale fires into six broad types of vegetation susceptible to burning: savanna, tropical forest, boreal forest, temperate forest, peatlands, and chaparral. We split the category “extratropical forest” used by Andreae and Merlet (2001) into “boreal” (high latitude ~50–70° forested regions) and “temperate” forest. We also derive EF for “extratropical” forest fires using a weighted average of boreal and temperate emission factors (86.5% and 13.5%, respectively) based on GFED3 biomass consumption estimates (van der Werf et al., 2010) to preserve the option of using this category. We present a specific category for chaparral (a type of temperate shrubland) since the emissions from chaparral fires are important in the southwestern US and shrublands are widespread globally (Friedl et al., 2002). (Some of the temperate forest and chaparral EF we include are flagged as preliminary in the Supplement Tables.) Our category “tropical forest” includes tropical evergreen forest deforestation fires, tropical dry forest deforestation fires, and tropical dry forest understory fires. Tropical dry forest is also called “seasonal” or “monsoon” forest. Tropical dry forests (TDF) differ from “woody” savanna regions in that TDF are characterized by a significant (>60%) canopy coverage or closed canopies (Mooney et al., 1995; Friedl et al., 2002). Savanna regions are qualitatively described as grassland with an “open” canopy of trees (if any). Our savanna category includes the savanna, woody savanna, and grassland categories

in the detailed MODIS land cover products (Friedl et al., 2002). Our savanna and tropical forest categories contribute the most open burning emissions globally (Andreae and Merlet, 2001). While peatlands represent 3% of terrestrial cover, they hold about one third of the world's soil carbon (Rein et al., 2009; Yu et al., 2010) and can be a significant contributor to annual carbon emissions (Page et al., 2002).

2.2.2 Biofuel

We use “biofuel” as a specific term denoting biomass used as a domestic or industrial energy source. In assessing the impacts of biofuel it is worth recalling that, in principle, it could be regrown so is potentially “renewable” unlike fossil fuel. Rural populations in developing countries rely heavily on biomass burning as a primary source of energy (Smil, 1979; Cecelski et al., 1979; Yevich and Logan, 2003). The amount of biofuel use in urban areas of the developing world is not known, but may be significant (Christian et al., 2010). Over the 50-yr period from 1950–2000, Fernandes et al. (2007) estimated a 70% growth in global annual biofuel consumption making it now the second largest type of global biomass burning after savanna fires (Andreae and Merlet, 2001), but future trends are hard to predict. In this work we present biofuel emission factors for open cooking fires, dung burning, Patsari cooking stoves, charcoal making, and charcoal burning. Open cooking fires are the single largest contributor to global biofuel emissions accounting for roughly 80% of current biofuel use worldwide (Dherani et al., 2008). Various stove designs are available, but the most complete emissions measurements have been made for Patsari stoves; therefore, we selected them to represent emissions from all types of biofuel stoves. Patsari stoves are used in Mexico and incorporate an insulated fire box that vents emissions outdoors via a metal chimney (Christian et al., 2010). The stoves are designed to replace traditional open three-stone fires and can reduce indoor air pollution by 70%. Stoves in general require less fuel per cooking task than open cooking fires, which reduces emissions and pressure on biofuel sources (Johnson et al., 2008; Masera et al., 2005; Zuk et al., 2007). For the above reasons there is considerable international activity to encourage switching from open cooking fires to stoves. In addition, the Patsari stove emissions were found to have different chemistry than open cooking fire emissions (Johnson et al., 2008; Christian et al., 2010), further justifying a separate category in this study. While not fully representative of all cooking stoves, the Patsari stove EF likely represent most stove emissions better than EF for open cooking fires and might be used to help assess the impact of changes in how biofuel is used.

Dung as a biofuel is mainly of note in Asia, dominated by use in India and China (Yevich and Logan, 2003). Its use in most other rural areas globally is less common than that of woodfuel (though sometimes still significant), and overall it comprises approximately 5% of the total dry matter burned

as biofuel (Yevich and Logan, 2003). Charcoal is mainly produced in rural areas and often consumed in urban areas, accounting for ~10% of global biofuel use (Bertschi et al., 2003a).

2.2.3 Agricultural/waste burning

Crop residue and pasture maintenance fires and open burning of garbage can be common both in rural agricultural regions and peri-urban areas. For instance, sugarcane burning is the main source of PM in some Brazilian cities (Lara et al., 2005; Cançado et al., 2006). Crop residue burning has been estimated as the fourth largest type of biomass burning (Andreae and Merlet, 2001), but these emissions could be greatly underestimated given the difficulty of detecting these often short-lived, relatively small fires from space (Hawbaker et al., 2008; Smith et al., 2007; Chang and Song, 2010a; van der Werf et al., 2010). Crop residue may be burned 1–3 times a year on a single site depending on the rate of annual harvest. Some crop residue is utilized as biofuel (especially in China), blurring the distinction between these categories (Yevich and Logan, 2003). A recent increase in crop residue burning is likely in large areas of the Amazon concurrent with a shift in land use from cattle ranching to crop production (Cardille and Foley, 2003; Morton et al., 2006). Pasture maintenance burning is performed every 2–3 yr to prevent reconversion of pasture to forest. These fires frequently include residual smoldering combustion of large logs that can burn for weeks after the flames have ceased (Kuffman et al., 1998). Garbage burning is normally overlooked as an emissions source. However, Christian et al. (2010) estimate that ~2000 Tg yr⁻¹ of garbage are generated globally and roughly half may be burned in open fires or incinerators. Partly because open garbage burning is often illegal, it is unmentioned in most inventories. We compile the few available EF for open burning of garbage as a separate category.

2.3 Assessment, calculation, and application of emission factors for specific fire types

This section provides the details of how we analyzed the emission factors. We classify biomass burning into 14 categories. For each of these categories, we organize the information by study in Supplement Tables S1–S14 for all studies meeting our selection criteria (updates at: <http://bai.acd.ucar.edu/Data/fire/>). For each included study we show the study-average emission factors and any additional specifics considered in calculating an overall average and estimate of the natural variation for the whole category. The rationale supporting the calculation of the category average and variation is summarized in the following sections. We present just the category average emission factors and category variability for all 14 BB categories in Tables 1 and 2. Our classification scheme allows consideration/assessment of fairly specific emission types while retaining the option of merging

Table 1. Emission factors (g kg^{-1}) for species emitted from different types of biomass burning^a.

	Tropical Forest	Savanna	Crop Residue	Pasture Maintenance	Boreal Forest	Temperate Forest	Extratropical Forest ^b
Carbon Dioxide (CO ₂)	1643 (58)	1686 (38)	1585 (100)	1548 (142)	1489 (121)	1637 (71)	1509 (98)
Carbon Monoxide (CO)	93 (27)	63 (17)	102 (33)	135 (38)	127 (45)	89 (32)	122 (44)
Methane (CH ₄)	5.07 (1.98)	1.94 (0.85)	5.82 (3.56)	8.71 (4.97)	5.96 (3.14)	3.92 (2.39)	5.68 (3.24)
Acetylene (C ₂ H ₂)	0.44 (0.35)	0.24 (0.10)	0.27 (0.08)	0.21 (0.29)	0.18 (0.10)	0.29 (0.10)	0.19 (0.090)
Ethylene (C ₂ H ₄)	1.06 (0.37)	0.82 (0.35)	1.46 (0.59)	1.28 (0.71)	1.42 (0.43)	1.12 (0.35)	1.38 (0.42)
Ethane (C ₂ H ₆)	0.71 (0.28)	0.66 (0.41)	0.91 (0.49)	0.95 (0.43)	1.79 (1.14)	1.12 (0.67)	1.70 (1.05)
Propadiene (C ₃ H ₄)	0.016 (0.0066)	0.012 (0.005)	–	0.020 (0.009)	–	–	–
Propylene (C ₃ H ₆)	0.64 (0.43)	0.79 (0.56)	0.68 (0.37)	0.85 (0.66)	1.13 (0.60)	0.95 (0.54)	1.11 (0.61)
Propyne (C ₃ H ₄)	–	–	–	–	0.059	–	0.059
Propane (C ₃ H ₈)	0.126 (0.060)	0.10 (0.067)	0.28 (0.15)	0.22 (0.10)	0.44	0.26 (0.11)	0.42 (0.18)
<i>n</i> -Butane (C ₄ H ₁₀)	0.038 (0.023)	0.016 (0.013)	0.072 (0.036)	0.040 (0.018)	0.12	0.083 (0.10)	0.12 (0.14)
<i>i</i> -Butane (C ₄ H ₁₀)	0.011 (0.009)	0.0043 (0.0027)	0.025 (0.013)	0.014 (0.0063)	0.042	–	0.042
1-Butene (C ₄ H ₈)	0.079 (0.024)	0.043 (0.022)	0.134 (0.060)	0.17 (0.077)	0.16	–	0.16
<i>i</i> -Butene (C ₄ H ₈)	0.11 (0.051)	0.024 (0.0051)	0.117 (0.060)	0.11 (0.05)	0.11	–	0.11
1,3-Butadiene (C ₄ H ₆)	0.039	0.052 (0.028)	0.151 (0.072)	–	0.14	–	0.14
trans-2-Butene (C ₄ H ₈)	0.029 (0.013)	0.011 (0.0055)	0.057 (0.030)	0.050 (0.023)	0.040	–	0.040
cis-2-Butene (C ₄ H ₈)	0.024 (0.010)	0.0084 (0.0043)	0.043 (0.023)	0.040 (0.018)	0.030	–	0.030
<i>n</i> -Pentane (C ₅ H ₁₂)	8.03×10^{-3} (8.03×10^{-3})	0.0032 (0.0032)	0.025 (0.012)	0.0056 (0.0025)	0.085	–	0.085
<i>i</i> -Pentane (C ₅ H ₁₂)	0.010 (0.010)	0.0022 (0.0032)	0.020 (0.012)	0.0074 (0.0033)	0.038	–	0.038
trans-2-Pentene (C ₅ H ₁₀)	3.30×10^{-3}	0.0045 (0.0028)	–	–	–	–	–
cis-2-Pentene (C ₅ H ₁₀)	1.90×10^{-3}	0.0025 (0.0018)	–	–	–	–	–
3-Methyl-1-Butene (C ₅ H ₁₀)	3.80×10^{-3}	0.0051 (0.0034)	–	–	–	–	–
2-Methyl-2-Butene (C ₅ H ₁₀)	4.00×10^{-3}	0.0048 (0.0035)	–	–	–	–	–
2-Methyl-1-Butene (C ₅ H ₁₀)	4.40×10^{-3}	0.0059 (0.0037)	–	–	–	–	–
Isoprene (C ₅ H ₈)	0.13 (0.056)	0.039 (0.027)	0.38 (0.16)	0.12 (0.055)	0.15	–	0.15
Cyclopentane (C ₅ H ₁₀)	–	–	0.0019 (0.0012)	–	–	–	–
2+3-Methylpentane (C ₆ H ₁₄)	–	–	–	–	0.036	–	0.036
2-Methyl-1-Pentene (C ₆ H ₁₂)	2.80×10^{-3}	0.0035 (0.0021)	–	–	–	–	–
<i>n</i> -Hexane (C ₆ H ₁₄)	0.010	0.013 (0.0074)	–	–	0.055	–	0.055
Heptane (C ₇ H ₁₆)	5.60×10^{-3}	0.0070 (0.0072)	–	–	0.048	–	0.048
Benzene (C ₆ H ₆)	0.39 (0.16)	0.20 (0.084)	0.15 (0.04)	0.70 (0.32)	1.11	–	1.11
Toluene (C ₆ H ₅ CH ₃)	0.26 (0.13)	0.080 (0.058)	0.19 (0.06)	0.34 (0.15)	0.48	–	0.48
Xylenes (C ₈ H ₁₀)	0.11 (0.082)	0.014 (0.024)	–	0.11 (0.050)	0.18	–	0.18
Ethylbenzene (C ₈ H ₁₀)	0.050 (0.036)	0.006 (0.010)	–	0.067 (0.030)	0.051	–	0.051
<i>n</i> -Propylbenzene (C ₉ H ₁₂)	–	–	–	–	0.018	–	0.018
α -Pinene (C ₁₀ H ₁₆)	–	–	–	–	1.64	–	1.64
β -Pinene (C ₁₀ H ₁₆)	–	–	–	–	1.45	–	1.45
Ethanol (CH ₃ CH ₂ OH)	–	–	–	–	0.055	–	0.055
Methanol (CH ₃ OH)	2.43 (0.80)	1.18 (0.41)	3.29 (1.38)	5.84 (3.42)	2.82 (1.62)	1.93 (1.38)	2.70 (1.75)
Phenol (C ₆ H ₅ OH)	0.45 (0.088)	0.52 (0.36)	0.52 (0.14)	1.68 (3.34)	2.96	0.33 (0.38)	2.60 (3.00)
Formaldehyde (HCHO)	1.73 (1.22)	0.73 (0.62)	2.08 (0.84)	1.90 (1.11)	1.86 (1.26)	2.27 (1.13)	1.92 (1.14)
Glycolaldehyde (C ₂ H ₄ O ₂)	2.84	0.81 (0.38)	2.01 (0.38)	–	0.77	0.25 (0.45)	0.70 (1.26)
Acetaldehyde (CH ₃ CHO)	1.55 (0.75)	0.57 (0.30)	1.24 (0.28)	2.40 (1.08)	–	–	–
Acrolein (C ₃ H ₄ O)	0.65 (0.23)	–	–	–	–	–	–
Furaldehydes	0.29 (0.0010)	–	–	–	–	–	–
Propanal (C ₃ H ₆ O)	0.10 (0.026)	–	–	0.16 (0.074)	–	–	–
Methyl Propanal (C ₄ H ₈ O)	0.18 (0.075)	–	–	0.33 (0.15)	–	–	–
Hexanal (C ₆ H ₁₂ O)	0.01 (0.005)	–	–	0.034 (0.015)	–	–	–
Acetone (C ₃ H ₆ O)	0.63 (0.17)	0.16 (0.13)	0.45 (0.07)	1.05 (0.47)	0.75	–	0.75
Methyl Vinyl Ether (C ₃ H ₆ O)	–	0.16 (0.045)	0.08 (0.01)	–	–	–	–
Methacrolein (C ₄ H ₆ O)	0.15 (0.045)	–	–	0.40 (0.18)	0.087	–	0.087
Crotonaldehyde (C ₄ H ₆ O)	0.24 (0.068)	–	–	0.60 (0.27)	–	–	–
2,3-Butanedione (C ₄ H ₆ O ₂)	0.73 (0.22)	–	–	1.58 (0.71)	–	–	–
Methyl Vinyl Ketone (C ₄ H ₆ O)	0.39 (0.11)	–	–	1.00 (0.45)	0.20	–	0.20
Methyl Ethyl Ketone (C ₄ H ₈ O)	0.50 (0.21)	–	–	0.94 (0.42)	0.22	–	0.22
2-Pentanone (C ₅ H ₁₀ O)	0.08 (0.024)	–	–	0.17 (0.077)	–	–	–
3-Pentanone (C ₅ H ₁₀ O)	0.03 (0.011)	–	–	0.08 (0.034)	–	–	–
Furan (C ₄ H ₄ O)	0.41 (0.10)	0.17 (0.058)	0.11 (0.04)	1.02 (0.43)	0.80 (0.50)	0.20 (0.21)	0.72 (0.62)
3-Methylfuran (C ₅ H ₆ O)	0.59 (0.20)	–	–	1.41 (0.64)	–	–	–
2-Methylfuran (C ₅ H ₆ O)	0.08 (0.028)	–	–	0.20 (0.091)	–	–	–
Other substituted furans	1.21 (0.016)	–	–	–	–	–	–
C ₆ Carbonyls	0.24 (0.11)	–	–	0.61 (0.28)	–	–	–
Acetol (C ₃ H ₆ O ₂)	1.13 (0.12)	0.45 (0.24)	3.77 (0.91)	6.18 (5.60)	–	–	–
Acetonitrile (CH ₃ CN)	0.41 (0.10)	0.11 (0.058)	0.21 (0.06)	0.55 (0.25)	0.61	–	0.61
Propenenitrile (C ₃ H ₃ N)	0.04 (0.01)	0.051 (0.022)	0.03 (0.002)	–	–	–	–
Propanenitrile (C ₃ H ₅ N)	0.090	0.031 (0.014)	0.06 (0.002)	–	–	–	–

Table 1. Continued.

	Tropical Forest	Savanna	Crop Residue	Pasture Maintenance	Boreal Forest	Temperate Forest	Extratropical Forest ^b
Pyrrole (C ₄ H ₅ N)	0.12 (0.038)	–	–	–	–	–	–
Formic Acid (HCOOH)	0.79 (0.66)	0.21 (0.096)	1.00 (0.49)	0.20 (0.64)	0.57 (0.46)	0.35 (0.33)	0.54 (0.47)
Acetic Acid (CH ₃ COOH)	3.05 (0.90)	3.55 (1.47)	5.59 (2.55)	10.4 (6.8)	4.41 (2.66)	1.97 (1.66)	4.08 (2.99)
Hydrogen Cyanide (HCN)	0.42 (0.26)	0.41 (0.15)	0.29 (0.38)	0.46 (0.45)	1.52 (0.82)	0.73 (0.19)	1.41 (0.60)
Dimethyl Sulfide (C ₂ H ₆ S)	1.35 × 10 ⁻³ (1.71 × 10 ⁻³)	0.0013 (0.0011)	–	–	4.65 × 10 ⁻³	–	4.65 × 10 ⁻³
Carbonyl Sulfide (OCS)	0.025	–	–	–	0.46 (0.47)	–	0.46 (0.47)
Chloromethane (CH ₃ Cl)	0.053 (0.038)	0.055 (0.036)	–	0.29 (0.13)	0.059	–	0.059
Dibromomethane (CH ₂ Br ₂)	–	–	–	–	8.28 × 10 ⁻⁵	–	8.28 × 10 ⁻⁵
1,2-Dichloroethane (C ₂ H ₄ Cl ₂)	–	–	–	–	1.29 × 10 ⁻³	–	1.29 × 10 ⁻³
Methyl Bromide (CH ₃ Br)	2.83 × 10 ⁻³ (2.38 × 10 ⁻³)	8.53 × 10 ⁻⁴ (8.62 × 10 ⁻⁴)	–	5.71 × 10 ⁻³ (2.57 × 10 ⁻³)	3.64 × 10 ⁻³	–	3.64 × 10 ⁻³
Methyl Iodide (CH ₃ I)	2.50 × 10 ⁻³ (3.45 × 10 ⁻³)	5.06 × 10 ⁻⁴ (3.88 × 10 ⁻⁴)	–	3.48 × 10 ⁻³ (1.56 × 10 ⁻³)	7.88 × 10 ⁻⁴	–	7.88 × 10 ⁻⁴
Trichloromethane (CHCl ₃)	2.94 × 10 ⁻⁴ (6.75 × 10 ⁻³)	0.012 (0.020)	–	6.32 × 10 ⁻⁴ (2.84 × 10 ⁻⁴)	–	–	–
Dichlorodifluoromethane (CCl ₂ F ₂)	2.80 × 10 ⁻³	–	–	–	–	–	–
Ethylchloride (C ₂ H ₅ Cl)	–	–	–	–	7.47 × 10 ⁻⁴	–	7.47 × 10 ⁻⁴
Ammonia (NH ₃)	1.33 (1.21)	0.52 (0.35)	2.17 (1.27)	1.47 (1.29)	2.72 (2.32)	0.78 (0.82)	2.46 (2.35)
Methyl Nitrate (CH ₃ ONO ₂)	8.29 × 10 ⁻³ (1.60 × 10 ⁻²)	5.1 × 10 ⁻⁴ (3.7 × 10 ⁻⁴)	–	–	2.83 × 10 ⁻³	–	2.83 × 10 ⁻³
Ethyl Nitrate (C ₂ H ₅ NO ₃)	5.70 × 10 ⁻³	–	–	–	1.78 × 10 ⁻³	–	1.78 × 10 ⁻³
<i>n</i> -Propyl Nitrate (C ₃ H ₇ NO ₃)	0.0003	–	–	–	3.23 × 10 ⁻⁴	–	3.23 × 10 ⁻⁴
<i>i</i> -Propyl Nitrate (C ₃ H ₇ NO ₃)	0.001	–	–	–	3.23 × 10 ⁻³	–	3.23 × 10 ⁻³
2-Butyl Nitrate (C ₄ H ₉ NO ₃)	0.0006	–	–	–	3.84 × 10 ⁻³	–	3.84 × 10 ⁻³
3-Pentyl Nitrate (C ₅ H ₁₁ NO ₃)	–	–	–	–	7.27 × 10 ⁻⁴	–	7.27 × 10 ⁻⁴
2-Pentyl Nitrate (C ₅ H ₁₁ NO ₃)	–	–	–	–	9.70 × 10 ⁻⁴	–	9.70 × 10 ⁻⁴
3-Methyl-2-Butyl Nitrate (C ₅ H ₁₁ NO ₃)	–	–	–	–	1.15 × 10 ⁻³	–	1.15 × 10 ⁻³
3-Ethyltoluene (C ₉ H ₁₂)	–	–	–	–	0.024	–	0.024
2-Ethyltoluene (C ₉ H ₁₂)	–	–	–	–	0.011	–	0.011
4-Ethyltoluene (C ₉ H ₁₂)	–	–	–	–	0.015	–	0.015
1,2,3-Trimethylbenzene (C ₉ H ₁₂)	–	–	–	–	0.051	–	0.051
1,2,4-Trimethylbenzene (C ₉ H ₁₂)	–	–	–	–	0.030	–	0.030
1,3,5-Trimethylbenzene (C ₉ H ₁₂)	–	–	–	–	5.86 × 10 ⁻³	–	5.86 × 10 ⁻³
Hydrogen (H ₂)	3.36 (1.30)	1.70 (0.64)	2.59 (1.78)	–	–	2.03 (1.79)	2.03 (1.79)
Sulfur Dioxide (SO ₂)	0.40 (0.19)	0.48 (0.27)	–	0.32 (0.14)	–	–	–
Nitrous Acid (HONO)	1.18	0.20	–	0.16 (0.07)	–	0.52 (0.15)	0.52 (0.15)
Nitrogen Oxides (NO _x as NO)	2.55 (1.40)	3.9 (0.80)	3.11 (1.57)	0.75 (0.59)	0.90 (0.69)	2.51 (1.02)	1.12 (0.69)
Nitrous Oxide (N ₂ O)	–	–	–	–	0.41	0.16 (0.21)	0.38 (0.35)
NMOC (identified)	26.0 (8.8)	12.4 (6.2)	25.7 (9.8)	44.8 (30.1)	29.3 (10.1)	11.9 (7.6)	27.0 (13.8)
NMOC (identified + unidentified) ^c	51.9	24.7	51.4	89.6	58.7	23.7	54.0
Total Particulate Carbon	5.24 (2.91)	3.00 (1.43)	–	10.6 (4.8)	–	–	–
Total Suspended Particulate (TSP)	13	–	–	–	–	–	–
CN (particles 0.003–3 μm diameter) ^d	5.90 × 10 ¹⁶	–	–	–	–	–	–
PM _{2.5} ^e	9.1 (3.5)	7.17 (3.42)	6.26 (2.36)	14.8 (6.7)	15.3 (5.9)	12.7 (7.5)	15.0 (7.5)
PM ₁₀	18.5 (4.1)	–	–	28.9 (13.0)	–	–	–
Black Carbon (BC)	0.52 (0.28)	0.37 (0.20)	0.75	0.91 (0.41)	–	–	0.56 (0.19) ^f
Organic Carbon (OC)	4.71 (2.73)	2.62 (1.24)	2.30	9.64 (4.34)	–	–	8.6–9.7 ^f
Oxylate (C ₂ O ₄)	0.04 (0.034)	0.0055 (0.0055)	–	0.040 (0.018)	–	–	–
Nitrate (NO ₃)	0.11 (0.050)	0.016 (0.013)	–	0.14 (0.063)	–	–	–
Phosphate (PO ₄)	5.56 × 10 ⁻³ (8.99 × 10 ⁻³)	0.0045 (0.0060)	–	1.07 × 10 ⁻³ (4.80 × 10 ⁻⁴)	–	–	–
Sulfate (SO ₄)	0.13 (0.088)	0.018 (0.009)	–	0.19 (0.086)	–	–	–
Ammonium (NH ₄)	5.64 × 10 ⁻³ (1.72 × 10 ⁻²)	0.0035 (0.0035)	–	3.97 × 10 ⁻³ (1.79 × 10 ⁻³)	–	–	–
Cl	0.15 (0.16)	0.23 (0.055)	–	0.24 (0.11)	–	–	–
Ca	0.085 (0.089)	0.021 (0.018)	–	0.020 (0.009)	–	–	–
Mg	0.040 (0.034)	0.016 (0.007)	–	0.030 (0.014)	–	–	–
Na	6.37 × 10 ⁻³ (5.46 × 10 ⁻³)	0.0055 (0.0045)	–	0.030 (0.014)	–	–	–
K	0.29 (0.28)	0.23 (0.053)	–	0.34 (0.15)	–	–	–

^a See Sect. 2.3 for guidance in use. Emission factors are shown with an estimate of the natural variation in parenthesis, when available.

^b EF calculated from a weighted average of boreal and temperate forest EF based on GFED3 biomass consumption estimates.

^c Estimated (see Sect. 3.4).

^d Number of particles per kg of fuel burned.

^e PM₁–PM₅ categorized as PM_{2.5}.

^f Source is Andreae and Merlet (2001).

categories at the user's discretion. As an example, we also derive values for an "extratropical forest" category (shown in Table 1) by merging the boreal and temperate forest EF with the formula described in Sect. 2.2.1. Some users may instead desire EF in more detail than is provided by our 14 categories in Tables 1–2 and this can often be retrieved by

consulting the Supplement Tables. For instance, the EF for smoldering combustion of hand-piled crop residue (common in much of Asia) are very different from the EF for flaming combustion of crop residue produced by mechanized agriculture and they can be found separately in Table S13.

Table 2. Emission factors (g kg^{-1}) for species emitted from different types of biomass burning^a.

Compound	Peatland ^b	Chaparral	Open Cooking	Patsari Stoves	Charcoal Making ^c	Charcoal Burning ^d	Dung Burning	Garbage Burning
Carbon Dioxide (CO ₂)	1563 (65)	1710 (39)	1548 (125)	1610 (114)	1626 (244)	2385	859 (15)	1453 (69)
Carbon Monoxide (CO)	182 (60)	67 (13)	77 (26)	42 (19)	255 (52)	189 (36)	105 (10)	38 (19)
Methane (CH ₄)	11.8 (7.8)	2.51 (0.72)	4.86 (2.73)	2.32 (1.38)	39.6 (11.4)	5.29 (2.42)	11.0 (3.3)	3.66 (4.39)
Acetylene (C ₂ H ₂)	0.14 (0.093)	0.20 (0.08)	0.97 (0.50)	0.28 (0.01)	0.21 (0.02)	0.42	–	0.40 (0.28)
Ethylene (C ₂ H ₄)	1.79 (0.72)	0.75 (0.18)	1.53 (0.66)	0.46 (0.12)	3.80 (1.15)	0.44 (0.23)	1.12 (0.23)	1.26 (1.04)
Ethane (C ₂ H ₆)	–	0.36 (0.11)	1.50 (0.50)	–	12.2 (9.3)	0.41 (0.13)	–	–
Propylene (C ₃ H ₆)	2.3 (0.74)	0.38 (0.13)	0.57 (0.34)	0.03	4.12 (1.89)	–	1.89 (0.42)	1.26 (1.42)
Propane (C ₃ H ₈)	–	0.19 (0.09)	–	–	–	–	–	–
Butane (C ₄ H ₁₀)	–	0.14 (0.07)	–	–	–	–	–	–
Isoprene (C ₅ H ₈)	1.07 (0.44)	–	–	–	–	–	–	–
Toluene (C ₆ H ₅ CH ₃)	1.21 (0.69)	–	–	–	–	–	–	–
Benzene (C ₆ H ₆)	2.46 (1.21)	–	–	–	–	–	–	–
Methanol (CH ₃ OH)	5.36 (3.27)	0.80 (0.28)	2.26 (1.27)	0.39 (0.39)	54.9 (27.9)	1.01	4.14 (0.88)	0.94 (1.25)
Acetol (C ₃ H ₆ O ₂)	1.92 (0.20)	–	–	–	21.6 (35.3)	–	9.60 (2.38)	–
Phenol (C ₆ H ₅ OH)	4.36 (5.06)	0.45 (0.21)	3.32	–	10.4 (6.6)	–	2.16 (0.36)	–
Furan (C ₄ H ₄ O)	1.51 (0.37)	0.18 (0.10)	0.40	–	3.94 (2.30)	–	0.95 (0.22)	–
Formaldehyde (HCHO)	1.69 (1.62)	0.83 (0.25)	2.08 (0.86)	0.37 (0.40)	3.62 (2.42)	0.60	–	0.62 (0.13)
Glycolaldehyde (C ₂ H ₄ O ₂)	2.62 (4.18)	0.23 (0.20)	1.42	–	–	–	–	–
Acetaldehyde (CH ₃ CHO)	2.81 (1.36)	–	–	–	–	–	–	–
Carbonyl Sulfide (OCS)	1.20 (2.21)	–	–	–	–	–	–	–
Acetic Acid (CH ₃ COOH)	7.08 (3.40)	1.10 (0.50)	4.97 (3.32)	0.34	44.8 (27.3)	2.62	11.7 (5.08)	2.42 (3.32)
Formic Acid (HCOOH)	0.54 (0.71)	0.06 (0.04)	0.22 (0.17)	0.0048	0.68 (0.20)	0.063	0.46 (0.31)	0.18 (0.12)
Acetone (C ₃ H ₆ O)	1.08 (0.29)	–	–	–	–	–	–	–
Hydrogen Cyanide (HCN)	5.00 (4.93)	0.38 (0.12)	–	–	0.21 (0.17)	–	0.53 (0.30)	0.47
Methyl Ethyl Ketone (C ₄ H ₈ O)	–	–	–	–	–	–	–	–
Hydrogen Chloride (HCl)	–	0.17 (0.14)	–	–	–	–	–	3.61 (3.27)
Methyl Vinyl Ether (C ₃ H ₆ O)	0.85	–	–	–	–	–	–	–
Acetonitrile (CH ₃ CN)	3.70 (0.90)	–	–	–	–	–	–	–
Sulfur Dioxide (SO ₂)	–	0.68 (0.13)	–	–	–	–	0.06	0.5
Hydrogen (H ₂)	–	–	–	–	–	–	–	0.091
Ammonia (NH ₃)	10.8 (12.4)	1.03 (0.66)	0.87 (0.40)	0.03	1.24 (1.44)	0.79	4.75 (1.00)	0.94 (1.02)
Nitrogen Oxides (NO _x as NO)	0.80 (0.57)	3.26 (0.95)	1.42 (0.72)	–	0.22 (0.22)	1.41	0.5	3.74 (1.48)
Nitrous Oxide (N ₂ O)	–	0.25 (0.18)	–	–	–	0.24	–	–
Nitrous Acid (HONO)	–	0.41 (0.15)	–	–	–	–	–	–
TNMHC as CH ₄	–	–	2.89 (1.21)	3.76 (4.53)	–	–	–	–
TNMHC as g C	–	–	2.27 (2.07)	–	–	–	–	–
NMOC (identified)	48.7 (32.4)	6.0 (2.4)	19.2 (7.6)	1.87 (0.92)	161 (115)	5.56	32.6 (10.2)	7.5 (7.6)
NMOC (identified + unidentified) ^e	97.3	12.1	57.7	5.62	321	11.1	97.7	22.6
Total Suspended Particulate (TSP)	–	15.4 (7.2)	4.55 (1.53)	3.34 (1.68)	0.7–4.2	2.38	–	–
Total Particulate C	–	–	–	–	–	–	22.9	–
PM _{2.5} ^f	–	11.9 (5.8)	6.64 (1.66)	–	–	–	–	9.8 (5.7)
Black Carbon (BC)	0.20 (0.11)	1.3	0.83 (0.45)	0.74 (0.37)	0.02 (0.02)	1.0 ^g	0.53 ^g	0.65 (0.27)
Organic Carbon (OC)	6.23 (3.60)	3.7	2.89 (1.23)	1.92 (0.90)	0.74 (0.72)	1.3 ^g	1.8 ^g	5.27 (4.89)

^a See Sect. 2.3 for guidance in use. Emission factors are shown with an estimate of the natural variation in parenthesis, when available.

^b EF include an assumed tropical forest overstorey.

^c EF reported in units of g of compound emitted per kg of charcoal produced.

^d EF reported in units of g of compound emitted per kg of charcoal burned.

^e Estimated (see Sect. 3.4).

^f PM₁–PM₅ categorized as PM_{2.5}.

^g Source is Bond et al. (2004).

2.3.1 Savanna

The emission factors from one laboratory study and four airborne studies of savanna fires are presented and averaged in Table S1. The savanna fire average and variation is also reported in Table 1. We make several points about three of the included studies next. During the Smoke, Clouds,

and Radiation-Brazil (SCAR-B) campaign, airborne EF measurements were made of fresh smoke from several different fire types. However, the EF were originally published as the overall regional average emission factors for the combination of all the different fire types observed (Ferek et al., 1998). We broke out the original fire-specific SCAR-B EF

into the appropriate fire-type categories in our classification scheme based primarily on the recorded visual observations from the aircraft. However, the delineation between TDF and “wooded” or “humid” savanna fires was difficult from the aircraft and the distinction is often unclear in the literature as well. We categorized three of the SCAR-B fires as savanna fires because the Advanced Very High Resolution Radiometer (AVHRR) Continuous Fields Tree Cover product (DeFries et al., 2000) showed that the area burned had a pre-fire canopy coverage less than 40% (Matthews, 1983; Hansen et al., 2000). We used the AVHRR product because the fires burned prior to coverage by the MODIS VCF product (Hansen et al., 2003). The gas and particle emissions data from the SCAR-B fires are also converted to units of g compound per kg fuel. “Xylenes” are calculated from the sum of p-xylene, m-xylene, and o-xylene. Since NO and NO₂ are rapidly interconverted in the atmosphere, we also calculate and report an EF for “NO_x as NO”. The estimate of the variation in the EF is taken as the standard deviation of the EF. The volume distribution for BB particles by aerodynamic diameter shows a minimum from about 1 to 5 microns (Ward and Radke, 1993). Thus, in all our tables, measurements of PM_{1.0}–PM_{5.0} are grouped together as PM_{2.5} to allow averaging data from more studies. We also note that PM_{2.5} is usually close to 80% of PM₁₀ or TPM when measured on the same BB sample (e.g. Artaxo et al., 1998). Finally, we group EF reported for elemental carbon (EC) or black carbon (BC) in a single “BC” category. If there are thermal and thermal-optical measurements of EC we take the results from the latter more advanced technique. Differences between the measurement techniques used for these species are the subject of ongoing research (Reid et al., 2005a, b; Bond and Bergstrom, 2006; Schwarz et al., 2008).

We include early dry season EF measured by Yokelson et al. (2011) in Mexico that may help our average EFs (Tables S1 and 1) better represent the full dry season. In addition, these early dry season EFs could be taken from Table S1 for an application targeted at that time of year.

We include EF from Christian et al. (2003) who measured emissions from burning grass and/or twig/leaf-litter fuels from Zambian humid savannas in 16 laboratory fires. Their reported uncertainty is $\pm 37\%$ factoring in 31% naturally occurring variability in NMOC (Yokelson et al., 2003), 15% prediction error (reflecting the uncertainty in using lab data to predict field emission factors for this fire type), and 5% error in measurement. Alang-alang (*Imperata cylindrica*) is a widespread fire-maintained grass subject to frequent burning in Indonesia (Jacobs, 1988; Seavoy, 1975; Pickford et al., 1992) that was burned in five fires by Christian et al. (2003) and we categorize it as a savanna-type fuel. Most of the data reported by Christian et al. (2003) were collected using open path FTIR (OP-FTIR) and PTR-MS. For this study and other studies with EFs measured by both FTIR and PTR-MS, the FTIR could sometimes quantify individual species when multiple species appeared on the same mass in the PTR-MS.

In these cases, we select the FTIR data with a notable exception for acetol. The coupling and/or selection of data from various instruments is described in more detail in the original papers and by Christian et al. (2004) and Karl et al. (2007). The EF for HCOOH and glycolaldehyde published prior to 2011 in FTIR-based studies have been rescaled to be consistent with new reference spectra (Rothman et al., 2009; Johnson et al., 2010).

For this category and for the other categories, when sufficient data are available, we provide a conservative estimate of the “naturally-occurring variation” in the average EF for a group of fires within the classification. It is common to report variability as “uncertainty,” but the measurement uncertainties associated with calculating individual EF are generally quite low for the studies we include in this compilation. We adopted a relatively simple approach to estimate the variability, which is described next in order of increasing complexity:

The case when only one study is available:

1. If there is only one EF value available, we do not estimate variability.
2. If there are only two EF values available, we estimate variability as the range.
3. If two or more EF values are given and both provide an estimate of variation, we average them to estimate variability.
4. If three or more EF values are given in just one study, we estimate variability as the standard deviation of the EF.

The case when two or more studies are available:

1. If more than one study reports EF, but only one study provides an estimate of variability, we estimate variability using the fractional variability from the one study provided.
2. If more than one study reports EF and an estimate of the variability, we took the average variability as our estimate of variability (we find that the range or standard deviation of study means can sometimes significantly underestimate natural variability).
3. When more than one study was available and there was a large difference in the amount of sampling between studies, we weighted the EF by the amount of sampling to derive a final average EF value reported in our tables, but our estimates of variation were obtained as above (without weighting).
4. Variability in total NMOC was taken as the sum of the variability of each individual NMOC (we find that equations propagating fractional uncertainties overemphasize the impact of compounds measured in low abundance on total variation).

Users preferring an alternate calculation of averages or variation can implement their scheme using the original data, which can be found in Supplement Tables S1–S14.

2.3.2 Boreal forest

Boreal forest fires can consume large amounts of both above-ground and below-ground biomass (Ottmar and Sandberg, 2003; French et al., 2004). We include lab or ground-based measurements of EF for burning organic soils, peat, and woody/down/dead vegetation; the latter term including stumps, logs, and downed branches (Tables 1, S2). Such fuels are likely to burn by RSC, which can continue long after flaming and strong convection from a fire have ceased (Bertschi et al., 2003b). We computed the average for five common components of the fuel in boreal organic soils that were burned individually by Bertschi et al. (2003b) (identified as Lolo1, 2, 3, NWT 1, 2 in original work) and took the standard deviation as the variability. Emissions from burning organic soil from Alaska (identified as sedge, sphagnum moss, feather moss, white spruce, and forest floor duff) were reported by Yokelson et al. (1997), for which we compute EF using the reported C content. Yokelson et al. (1997) also reported emissions measurements for boreal peat from Alaska and Minnesota. Given that the %C was not measured for Alaskan peat, we used the measured %C for MN peat (49.4%) in all of the boreal peat EF calculations. We also include Alaskan duff EF measured in a laboratory by Burling et al. (2010). Bertschi et al. (2003b) reported EF for woody/down/dead fuels (identified as Stump and Cwd 2), which are also included here. We are unaware of any measurements of the relative consumption of the different organic soil and woody fuel components for “typical boreal fires” so a straight average of the EF for the organic soil/duff and dead and down component in these lab/ground studies was used for a ground-based average (as shown in Table S2).

Four studies reported airborne measurements of boreal forest fire EF in fresh smoke for an extensive number of compounds. We include the average of the emission factors from three fires (B280, B349, and B309) sampled by Goode et al. (2000) (fire B320 was not included since the fuels were not representative of a boreal forest; see original work). Nance et al. (1993) and Radke et al. (1991) also reported boreal airborne EF measurements for one wildfire and four prescribed fires, respectively. These are included in this compilation. We include airborne EF measurements for boreal wildfires from the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) campaign (Simpson et al., 2011). Whole air samples (canisters) were collected in smoke plumes over Saskatchewan, Canada. Emission factors for long-lived species were based on all the canisters collected in 5 plumes. EFs of “short-lived” ($k_{OH} \geq 8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) species were calculated using only samples of fresh smoke collected <7.3 km from the source.

Due to slow decomposition, large amounts of carbon are stored in boreal soils and dead/down woody fuels that burn by smoldering combustion and thus account for much of the total fuel consumption. To take this into consideration, we calculate the overall boreal forest fire EF in Table 1 (and Table S2) from a straight average of the airborne and ground-based EF averages, which is roughly equivalent to assuming ~70% of the fuel consumption is by smoldering combustion. In fact, data in Table 4 of van der Werf et al. (2010) suggest that an even larger weighting of the ground-based “smoldering” EF could be appropriate. Using Table S2, EF can be calculated based on other relative contributions of flaming and smoldering. Some smoldering compounds were measured only from the air. For these compounds we multiply the airborne EF by the average ratio of the “50-50” average to the airborne average (2.02 ± 0.070). A similar approach is used for smoldering compounds measured only from the ground; they were multiplied 0.70 ± 0.11 to obtain the 50-50 average. Finally, we point out that the flaming and smoldering emissions can have different injection altitudes, which could be important to recognize in some applications. For instance, the boreal airborne average in Table S2 would likely agree well on average with airborne measurements of fresh smoke from boreal forest fires, but the overall boreal average shown in Tables 1 and S2 may better represent the true average regional fire emissions.

2.3.3 Tropical forest

Our emission factors for tropical forest fires are in Table 1. We derive the EFs by averaging over several types of tropical forest fires in Table S3. For tropical evergreen forest deforestation fires we include EFs cited in Yokelson et al. (2008) and EFs retrieved from the original SCAR-B data of Ferek et al. (1998). The EFs in Yokelson et al. (2008) (all from the Tropical Forest and Fire Emissions Experiment – TROF-FEE) were derived using a 0.05/0.95 weighted average of the Christian et al. (2007) ground-based measurements (dominated by residual smoldering combustion) and the Yokelson et al. (2007a) airborne measurements (dominated by flaming combustion). For these types of fires, available evidence suggests that approximately 5% of biomass consumption is by residual smoldering combustion and 95% of consumption is during the convective plume forming phase of the fire (Christian et al., 2007). The average of the EF for residual smoldering and the EF for initially lofted emissions, weighted by the above fuel consumption, gives fire-average EF for smoldering compounds that were 1.12 ± 0.11 times higher than the EF from just the airborne data. Thus, since some smoldering compounds were measured only in the air, their emission factors are computed from 1.12 times the airborne average in both this work and Yokelson et al. (2008). The EF and variation for pyrrole can be found in the discussion version of Yokelson et al. (2007a). The variation for all the other species is taken as the standard deviation in the airborne EF

in Table 2 of Yokelson et al. (2007a). We also average EF from 12 airborne samples of fires from the SCAR-B campaign (Ferek et al., 1998) that represented emissions from six flaming and six smoldering fires classified as tropical evergreen deforestation fires. We do not make the small adjustment to the smoldering compounds for RSC in the SCAR-B data (Ferek et al., 1998). Average EF for the “subcategory” tropical evergreen deforestation fires are included in Table S3.

For tropical dry forest (TDF) fires we consider both deforestation and understory fire emissions. The studies we include are Yokelson et al. (2009, 2011), Ferek et al. (1998), and Sinha et al. (2004). Yokelson et al. (2011) report EFs for nine TDF fires sampled in Mexico (six of which were originally published in Yokelson et al., 2009). These were early dry season fires, which should help the average EF we derive for this category reflect the entire dry season since the other studies measured EF later in the dry season. We calculate an EF for nitrous acid (HONO) from the mass emission ratio $\Delta\text{HONO}/\Delta\text{NO}_x$ measured on one tropical dry deforestation fire (Fire #2 on 23 March 2006 from Yokelson et al., 2009) times our average EF(NO_x) for TDF. We classify three SCAR-B fires from Ferek et al. (1998) as TDF fires and estimate the variation as the standard deviation of these EF. Sinha et al. (2004) measured numerous emissions from one African tropical dry forest (Miombo) understory fire. That work includes an EF for condensation nuclei in the diameter range 0.003–3 μm expressed as number of particles per kg fuel burned. Finally, in theory, to derive average EF for tropical dry forest fires from the available measurements we would need to know the relative importance of understory and deforestation burns in this ecosystem globally (Desanker et al., 1997). Since this information is not available to our knowledge, we weight them equally here to obtain average EF for TDF. We then weight all the studies in Table S3 equally to obtain the tropical forest fire average EF that we carry over to Table 1.

2.3.4 Temperate forest

We include the average and standard deviation of EFs from three temperate evergreen forest fires (two wild and one prescribed) from Radke et al. (1991) and seven pine-oak forest fires sampled in remote mountain areas of Mexico by Yokelson et al. (2011), as seen in Table S4. We do not include the EFs for pine-oak forest fires measured in the Mexico City area by Yokelson et al. (2007b), since they were likely at least partially affected by nitrogen deposition from the urban area. We also include the average and standard deviation of the preliminary EFs from a recent study that sampled two prescribed understory fires in coniferous forest in the Sierra Nevada Mountains of California and six prescribed understory fires in coniferous forest in coastal North Carolina (Burling et al., 2011).

2.3.5 Peatland

Peat burns almost entirely by smoldering combustion. Christian et al. (2003) made laboratory measurements on a single Indonesian peat fire. We provide no estimate of variation for EF from Christian et al. (2003) as only one fire was measured, though a general range of at least 20–40% uncertainty could be assumed. The boreal peat EF reported in Yokelson et al. (1997) and considered in calculating the boreal forest EF (Table S2) are also used in computing our global peatland EF in Table S5. The Indonesian peat sample had a 54.7% carbon content, which contributed to a significantly higher EF(CO_2) compared with boreal peat, but we do not imply that tropical peat always has higher C content. We calculated the average peat EF in Table S5 by averaging the studies of boreal (Yokelson et al., 1997) and Indonesian (Christian et al., 2003) peat and estimate an average variability from the fractional variation in EF in Yokelson et al. (1997). Smoldering peat accounts for the bulk of the emissions from most fires in peatlands and our average peat EFs in Table S5 are based only on the smoldering peat measurements. However, Page et al. (2002) estimated that 0.19–0.23 Gt of carbon was released into the atmosphere through peat combustion in tropical peat swamp forests, while 0.05 Gt of carbon was released from overlying vegetation during the 1997 El Niño year in central Borneo. From these estimates we took a weighted average of the peat EFs (73%) in Table S5 with the tropical evergreen forest deforestation fire EFs (27%) in Table S3 to derive a peatland average shown in Table 2 that accounts for consumption of a (tropical) forest overstory. The user can apply the average EFs most suited to their application.

2.3.6 Chaparral

We include the average EF from three studies that measured emissions from California chaparral fires. The average EF from three fires sampled by Radke et al. (1991) was taken (Eagle, Lodi 1, and Lodi 2). We converted their EF(NO_x), which assumes a 50/50 mix to an EF for “ NO_x as NO” by multiplying their original EF by a mass factor of (30/38). We include the emission factors from a laboratory study that sampled ~ 40 carefully replicated fires in six types of chaparral fuels (Burling et al., 2010). We also include the average EF from five chaparral fires measured during a recent field campaign (Burling et al., 2011). The emission factors from the latter campaign are flagged as preliminary, but subject to only minor changes by the time of publication.

2.3.7 Open cooking

Christian et al. (2010) reported the average EF of eight open cooking fires sampled in Mexico. Brocard et al. (1996) and Brocard and Lacaux (1998) reported the average emission factors for 43 open cooking fires in Ivory Coast. We

multiply their EF and variation by MW_X/MW_C to convert from g C kg^{-1} dry fuel to g X kg^{-1} dry fuel. Some updated EF reported by Brocard and Lacaux (1998) supersede those found in Brocard et al. (1996). Smith et al. (2000) sampled six open cooking fires in a lab using Indian fuels: variation was taken as the fractional variation in ER as seen in Bertschi et al. (2003a). We include the EF measured by Zhang et al. (2000) for wood burning in open stove types in China and EF measurements made in Honduras for traditional open “stoves” (designated as “no chimney”) from Roden et al. (2006, 2009). CO_2 data were not included in the published work of the latter, but were graciously provided by Tami Bond and Christoph Roden. Johnson et al. (2008) included EF for 8 open cooking fires in Mexico, which we convert from g C kg^{-1} fuel to g X kg^{-1} fuel. Bertschi et al. (2003a) report the average EF for three open wood cooking fires in Zambia and we estimate variation from the fractional variation in their ER. We weight all 8 included studies equally to obtain the average EF shown in Tables 2 and S7.

2.3.8 Patsari cooking stoves

We assume a fuel C content of 50% when converting all cook stove ER to EF. Christian et al. (2010) analyzed 26 samples collected from chimney outlets of two Patsari stoves in Mexico. Our estimate of variation is the range in the two EF measurements. We also include Patsari stove EF measurements from Johnson et al. (2008) made in 13 homes in Mexico. We report the overall Patsari stove average emission factors and variation in Tables 2 and S8.

2.3.9 Charcoal making

Most of the global charcoal production is carried out in temporary kilns constructed mainly from dirt (Bertschi et al., 2003a). Charcoal making EF have been reported in the literature in at least four types of units: g compound or g C emitted, referenced to either kg of wood used or kg of charcoal made. We convert as needed and report all EF here in units of g compound per kg charcoal produced. In Bertschi et al. (2003a), the kiln was charged with a tree species with a known carbon content of 48% (Susott et al., 1996). Coupling several other studies they concluded that $\sim 45\%$ of the wood carbon is given off as gases so that approximately 216 g C is volatilized per kg of dry wood used. Dividing up those 216 g according to their measured ER (which included the major emissions CO_2 , CO, and CH_4) then allowed straightforward calculation of the reported EF per kg wood used. Conversion to EF per kg charcoal produced was based on assuming an average charcoal yield per mass of dry wood of 28%, a factor that varies little between the many reported measurements (Bertschi et al., 2003a; Chidumayo, 1994; Pennise et al., 2001; Lacaux et al., 1994; Smith et al., 1999). Bertschi et al. (2003a) obtained their ER from averaging three 1–2 h measurements made on one kiln on three different days

spread over the 4 days required to produce a batch of charcoal. They then derived EF as just described. Christian et al. (2010) made 36 spot measurements of ER (with ~ 1 min sampling time) during days 2–5 from three kilns that had 8-day “lifetimes”; they then converted to EF with the procedure of Bertschi et al. (2003a). Our estimate of variation for Bertschi et al. (2003a) and Christian et al. (2010) is the fractional uncertainty in ER. Christian et al. (2007) made three spot measurements (1 min sampling time) from a single kiln in Brazil; however, measurements were made only in the last stage of the kiln lifetime and may not be representative of emissions occurring throughout the charcoal making process. The FTIR-based studies of Bertschi et al. (2003a) and Christian et al. (2007, 2010) measured a substantially different suite of NMOC than the other available studies and also differed in sampling approach so data from these 3 studies was averaged together separately using the weighting factors described next. Since Christian et al. (2007) collected only three 1 min spot measurements, we employed a weighting factor (4%) based on the minutes of actual sampling. The kiln measurements of Christian et al. (2010) and Bertschi et al. (2003a) were roughly equivalent in the extent of sampling and were weighted equally at 48%. The FTIR-based average values were then averaged with 4 other studies to obtain the overall charcoal making EF shown in Tables 2 and S9. The four additional studies are described next. Lacaux et al. (1994) continuously monitored the emissions from a charcoal kiln in the Ivory Coast over its whole “lifetime”. We assume that any differing EF found in a later paper that discusses that project (Brocard and Lacaux, 1998) supersede those found in Lacaux et al. (1994). We also include EF from Smith et al. (1999) and Pennise et al. (2001) measured in Thailand and Kenya, respectively.

2.3.10 Charcoal burning

We report all EF in units of g compound per kg charcoal burned (Tables 2 and S10). Unless otherwise stated, the charcoal fuel carbon content was assumed to be $72 \pm 3\%$ (Lacaux et al., 1994; Chidumayo, 1994; Ishengoma et al., 1997; Smith et al., 1999). We recalculate the EF from the ER reported in Bertschi et al. (2003a) and a few of our EF values differ slightly from those originally reported in their work. No variation was reported for the Bertschi et al. (2003a) study as emissions were measured from only one fire. Brocard et al. (1998) reported ER and fractional variation in those ER for charcoal burning, which we converted to EF. For the compounds they reported relative to CO_2 , we estimate variation from the fractional variation in the ER. To estimate variation for the compounds they reported relative to CO, we also consider their uncertainty in $\Delta\text{CO}/\Delta\text{CO}_2$. We include Smith et al. (2000) and Kituyi et al. (2001) EF measured in India and Kenya, respectively.

2.3.11 Dung

Keene et al. (2006) reported the median EF of gases and total particulate carbon from two laboratory fires that burned dung collected in India. Christian et al. (2007) measured the emissions from three burning cattle dung piles encountered on a subsistence farm in Brazil. We calculate all EF assuming a 32.6% fuel carbon content on a dry weight basis, as reported by Keene et al. (2006). We compute a weighted average based on the number of samples from each study (Tables 2 and S11).

2.3.12 Pasture maintenance

In Brazil many cattle ranches have been established in areas that were previously tropical forest. Pasture maintenance fires are used to prevent the re-establishment of the forest and they burn both grass and residual wood from the original forest. Within Brazil, these fires are estimated to consume as much biomass annually as primary deforestation fires (Kauffman et al., 1998). Pasture maintenance fires are thought to be much less abundant in most other tropical forest areas. Yokelson et al. (2007a) sampled one Brazilian pasture fire from an airborne platform (Table S12). We include no estimate of variation as only one fire was measured. The EF for pyrrole for that fire was reported in the discussion version of Yokelson et al. (2007a). The SCAR-B study of Ferek et al. (1998) included airborne samples of six pasture fires. We use the standard deviation in EF from their pasture fire measurements to estimate the variability in EF and we compute a weighted airborne average EF based on the number of fires sampled in these two studies. A significant fraction of the fuel consumption in pasture fires produces unlofted emissions via residual smoldering combustion of the residual woody debris (RWD) from the former forest (Barbosa and Fearnside, 1996; Guild et al., 1998; Kauffman et al., 1998). These emissions must be sampled from the ground. We are aware of one ground-based study (Christian et al., 2007) that reported EF for RSC of RWD in pastures, and we also obtained originally unpublished EF from that study for “NO_x as NO,” NO, and NO₂. For all species with both airborne and ground-based data we obtained a “EF(total)” for pasture fires from a weighted average based on the assumption that 40% of the fuel consumption was by RSC and 60% generated lofted emissions that could be sampled from the air (Christian et al., 2007).

Some compounds were measured only from the air. The EF(total) for the smoldering compounds that were measured only from an aircraft is estimated by multiplying the average EF(air) by 2.00 ± 0.90 , which was the average value of the ratio EF(total)/EF(air) for smoldering compounds not containing N that were measured from both platforms (Yokelson et al., 2008). Two flaming compounds were measured only from the air. EF(total) for SO₂ is estimated by multiplying EF(air) for SO₂ by EF(air)/EF(total)

for NO_x which was measured from both platforms. Our estimate of EF(HONO) is obtained by multiplying the $\Delta\text{HONO}/\Delta\text{NO}_x$ mass ER in Yokelson et al. (2007a) times our final EF(NO_x). Two smoldering compounds were measured only on the ground. EF(total) for acetol (1-hydroxy-2-propanone, C₃H₆O₂) and phenol (C₆H₆O) are estimated by multiplying the EF(ground) times the average EF(total)/EF(ground) for the (non-N) smoldering compounds measured from both ground and air. We use the fractional variation in the ground-based EF to estimate the variation in species with ground or both ground and airborne data, since ground-based data appear to have greater variability than airborne data (see Figs. 2 and 4 in Yokelson et al., 2008). For species with only airborne data we estimate the uncertainty as 45% (Yokelson et al., 2008) (Table 1).

2.3.13 Crop residue

Post harvest crop residue is a fine fuel that burns directly in the field and mostly by flaming in many mechanized agricultural systems. In contrast, when crops are harvested by hand the residue is often burned in large piles that may smolder for weeks. Yokelson et al. (2009) reported emission factors from airborne measurements of six crop residue fires associated with mechanized agriculture in the Yucatan, Mexico. Christian et al. (2010) made ground-based measurements of EF from mostly smoldering combustion during two similar burns in Central Mexico. Yokelson et al. (2011) made airborne measurements of the EFs for 6 additional crop residue fires associated with mechanized agriculture in central Mexico and derived overall averages that included their EFs and those from Yokelson et al. (2009) and Christian et al. (2010). We use the overall averages for mechanized agriculture from Yokelson et al. (2011) in Table S13. Christian et al. (2003) measured the mostly smoldering emissions from three laboratory fires burning manually piled Indonesian rice straw. Because of the significantly different EFs for these agricultural burning types it would be preferable to apply the specific EFs for each type of agriculture, when possible, by referring to Table S13 and the original papers. Because some users may require or prefer a global average for this category we present an estimate of this in Tables 1 and S13. In our overall average for crop residue fires, the EFs from the manual and mechanical agriculture subcategories are weighted based on the number of fires sampled, which is equivalent to assuming a 3:14 ratio of manual to mechanized harvesting on the global scale. The actual value of this ratio is not known to us and the reader can adjust the weighting if they prefer. In addition, because of the very large difference in EFs for these two types of burning, for this category only, we calculated the overall average by assuming a value of zero for the EF of 13 species that were not detected from fires associated with mechanical agriculture, but very high from smoldering rice straw (see Table S13). This procedure gives a weighted

EF value for these 13 compounds that is more consistent with the overall average values for the other compounds.

2.3.14 Garbage burning

We consider field and laboratory measurements from Christian et al. (2010) and Lemieux et al. (2000), respectively. Christian et al. (2010) made 72 spot measurements at four Mexican landfills using a rolling, land-based FTIR and filter sampling apparatus. Emission factors were computed assuming the landfill waste was 40% C by mass. Their estimate of EF(PM_{2.5}) is the sum of particle components measured on quartz filters with a small allowance for unmeasured species (Christian et al., 2010). We report the average EF(PM_{2.5}) and EF(HCl) from Lemieux et al. (2000) for the burning of recycled and non-recycled waste in barrels. We obtain the average from four “runs” – emissions from two avid recyclers and two non-recyclers – with PM_{2.5} emissions from non-recyclers notably higher than those of avid recyclers (see Table 1 in Lemieux et al., 2000 for study details and garbage composition). We include airborne EF measurements from a garbage burning fire in Mexico (Yokelson et al., 2011). We also include the few available USEPA (1995) AP-42 EF for open burning of municipal waste.

2.4 Estimates of biomass loading and biomass consumption

To project total emissions from a fire or region the EF presented above must be multiplied by the mass of biomass consumed in the fire or region. For open burning the total mass of biomass consumed is usually estimated from the product of two other estimates: (1) the mass of biomass consumed per unit area, and (2) the area burned. Airborne or ground-based measurements of the area of individual burn scars can be fairly accurate, but they are usually not available for the tropics and space-based measurements of burned area are still highly uncertain (Korontzi et al., 2004; Roy and Boschetti, 2009; Giglio et al., 2006, 2010). The biomass consumption per unit area has been measured for examples of most major types of open burning. Another approach involves calculating the fraction of the total biomass that was exposed to a fire that actually burned to determine a combustion factor (sometimes called “combustion completeness”). The combustion factor (CF) can then be multiplied by spatially varying estimates of biomass loading (Brown and Lugo, 1992; Brown, 1997) to estimate the biomass consumption per unit area for any burned location. The CF need not be a constant for an ecosystem. The small diameter biomass components in a “fuel complex” tend to have larger CFs than the larger diameter biomass components (Table 2 in Kauffman et al., 2003). Considering the season of CF measurements (available in the references for Table 3) reveals that CF tend to increase strongly as periods of dry weather lengthen and dry out the larger diameter fuels (van der Werf

et al., 2006). Additional variation in CF results from natural variation at burn time in any of numerous factors that affect fire behavior such as relative humidity, temperature, winds, fuel geometry, etc. (Kauffman et al., 2003). For example, CF for Brazilian pasture fires ranged from 21–83% due mainly to variable consumption of the large diameter residual woody debris (Kauffman et al., 1998; Guild et al., 1998). In southern Africa the percentage of available fuel that burned in understory fires in June (at the beginning of the dry season) in the Miombo tropical dry forest was 1% and 22% ($n = 2$, Hoffa et al., 1999), while Shea et al. (1996) observed that 74% and 88% ($n = 2$) of the understory fuels burned in Miombo fires in late August-early September (their Table 4). We have compiled many of the literature data for biomass loading, combustion factor, and biomass consumption sorted by vegetation/fire type in Table 3. GFED3 estimates for biomass consumption are also shown in Table 3 whenever their regional estimates for fuel consumption per unit area were likely dominated by one vegetation type. GFED estimates 46% higher biomass consumption for North American boreal fuel types compared to the average of the other referenced measurements. However, estimates of Asian boreal biomass consumption by GFED lie within 4% of the average of the few measurements. A comparison for other fire types is difficult because the GFED biomass consumption data is presented by geographic regions that usually contain multiple fire types (van der Werf et al., 2010).

2.5 Global emission estimates

Operationally, most global models use temporally and spatially explicit products such as monthly GFED (van der Werf et al., 2006, 2010) or hourly FLAMBE (Reid et al., 2004, 2009) to generate open burning emissions over the course of a model run. However, estimates of the total annual biomass consumed globally by all the various fire types are needed, at the global scale, to assess the importance of various fire types, to develop emissions inventories for an average or model year, and to factor into budgets. We report several global estimates of combusted biomass (dry matter) for different fire types in Table 4. The individual estimates are based on data collected anywhere from 1987–2000, which explains some of the variability in comparisons. Global estimates from Andreae and Merlet (2001) and Bond et al. (2004) agree well for the main types of open burning: savanna, forest, and crop residue fires. The annual means for 1997–2009 from GFED3 (van der Werf et al., 2010) are about 20% lower than the widely used estimates in Andreae and Merlet (2001) for both savanna burning (2460 versus 3160 Tg) and total forest burning (1591 versus 1970 Tg). The Andreae and Merlet (2001) estimate of crop residue burning is about 75% higher than GFED3, but the latter assume that they underestimate this source. Kopacz et al. (2010) suggest that GFED3 underestimates BB in several important tropical regions. Detailed discussion and comparison of

Table 3. Biomass loading, combustion factor, and biomass consumption estimates for various fuel types.

Fuel Type	Reference	Location	Vegetation specifics	Biomass Loading (Mg ha ⁻¹)	Combustion Factor (%)	Biomass Consumption (Mg ha ⁻¹)
Tropical Dry Forest	Kauffman et al. (2003)	Mexico	Deforestation	118.2–134.9	62.4–80.2	73.7–108.1
	Kauffman et al. (1993)	Brazil	Deforestation	73.8	87	64
	Jaramillo et al. (2003)	Mexico	Deforestation	112.2	–	–
	Shea et al. (1996)	Zambia	Understory	5.1–5.8	88–74	4.5–4.3
	Hoffa et al. (1999)	Zambia	Understory	10.4	22.3	2.30
	Ward et al. (1992)	Brazil		9.3	78	7.3
	van der Werf et al. (2010), GFED3	Central America	Central America (CEAM)	–	–	29.8
Evergreen Tropical Forest	Ward et al. (1992)	Brazil		292.4	53	155
	Fearnside et al. (1993)	Brazil		265	27.5	73
	Carvalho Jr. et al. (1998)	Brazil		401.5	20.47	82
	Carvalho Jr. et al. (2001)	Brazil		496	50	248
	Hughes et al. (2000)	Mexico		403	95	380
	Kauffman et al. (1995)	Brazil		355.4	51.6	185
	Guild et al. (1998)	Brazil		354.8	47	167
	van der Werf et al. (2010), GFED3	Equatorial Asia	Equatorial Asia (EQAS)	–	–	190
Crop Residue	Zárate et al. (2005)	Spain	Cereal crops	–	80	1.14
	Hughes et al. (2000)	Mexico	Cornfield	23	–	–
	Lara et al. (2005)	Brazil	Sugarcane	–	–	20
Peatland	Page et al. (2002)	Indonesia	Peat plus overstory	–	–	510
	Ballhorn et al. (2009)	Indonesia	Peat only	–	–	383
Pasture	Hughes et al. (2000)	Mexico		24	–	–
	Guild et al. (1998)	Brazil		66.3	31	21
	Kauffman et al. (1998)	Brazil		53–119	21–84	24.5–44.5
	Kauffman et al. (2003)	Mexico		29.0–40.3	75–63	21.8–25.4
	Jaramillo et al. (2003)	Mexico		26.9	–	–
Savanna	Ward et al. (1992)	Brazil	Tropical savanna	7.2	99	7.1
	Savadojo et al. (2007)	West Africa	Woodland savanna	–	–	4.1
	Shea et al. (1996)	South Africa		3.8	76	2.9
Boreal Forest	Goode et al. (2000)	Alaska, USA		–	–	36
	S. Drury (unpublished data, 1998)	Alaska, USA	Wildfire B309, 28 June 1997	–	–	37
	van der Werf et al. (2010), GFED3	North America	Boreal North America (BONA)	–	–	53.2
	FIRESCAN Science Team (1996)	Bor Forest Island, Siberia	Prescribed crown fire	–	–	38
	Cofer III. et al. (1998)	Northwest Territories, Canada	Prescribed crown fire	–	–	42.7
	van der Werf et al. (2010), GFED3	Asia	Boreal Asia (BOAS)	–	–	39.6
	Kasischke et al. (1999)	Global estimate		–	–	10–60
	Stocks (1991)	Global estimate		–	–	25
	Cahoon Jr. et al. (1994, 1996)	Global estimate		–	–	25
	de Groot et al. (2009)	Canada		–	–	22
Temperate Forest	Sah et al. (2006)	Florida, USA	Florida Keys pine forests	60.6	–	–
	Snyder (1986)	Florida, USA	Everglades NP	75–90	–	–
	van der Werf et al. (2010), GFED3	North America	Temperate North America (TENA)	–	–	12.5
	Yokelson et al. (2007b)	Mexico	Pine dominated forest	–	–	6.5–32
	Campbell et al. (2007)	Oregon, USA	Mixed conifer forest	–	–	34–44
Chaparral/Shrub	Cofer III. et al. (1988)	S. California, USA	Chaparral	–	–	20–70
	Clinton et al. (2006)	S. California, USA	Chaparral	28.3	–	–
	Ottmar et al. (2000)	S. California, USA	Chaparral	–	–	15.0
	Hardy et al. (1996)	S. California, USA	Chaparral	–	–	24.5

current inventories can be found in Reid et al. (2009), Kopacz et al. (2010), Wiedinmyer et al. (2010) and the references therein. Yevich and Logan (2003) estimated biofuel biomass consumption at 2447 Tg yr⁻¹ for 1985, which suggested a dominant role of biofuels in global emissions even 25 yr ago. They also estimated that biofuel use was growing at 20% per

decade. Consistent with that growth, Bond et al. (2004) and Fernandes et al. (2007) independently estimated higher biofuel use for 1996 and 2000, respectively. If savanna burning remains constant on average, biofuel burning could overtake it as the primary source of BB emissions by approximately 2030; assuming the average emissions presented in Table 4

Table 4. Global estimates of biomass consumption in units of mass of dry matter burned (Tg) per year.

Year measured	1990's	mid 1990's	2000	1993/1995	1985		
	Andreae and Merlet (2001) ^a	Bond et al. (2004) ^b	Fernandes et al. (2007) ^c	Ludwig et al. (2003) ^d	Yevich and Logan (2003) ^e	Other ^f	Average
Savanna	3160	3572	–	–	–	–	3366
Forest	1970	1939	–	–	–	–	1955
Tropical forest	1330	–	–	–	–	–	1330
Extratropical forest	640	–	–	–	–	–	640
Biofuel	2897	–	2458	–	2447	–	2601
Cooking Stoves	–	–	1351	–	–	–	1351
Open Cooking (fuelwood)	–	–	–	1062	1714	–	–
Charcoal Burning	38	–	39	24	–	–	39
Charcoal Making	43	–	–	–	–	–	43
Crop Residue (for biofuel)	–	–	495	–	597	–	546
Dung	–	–	75	–	136	–	106
Industrial	–	–	498	–	–	–	498
Peat	–	–	–	–	–	3400	3400
Pasture Maintenance	–	–	–	–	–	240	240
Crop Residue (field burning)	540	475	–	–	451	–	489
Garbage Burning	–	–	–	–	–	1000	1000

^a Source is Andreae and Merlet (2001). Value of 640 Tg yr⁻¹ is cited in original work as “extratropical forest”, which encompasses both boreal and temperate forest types. “Biofuel” global estimate derived from the sum of biofuel burning, charcoal making, and charcoal burning estimates. Charcoal making estimate of 43 Tg yr⁻¹ was calculated assuming a 27% charcoal yield (Bertschi et al., 2003a). The biomass consumption estimates were derived using methods described in Lobert et al. (1999).

^b Source is Bond et al. (2004). Estimates from Table 4 in original work.

^c Source is Fernandes et al. (2007). Original work defines “biofuel” as fuelwood (open cooking), charcoal burning, crop residues and dung.

^d Source is Ludwig et al. (2003).

^e Source is Yevich and Logan (2003). “Biofuel” defined as woodfuel, charcoal burning, crop residues and dung.

^f Other. Garbage burning estimate of 1000 Tg yr⁻¹ from Christian et al. (2010), peat estimate of 3400 Tg yr⁻¹ from Page et al. (2002), and pasture maintenance estimate of 240 Tg yr⁻¹ from Yokelson et al. (2008).

represent global emissions from the year 2003 with a 20% growth rate per decade. This projection is included to highlight the importance of biofuel use, but it is based mostly on past population/development trends and a rigorous projection of future trends is beyond the scope of this work. In general, large uncertainties in biofuel use stem from the difficulty in monitoring its usage in developing countries (Bond et al., 2004). The magnitude of industrial biofuel use remains especially uncertain given the diverse range of fuels used and the subjectivity of user surveys coupled with financial and legal issues for micro-enterprises, which form a large part of the economy of the developing world (Christian et al., 2010). A quantity with extreme uncertainty is the amount of global garbage burning with estimates ranging up to 1000 Tg yr⁻¹ (Christian et al., 2010 and references therein).

3 Discussion

We begin this section with a brief comparison to two widely used compilations of emission factors and then provide guidance on estimating EFs for individual, unmeasured species. We then discuss a few individual BB emissions that are important as a radical source (HONO) or for use as BB tracers (HCN, CH₃CN) and for which a significant amount of new

information has been recently obtained. We then briefly discuss progress in NMOC measurements as well as the large amount of NMOC emitted by BB that so far remain unidentified. We offer a new estimate for total global BB NMOC emissions. An overview of the sparse information available about atmospheric processing of BB emissions is presented. We then conclude with a brief summary of the state of the field identifying a few key gaps in our knowledge that should be targeted for future research.

3.1 Summary comparison to previous compilations

Because of the large number of compounds and fire types involved, a comprehensive comparison of the EFs presented here to all previous compilations is beyond the scope of this paper. In this section we present an overview comparison of our open burning EFs with the widely used review of Andreae and Merlet (2001, hereafter AM2001). We also compare our biofuel EFs with those in the extensive reference work of Yevich and Logan (2003). We acknowledge that a comparison of 2011 values to those from 2001 or 2003 should be seen partly as documentation of how values evolve as new information becomes available rather than as a traditional direct comparison. In addition, more than one

averaging scheme may be adequate or appropriate since the applications of these data are diverse. In particular, AM2001 takes an inclusive approach while we take a highly selective approach, with each having their own strengths and weaknesses. An overly selective approach may inadvertently omit useful data while the full literature average may not reflect the ecosystem average for a large variety of reasons discussed earlier. The fact that many compounds are close in all compilations suggests some additional confidence for those species. A user may be well-advised to consider all compilations and the original work in many applications.

To keep the discussion at a reasonable length and focus it on differences outside the commonly observed variability, we limit our comparison to AM2001 to “major” emissions for which the recommended EF changed by more than 50% between 2001 and 2011. We loosely define major emissions as those with $EF > 0.2 \text{ g kg}^{-1}$ in our compilation. As an exception, we track the NO_x and $\text{PM}_{2.5}$ EFs even when they do not meet these two selection criteria since they are critical to so many applications. Many other major emissions differ by less than 50% and many minor emissions change by more than 50%, but they are not discussed here. The comparison is influenced by the fact that AM2001 provided best guesses for a significant number of unmeasured species while we do not. Instead, we discuss application-specific options for estimating values for unmeasured species separately in Sect. 3.2. In addition, we discuss HONO, HCN, and CH_3CN in separate sections following this overview.

We make three general points before discussing specific compounds. We provide averages for 8 fire types not found in AM2001: boreal forest, temperate forest, chaparral, cooking stoves, peat, dung, pasture maintenance, and garbage burning, with possibility for even further subdivision using the Supplement Tables. For many fire types we include some new major emissions: e.g. HONO (see also Sect. 3.3), acetol, and glycolaldehyde. Our PM EFs are generally modestly higher.

We present a compact summary of the comparison with AM2001 for the selected major EFs in Fig. 1, where the black columns indicate the ratio of our EF to the AM2001 EF for each species. If a species has a blue column, this indicates that a EF was not available in AM2001 and, for the blue columns only, the height shows our actual EF in g kg^{-1} to verify that it is a major emission. For example, referring to the top panel of Fig. 1 (savanna fires), we see that our $\text{EF}(\text{C}_2\text{H}_6)$ is 2.06 times higher than the $\text{EF}(\text{C}_2\text{H}_6)$ in AM2001. For phenol, our EF is 175 times larger than that reported in AM2001 as indicated by the number above the column. While our values are higher for most of the EFs shown, the AM2001 values are significantly higher for NH_3 and HCOOH . Our EF for NO_x is identical to that in AM2001 and our $\text{EF}(\text{PM}_{2.5})$ is 33% higher. Finally, EF for HONO, glycolaldehyde, and acetol are not found in AM2001 and they are now seen to be “major” emissions (EFs of 0.20, 0.81, and 0.45 g kg^{-1} , respectively).

The underlying causes of all the differences depicted in Fig. 1 cannot be discussed in detail here, but they can be gleaned from the original papers and consideration of the various averaging schemes. However, for one category, much of the difference with AM2001 can be summarized succinctly, which we do next. Our extratropical smoldering compounds are generally higher than AM2001, which is mostly due to two factors. (1) Our total EFs for boreal fires reflect the large component of smoldering combustion in this region and are calculated by equally weighting the ground-based and airborne averages. (2) We also weight the boreal forest fire EFs more than the temperate forest fire EFs (87:13, based on relative global fuel consumption) to generate our extratropical EF. Conversely, our $\text{EF}(\text{NO}_x)$ for extratropical forest fires is about three times lower than $\text{EF}(\text{NO}_x)$ for extratropical fires in AM2001. This is because the $\text{EF}(\text{NO}_x)$ for temperate fires is higher than for boreal fires, but the temperate forest fire contribution is minimized in our extratropical average by our weighting scheme. However, our temperate forest fire $\text{EF}(\text{NO}_x)$ is similar to the AM2001 $\text{EF}(\text{NO}_x)$ for extratropical fires. For crop residue fires, the comparison to AM2001 is complex. The original AM2001 EFs relied on very limited data and extrapolations and AM2001 use a different averaging scheme than that applied in this work. In fact, we recommend using the EF measured specifically for mechanized or manual-harvest agriculture explicitly when possible (Sect. 2.3.13).

In comparison to Yevich and Logan (2003), the main difference is that they reported five major emitted species (CO_2 , CO , CH_4 , NO_x , and PM) whereas we include many more species (nearly all recently-measured) in this work. For species reported in both compilations most of the values are within 40% of each other, but a few changed by a factor of 2 or more. Ratios of this work to Yevich and Logan (2003) for a given EF are shown in parentheses. The large changes are: lower NO_x from charcoal burning (0.17) and dung burning (0.10); higher CH_4 (4.07) and PM (18.8) from dung burning; and higher CO , CH_4 , and NO_x emissions from crop residue burned in field (2.00, 2.65, and 2.79, respectively). For the main type of biofuel burning (open wood cooking fires) the Yevich and Logan (2003) EFs are mostly very close to our EFs and all their EFs are within 48% of our updated values.

3.2 Estimating unmeasured emission factors

In general, estimating unmeasured values can improve model performance although this is not a guaranteed outcome. Our compilation does not tabulate estimates for unmeasured, individual species because the best estimation method depends on the application. The simplest estimates are obtained by using the EF values that may be available for the most similar fuel type. For example, filling in with EF values from one forest type for another, or using savanna fire EFs to estimate missing EFs for mechanized agriculture crop residue fires. To account for MCE differences between fire types,

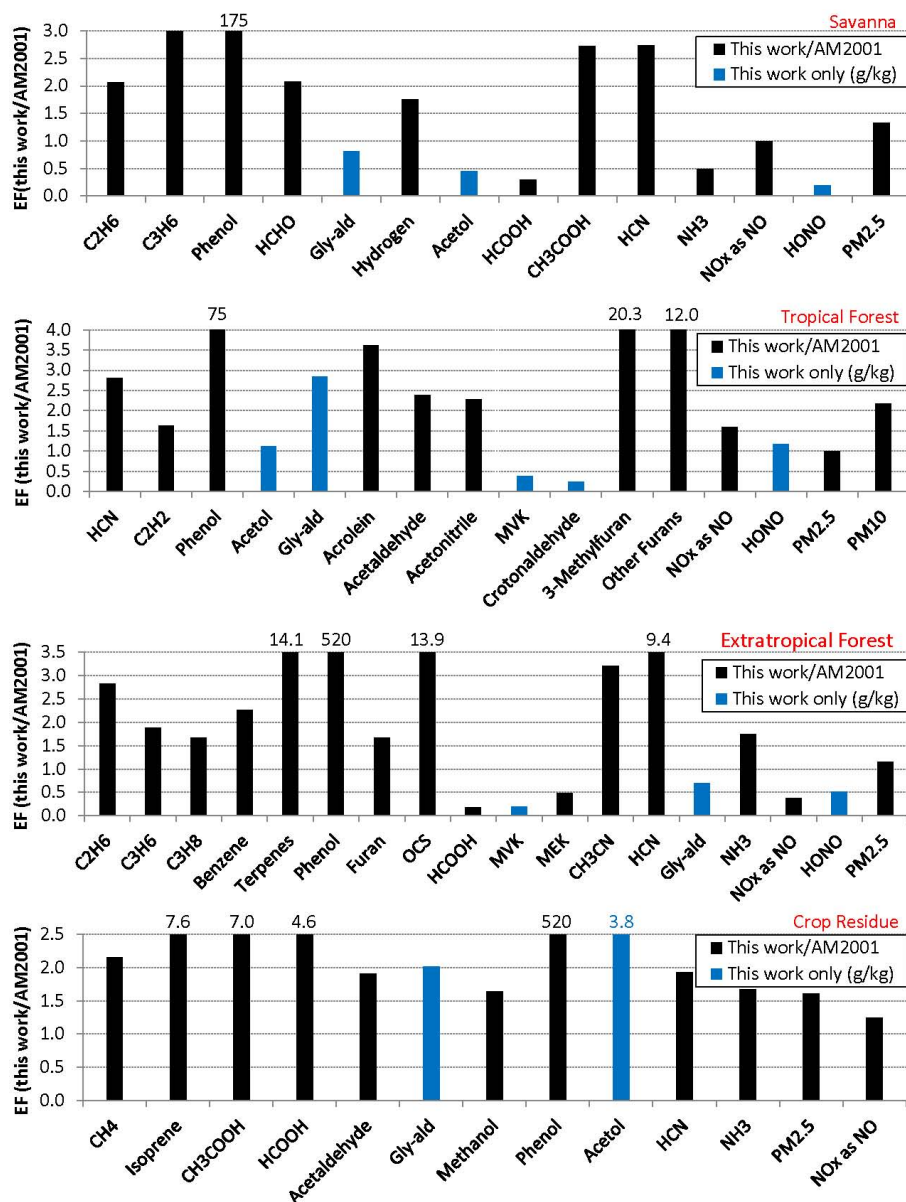


Fig. 1. The black columns show the EF in this work divided by the EF in Andreae and Merlet (2001) for the indicated species. The blue columns show the EF in g kg^{-1} for species not found in Andreae and Merlet (2001). “Gly-ald”, “MVK”, and “MEK” indicate glycolaldehyde, methyl vinyl ketone, and methyl ethyl ketone, respectively. See Sect. 3.1 for discussion.

one can calculate missing EFs at the average MCE for a fire type using the relationships between EF and MCE for a similar fuel type. Or one can use the inter-compound ratios from the most similar fuel type. For example, assume compounds X and Y have both been measured for fuel type A, but only compound X has been measured for a similar fuel type B. The emissions of compound Y from fuel type B can be estimated from: $Y_B = (Y/X)_A \times X_B$. If laboratory data is used it is critical to consider how realistic the fire simulations were. In addition, lab EFs may require some mathematical processing to project EF that better reflect field burning conditions.

These latter two issues are discussed in detail in Christian et al. (2003) and Yokelson et al. (2008). Another general principle is to use data relying on the most appropriate measurement technique available. For instance, in complex mixtures featuring sticky gases, some techniques may be more prone to chemical interference or positive or negative sampling artifacts. It is best to use sources where the smoke age and MCE are available in addition to the EF for the species of interest. Finally, if possible, estimates should be obtained from studies where the data for all the reported species seems reasonable. For example, BC values would be preferred from

a study where all the trace gas EFs, particle size distributions, etc. are in the normal range as this indicates overall representative sampling. Sometimes a study may report a useful upper limit for a compound even though it does not report an EF. For instance, an upper limit is reported for glyoxal/acetone of 20% in OP-FTIR studies (Christian et al., 2003) or 10% in on-line, pre-separation MS studies (Karl et al., 2007; Warneke et al., 2011). In some cases, inspection of mass spectra can put an upper limit on the emissions of a compound, but it is frequently the case at high masses that many species appear at one nominal mass. Our estimates of total NMOC in Sect. 3.4 also provide very rough guidance for the sum of the compounds that are unmeasured.

3.3 Specific compounds

3.3.1 HONO

Given the abundance of highly reactive species present in fresh smoke, OH plays a key role in the “fast chemistry” of young plumes (Hobbs et al., 2003). Photolysis is the primary daytime fate of nitrous acid (HONO), which forms OH and NO with unit quantum yield within 10–20 min (Sander et al., 2006). Thus, HONO can be an important source of the OH radical, which then initiates attack on NMOCs (Finlayson-Pitts and Pitts, 2000). Significant, direct emissions of gas-phase HONO from BB at $\sim 3\%$ of NO_x was first reported for a savanna fire by Trentmann et al. (2005). A range of $\Delta\text{HONO}/\Delta\text{NO}_x$ (5–30%) was then observed in a laboratory experiment burning various types of southern African biomass (Keene et al., 2006). A comparable molar ratio of $\Delta\text{HONO}/\Delta\text{NO}_x$ ($\sim 14\%$) was observed by Yokelson et al. (2007a) from a pasture fire in the Amazon (Table S12). The Caltech chemical ionization mass spectrometer (CIMS) measured similar HONO/ NO_x ER for Yucatan BB (Yokelson et al., 2009). OP-FTIR and the NOAA negative ion proton transfer CIMS were in good agreement with each other and observed HONO/ NO_x ratios similar to those mentioned above when sampling laboratory fires burning North American biomass fuels (Roberts et al., 2010; Burling et al., 2010; Veres et al., 2010). A subsequent aircraft field campaign confirmed the lab HONO/ NO_x ratios by airborne FTIR (Burling et al., 2011) for the same fuel types on open fires and also documented rapid post-emission HONO loss (Akagi et al., 2011). Similar HONO/ NO_x ER were observed for boreal forest fires during ARCTAS (J. M. St. Clair, personal communication, 2010). The collective range of $\sim 3\text{--}30\%$ in the ER $\Delta\text{HONO}/\Delta\text{NO}_x$ from all studies suggests that HONO emissions may be highly dependent on fuel type (Keene et al., 2006; Burling et al., 2010). High levels of OH in young BB plumes that are consistent with photolysis of significant amounts of HONO have been observed at least twice (Hobbs et al., 2003; Yokelson et al., 2009) (discussed further in Sect. 3.5). In two prognostic model applications both Trentmann et al. (2005) and Alvarado and Prinn (2009) found that adding both a “reasonable” amount of initial HONO and a

continuous source from heterogeneous chemistry to detailed photochemical models of BB plumes improved the agreement between simulated and observed ozone formation.

3.3.2 HCN

Andreae and Merlet (2001) reported HCN emission factors only from Hurst et al. (1994a, b) and stressed the need for more measurements of this species given its potential value as a biomass burning tracer (Li et al., 2000). Within the past decade EF(HCN) has been measured frequently and the results have high variability. However, the bulk of the new data suggest average EF for most types of biomass burning that are about ten times higher than obtained in the first measurements (Tables 1 and 2). HCN has also proved useful as a tracer to deconvolute mixtures of urban and BB emissions (Yokelson et al., 2007b; Crouse et al., 2009). Currently there appears to be two main limitations in the use of HCN as a BB tracer. First, there is a high natural variability in HCN emissions even within a single or similar fire types. For example, Yokelson et al. (2009) note that the ER $\Delta\text{HCN}/\Delta\text{CO}$ for Brazilian tropical evergreen forest deforestation fires (0.0063 ± 0.0054) does not differ significantly from that of tropical dry forest deforestation fires in the Yucatan (0.0066 ± 0.0041). While it is encouraging that the mean, observed ER for these two fuel types are similar, the 1σ standard deviation uncertainty in the mean is greater than 60% of the mean for both fuel types, which then contributes large uncertainty to HCN-based estimates of the BB contribution to regional pollutant levels as discussed elsewhere (Yokelson et al., 2007b; Crouse et al., 2009). Second, there is a large difference in the $\Delta\text{HCN}/\Delta\text{CO}$ ER that can occur for some different fire types, which impacts estimates in the many areas featuring many types of biomass burning. For example, Christian et al. (2010) note that HCN levels fell below FTIR detection limits when sampling cooking fire emissions in both Mexico and Africa. Thus, more sensitive measurements of biofuel sources are needed for this fire type. On the other hand the EF(HCN) measured for peat fires appear to be about ten times larger than for other types of open burning (Tables 1, 2, and S5). Indonesia, as one example, can have large amounts of peat fires, forest fires, and biofuel use, complicating the use of HCN as a tracer in that region.

3.3.3 CH_3CN

Biomass burning is thought to be the primary source of acetonitrile in the atmosphere (de Gouw et al., 2003). Its relatively long lifetime (5–6 months, Li et al., 2003) and near exclusive production from biomass burning suggests great potential as a biomass burning tracer. Many groups have now measured CH_3CN in smoke plumes by MS (Andreae et al., 2001; Jost et al., 2003; Holzinger et al., 1999; Karl et al., 2003, 2007; Christian et al., 2003; Yokelson et al., 2007a, 2009; Crouse et al., 2009). The $\Delta\text{CH}_3\text{CN}/\Delta\text{HCN}$ ER has

been shown to be quite robust in both laboratory and field measurements with molar ER of 0.39–0.56 being observed for a wide range of non-boreal fuel types burned (Crouse et al., 2009; Yokelson et al., 2008, 2009; Christian et al., 2003). The $\Delta\text{CH}_3\text{CN}/\Delta\text{HCN}$ ER for 4 boreal plumes sampled during ARCTAS was 0.30 ± 0.11 (Simpson et al., 2011). Analogous to HCN, CH_3CN is both unmeasured for cooking fires and was produced at order of magnitude higher levels by peat fires (Table S5).

3.4 Gas-phase non-methane organic compounds (NMOC)

Most NMOC are reactive so it is important to speciate as many as possible and to know the total amount. Early attempts to measure total gas-phase NMOC from BB relied on instruments designed to measure total NMHC (TNMHC, e.g. Cofer III. et al., 1993) and returned ER for $\Delta\text{TNMHC}/\Delta\text{CO}$ on the order of 24%. However, it is now known that ~60–80% of the NMOC emitted by BB are OVOC on a molar basis and that TNMHC instruments have a response to oxygenated compounds that is poorly characterized (Kállai et al., 2003). More recent attempts to estimate total NMOC are described next. PTR-MS is a “soft ionization” technique for measuring gas-phase NMOC with proton affinity higher than water (most NMOC) that produces essentially one peak per molecular mass and for which the proportionality between signal level and concentration falls within a narrow range for all compounds detected at each mass (Lindinger et al., 1998; Karl et al., 2007). GC and FTIR techniques can be useful for species identification when more than one compound appears at a mass, but their response factors to individual species vary over a greater range than for PTR-MS. In addition, many of the NMOC emitted by BB are too “sticky” or reactive to be measured by GC while FTIR works best for smaller molecules whose strongest absorption features are not severely overlapped by water or other co-emitted species (Goode et al., 1999). In BB studies that synthesized all three techniques the amount of MS signal due to identified and un-identified peaks was compared in a few selected “typical” PTR-MS mass spectra. In this way both Christian et al. (2003) and Karl et al. (2007) estimated that ~72% of the NMOC in fresh smoke could be identified (on a molar basis) when considering all m/z up to 205. Since most of the unidentified species are heavier in mass (>100 amu) this corresponds to successful identification of about 50% of the NMOC on a mass basis. In a recent laboratory-based fire study, additional advanced species identification processes were employed, but the unidentified species still ranged from 25–51% on a mass basis (Warneke et al., 2011).

Two major concerns regarding this large amount of unidentified (and often overlooked) NMOC species are (1) the additional reactivity they contribute to plume gas-phase chemistry should be recognized in models, and (2) because of their high mass, on average, many are likely to

be SVOC that could also condense after cooling or oxidation (Robinson et al., 2007). Consistent with the first effect, Trentmann et al. (2005) showed that tripling the NMOC/ NO_x ratio above the measured amount improved model-measurement agreement for ozone. Alvarado and Prinn (2009) added monoterpenes to the BB initial emissions in their smoke model to increase the total organic gas-phase emissions by 30% as a surrogate for unidentified NMOC and this enabled their model to better reproduce the secondary formation of particulate organic carbon observed in a plume. Both findings suggest that model simulations can be improved by including NMOC that have not been identified to date.

Because unidentified NMOC emissions are both abundant and important, we have included their estimated EF for each fire type in Tables S1–S14 and in Tables 1 and 2 as described above. In addition, we provide a new global estimate of total NMOC emissions in Table 5, which supersedes the estimate in Table 5 of Yokelson et al. (2008). For most fuel types we calculated total identified NMOC by summing the individual average NMOC emission factors reported in Tables S1–S14. We then estimated the potential total NMOC (identified plus unidentified) in g kg^{-1} for each fire type by multiplying identified NMOC by a factor of 2 or 3 as needed. Based on the findings of Christian et al. (2003) and Karl et al. (2007) that only about half of the NMOC mass can be identified when the emissions are measured by FTIR, GC, and PTR-MS, we employed a factor of 2 to estimate total NMOC from fire types where the emissions were measured with all these instruments. Yokelson et al. (2009) found that studies using 2 of these techniques identified only about 40% as much NMOC by mass compared to studies using all three techniques. Therefore, we use a factor of 3 to calculate potential total NMOC for those fire types that have so far only been sampled with minimal instrumentation (e.g. biofuel burning).

To scale to global production of gas-phase NMOC in Tg yr^{-1} in Table 5, we multiply the total NMOC in g kg^{-1} for each fire type by the estimated biomass consumption for that fire type from Table 4. Global production of NMOC from biofuels is calculated using EF(NMOC) of open cooking fires, since these types of fires are the dominant source of biofuel emissions on a global scale (Dherani et al., 2008). Summing the annual gas-phase NMOC from each fire type results in a total BB gas-phase NMOC source of 406 Tg yr^{-1} (383 Tg yr^{-1} without garbage burning). We then show that adding the estimated NMOC emissions from peat fires in the 1997 El Niño year brings the global total to 737 Tg yr^{-1} . The latter estimate is an upper limit for emissions during an El Niño year when a large number of fires affected the Indonesian tropical peatlands. The lower value of 383 Tg yr^{-1} ignores the contribution from peat and garbage burning entirely. We note that Table 2 of AM2001 estimates that about 100 Tg yr^{-1} of identified NMOC are emitted by BB when considering all the NMHC and several of the main OVOC. If the other OVOC from their Table 1 (that are not

Table 5. Measured and predicted estimates of NMOC emitted from biomass burning on an annual basis.

Fuel Type	Total Combusted Biomass (Tg yr ⁻¹) ^a	EF(CO) (g kg ⁻¹ dry biomass) ^b	CO global production (Tg yr ⁻¹)	EF (NMOC, identified) (g kg ⁻¹ dry biomass) ^b	EF (NMOC, estimation of total) (g kg ⁻¹ dry biomass) ^c	NMOC global production (Tg yr ⁻¹)	EF (BC) (g kg ⁻¹ dry biomass)	BC global production (Tg yr ⁻¹)
Savanna	3366	63	212	12.4	24.7	83	0.37	1.25
Extratropical	640	122	78	27.0	54.0	35	0.56	0.36
Tropical Forest	1330	93	124	26.0	51.9	69	0.52	0.69
Biofuel	2601	77	200	19.2	57.7	150	0.83	2.16
Open Cooking/Cooking Stoves	1351	59.5	80	10.5	31.6	42.7	0.79	1.06
Dung Burning	106	105	11.1	32.6	97.7	10.4	0.53	0.056
Charcoal Making	43	255	11.0	161	321	13.8	0.02	8.6 × 10 ⁻⁴
Charcoal Burning	39	189	7.4	5.56	11.1	0.43	1.0	0.039
Pasture Maintenance	240	135	32	44.8	89.6	21.5	0.91	0.22
Crop Residue	489	102	50	25.7	51.4	25.1	0.75	0.367
Garbage Burning	1000	38	38	7.5	22.6	22.6	0.65	0.65
Peat ^d	3400	182	619	48.7	97.3	331	0.20	0.68
Avg. model year – global estimate	–	–	734	–	–	406	–	5.69
El Niño year – global estimate	–	–	1353	–	–	737	–	6.37

^a Total combusted biomass estimates are from Table 4 averages (this work), unless otherwise noted. Charcoal making estimate is in units of Tg charcoal made per year. Charcoal burning estimate is in units of Tg charcoal burned per year.

^b Data are from Tables 1 and 2 of this work. EF for open cooking fires was used to represent EF for all biofuel since cooking fires are the dominant source of biofuel emissions globally. EF for open cooking/cooking stoves was taken as the averages of open cooking and cooking stove EF. Charcoal making EF in units of g kg⁻¹ charcoal made. Charcoal burning EF in units of g kg⁻¹ charcoal burned.

^c Multiplication factors to estimate total EF(NMOC) (as identified + unidentified NMOC) is described in Sect. 3.4.

^d Emissions from peat are added to global totals to estimate a typical emissions during an El Niño year.

included in their Table 2) are considered, it suggests that about 150 Tg yr⁻¹ of identified NMOC are emitted by BB globally. Doubling this value to account for unidentified species suggests a true global total near 300 Tg yr⁻¹, however, this has not been widely realized. The latter value is only 20–30% lower than our estimate in Table 5. Clearly biomass burning emissions of NMOC rank well ahead of urban NMOC emissions globally and are second only to biogenic emissions (~1000 Tg yr⁻¹) as discussed in Yokelson et al. (2008). CO and black carbon (BC) are also important BB emissions. Both as a demonstration of (and a check on) our methodology in Table 5, we also combine our biomass consumption values with the measured EF(CO) and EF(BC) for each fire type to produce global BB central estimates for CO (734 Tg yr⁻¹) and BC (5.69 Tg yr⁻¹) that are in good agreement with other recent estimates (Kopacz et al., 2010; Bond et al., 2004).

3.5 Post emission processing

The emission factors presented herein were calculated from fresh smoke sampled at the source that had usually cooled to ambient temperature, but undergone minimal photochemical aging. In nearly any application of this data, it is important to realize that rapid, complex photochemistry can cause large changes in smoke composition within minutes after its initial emission. There is a not a single standard process-

ing scenario that can be applied to all smoke. Rather, there are numerous possible fates of smoke given differences in initial emissions, degree of cloud processing, dispersion altitude, temperature, humidity, time of day or night, small vs. large-scale fires (e.g. cooking fires vs. forest fires), the degree of mixing with other BB plumes or biogenic or urban emissions, etc. In theory, almost any realistic processing scenario can be modeled. In practice, very few detailed smoke evolution data have been acquired that are of value for testing or constraining the chemical mechanism in smoke photochemistry models. Next we summarize the measurements that have been made and draw a few conclusions.

The type of measurements that provide the most straightforward test of photochemical models are those that trace the evolution of a single, isolated BB plume. Measurements of this type have been obtained in Alaska, Africa, California, Mexico, and Canada. Goode et al. (2000) sampled two very large plumes up to ~56 km downwind in Alaska (their Table 6). The B280 fire plume was sampled well below the top of the plume and no ozone formation or change in a reactive hydrocarbon (C₂H₄) was observed over ~2.8 h of aging. However NH₃ decreased about 70% over that time. The B309 fire plume was sampled closer to the top and within ~2 h of aging the ΔO₃/ΔCO ratio had risen to ~9% (from negative values at initial injection). Both ΔHCOOH/ΔCO and ΔCH₃COOH/ΔCO doubled on that time scale, but the decrease in C₂H₄, which would have

accompanied high OH, was small enough to be insignificant. The chemical evolution of five different isolated BB plumes was tracked by various aircraft during the Southern Africa Fire Atmosphere Research Initiative (SAFARI) 2000. Three of these plumes were sampled by the University of Washington Convair 580 (Fig. 5 in Yokelson et al., 2003) and $\Delta\text{O}_3/\Delta\text{CO}$ rose to $\sim 9\%$ in only ~ 40 min of aging. In addition $\Delta\text{CH}_3\text{COOH}/\Delta\text{CO}$ more than tripled from its initial value to $\sim 9\%$ within the same aging interval. Additional detailed analysis of the most extensively sampled plume (Hobbs et al., 2003), the Timbavati plume, revealed a rapid loss of NO_x and 16 reactive hydrocarbons consistent with an average OH of 1.7×10^7 molecules cm^{-3} . Technical issues involving the sampling system preclude us from making conclusive quantitative statements about the evolution of the particles in that plume (Alvarado and Prinn, 2009; Magi, 2009), but particle nitrate definitely increased and OC likely did also. Jost et al. (2003) sampled a Namibian BB plume at 11 different smoke ages and observed $\Delta\text{O}_3/\Delta\text{CO}$ rise to $\sim 10\%$ in ~ 2 h and also a tendency for acetone to be enhanced in the downwind plume. In another African plume, Abel et al. (2003) measured an increase in single scattering albedo from 0.84 to 0.885 over 2.4 h of aging that they attributed to condensation of non-absorbing (organic) species.

Yokelson et al. (2009) described the evolution during 1.5 h of aging of a single BB plume in the Yucatan sampled by the NCAR C-130. $\Delta\text{O}_3/\Delta\text{CO}$ rose to 10–15% in about one hour, which is almost identical to the O_3 formation rate observed by Hobbs et al. (2003). Rapid secondary production of peroxyacetyl nitrate (PAN), hydrogen peroxide, formic acid, and peroxyacetic acid was observed. The post emission loss rates were measured for SO_2 , NO_x , and HONO. No reactive NMOC were measured in the down-wind plume, but in-plume OH was directly measured for the first time in a BB plume and averaged 1.14×10^7 molecules cm^{-3} for the plume age interval 22–43 min. Significant post-emission formation rates for particle nitrate, ammonium, sulfate, organic aerosol (OA), and an increase in single scattering albedo were measured. Aerosol mass spectrometry and light scattering measurements both indicated that the aerosol to CO ratio increased by a factor of ~ 2.4 in 1.5 h. In another isolated Yucatan plume TEM analysis indicated that slightly aged smoke had a higher abundance of tar balls (Yokelson et al., 2009), which have been linked to the concept of brown carbon (Adachi and Buseck, 2008; Andreae and Gelencsér, 2006; Chakrabarty et al., 2010). Recently the evolution of an isolated BB plume was measured in mid-coast California for ~ 4.5 h. A rapid increase in light scattering and formation of O_3 , HCOOH , CH_3COOH , and PAN was observed along with loss of NO_x , HONO, C_2H_4 , C_3H_6 , and NH_3 (Akagi et al., 2011).

The chemical evolution of one boreal forest fire plume (Flight 18, McKay Lake Fire) was extensively measured during ARCTAS (Alvarado et al., 2010). This fire plume exhibited two different types of behavior on the same day.

In particular, the early evening samples were divided into two groups: those obtained below 1 km and those obtained above 2 km. The low altitude samples had low MCE (more smoldering, 0.85–0.92) and low $\Delta\text{NO}_y/\Delta\text{CO}$ (0.34–0.55%). After ~ 4 h of aging $\Delta\text{PAN}/\Delta\text{CO}$ reached 0.23–0.36% and $\Delta\text{O}_3/\Delta\text{CO}$ ranged from -1% to 3%. The higher altitude samples had higher MCE (more flaming, 0.96) and a higher $\Delta\text{NO}_y/\Delta\text{CO}$ (1.1–1.7%). In the high altitude samples (produced by more vigorous combustion) $\Delta\text{PAN}/\Delta\text{CO}$ reached 0.51% after only one hour, by which time $\Delta\text{O}_3/\Delta\text{CO}$ had already reached 5%. These results nicely illustrate the high natural variability in post-emission processing that can be expected for fires, which was, in this case, driven partly by variable initial emissions. In light of the potential connection between plume chemistry and plume injection altitudes it is significant that large numbers of BB plume heights can now be measured from space about once per day (Val Martin et al., 2010). However, in the boreal forest, where individual fires can burn for weeks, the fire radiative energy (and likely the biomass consumption rate and injection altitude) may not peak at mid-day in a simple diurnal cycle. In fact, the regional fire radiative energy can be higher at night (see Fig. 4b of Vermote et al., 2009), which could be driven by frontal passage or other weather or fuel conditions.

Several authors have constructed detailed photochemical models for direct comparison to the measurements in some of the plumes mentioned above (Jost et al., 2003; Trentmann et al., 2005; Mason et al., 2006; Alvarado and Prinn, 2009; Alvarado et al., 2010). Taken together, these studies show that model performance is improved by considering the initial emissions of HONO, a continuous heterogeneous source of HONO, and unidentified NMOC. In addition, Alvarado et al. (2010) discuss application-specific techniques to improve model performance at larger geographic scales.

It is also useful to compare data acquired in “intercepted”, aged plumes to “probable” initial values. Yokelson et al. (2009) discuss sources of uncertainty in interpretation of data from aged smoke only in their Sect. 3.5. The comparison is least uncertain for species which have tightly constrained initial values such as $\Delta\text{O}_3/\Delta\text{CO}$, which is negative in fresh plumes (Yokelson et al., 2003). For example, Andreae et al. (1994) described encounters with 40 different tropical BB plumes about 7–10 days old for which $\Delta\text{O}_3/\Delta\text{CO}$ averaged $43 \pm 26\%$ (ranging from 11–89%) and where $\Delta\text{O}_3/\Delta\text{CO}$ correlated positively with $\Delta\text{NO}_y/\Delta\text{CO}$ (their Table 1 and Fig. 14). At the other end of the spectrum, 1–2 day old plumes from smoldering tundra fires in the Arctic had an average $\Delta\text{O}_3/\Delta\text{CO}$ of $9.5 \pm 6\%$ (Wofsy et al., 1992; Jacob et al., 1992). The smaller O_3 enhancements in the arctic plumes were attributed to younger plume age and a factor of ten lower initial $\Delta\text{NO}_x/\Delta\text{CO}$ (inferred from lower $\Delta\text{NO}_y/\Delta\text{CO}$) (Andreae et al., 1994). Nine plumes from boreal wildfires that were 6–15 days old were sampled at the PICO-NARE station in 2004 and eight of the plumes had $\Delta\text{O}_3/\Delta\text{CO}$ ranging from 9% to 89% (Table 3

of Val Martín et al., 2006; Lapina et al., 2006). However one aged plume had $\Delta\text{O}_3/\Delta\text{CO}$ of -42% (vide infra). Higher O_3 enhancements were correlated with higher NO_y . Yokelson et al. (2007a) sampled a large regional plume in Brazil containing the mixed output from many regional fires with smoke age likely ranging from 1–20 h that had enhanced O_3 , HCOOH , and CH_3COOH . Reid et al. (1998) compared regional haze dominated by aged BB smoke to BB smoke <4 min old in Brazil. Smoke aging was associated with loss of gas-phase NMHC and growth of particle ammonium, organic acids, and sulfate as well as other changes including increases in particle size and single scattering albedo.

The observation at PICO-NARE that some plumes may have little or no photochemical activity is consistent with some airborne observations. One of two Alaskan plumes traced by Goode et al. (2000) and several aged plumes encountered at high altitude off the coast of the US by de Gouw et al. (2006) or in Africa by Capes et al. (2009) showed little evidence of oxidation. Most of the boreal forest fire plumes sampled during ARCTAS were photochemically active enough to generate substantial amounts of PAN, but very little O_3 (Alvarado et al., 2010; Singh et al., 2010). A variety of plume chemistry regimes has been observed in remote sensing studies. For example, Fishman et al. (1991) attributed widespread O_3 enhancements in the Southern Hemisphere to BB, while Verma et al. (2009) observed both O_3 formation and O_3 destruction in boreal forest fire plumes. In summary, the airborne, ground-based, and space-based observations consistently demonstrate that a large range in post-emission outcomes is possible. An important aspect of this variability is that despite the difficulty of using reactive initial emissions as input for regional-global models, there may not be an advanced smoke age that provides significant advantages as a starting point at which emissions could be tabulated.

A few observations have been made of cloud processing of smoke. Yokelson et al. (2003) observed rapid reduction in NO , CH_3OH , NH_3 , and CH_3COOH and concurrent fast NO_2 and HCHO formation within a small pyrocumulus cloud that capped a vertical column of smoke ~ 3 km above the flame front. This was modeled as the product of heterogeneous reactions of CH_3OH on droplet surfaces combined with enhanced photochemistry in the cloud (Tabazadeh et al., 2004; Madronich, 1987). Unpublished data from the Yucatan plume described earlier in this section shows a very large step increase in $\Delta\text{HCHO}/\Delta\text{CO}$ immediately after the plume RH briefly exceeded 100%, a potential sign of cloud-processing (A. Fried and T. Campos, personal communication, 2010). A large fraction of the smoke on Earth resides in hazy boundary layers that are “topped” with a layer of embedded cumulus clouds. These clouds also play a role in “pumping” smoke from the boundary layer to the free troposphere. For these reasons, smoke-cloud interactions require much more research.

3.6 Knowledge gaps and sources of uncertainty

3.6.1 Poorly characterized combustion/fire types and post-emission processing scenarios

The emissions from residual smoldering combustion have rarely been measured and measurements of fuel consumption by RSC are also rare. This is a major source of uncertainty for every type of open burning except grass fires. For instance, Bertschi et al. (2003b) showed that if RSC accounted for 10% of fuel consumption on woody savanna fires, the fire-average EF for some species would be ~ 2.5 times larger. Biofuel use (e.g. cooking fires) is the second largest type of global BB, but often overlooked as these small fires elude satellite detection. Biofuel consumption is estimated from questionnaires distributed in rural areas (Yevich and Logan, 2003), which may underestimate urban and industrial biofuel use. The NMOC emissions from biofuel use have not been measured with mass spectrometry, which is required for comprehensive smoke analysis. Thus, HCN and CH_3CN emissions have not been quantified for biofuels and there is no chemical tracer to validate survey results (Christian et al., 2010). The lack of a tracer to verify surveys is especially problematic for industrial biofuel use. Small informal firms account for over 50% of non-agricultural employment and 25–75% of gross domestic product in both Latin America and Africa (Ranis and Stewart, 1994; Schneider and Enste, 2000). These firms use a variety of fuels (wood, sawdust, crop residue, coal, used motor oil, tires, garbage, boards with lead paint, etc.) and some are illegal, which can affect survey results (Christian et al., 2010). More biofuel measurements, with more complete instrumentation, are needed to characterize the diverse emissions, which depend on fuel, geography, local customs, climate, and season (Yevich and Logan, 2003).

Garbage burning (GB) is a poorly characterized emission source that can be significant in urban-rural areas of developing and developed nations. Christian et al. (2010) made seminal measurements of open GB. High EF(HCl) ($1.65\text{--}9.8\text{ g kg}^{-1}$) traceable to waste polyvinyl chloride suggest that GB is the main global source of HCl. GB emits large amounts of PM, HCl, and NO_x (Yokelson et al., 2011) and interaction between these species could impact O_3 formation (Osthoff et al., 2008; Raff et al., 2009; Thornton et al., 2010). GB is the main global source of dioxins (Costner, 2005, 2006) and the emissions of other toxic chlorinated compounds should be measured. GB could impact source apportionment studies because it emits high levels of several compounds used as tracers for BB such as levoglucosan (Christian et al., 2010).

Relatively few measurements have been made of BB in temperate regions where much of the burning is prescribed for land management, but controlled to protect air quality (Mutch, 1994; Neary et al., 2005; Wiedinmyer and Hurteau, 2010). Models often assess the air quality impacts using

EFs from tropical and boreal forest fires, which adds uncertainty. Preliminary results from recent laboratory and field campaigns in temperate regions are included in this compilation. Finally, there are very few measurements of important post-emission processing scenarios such as nighttime smoke chemistry and mixing with clouds or other plumes.

3.6.2 Measurement challenges

The proper measurement of particle-phase light absorbing carbon (LAC, including BC, weak absorption by organic carbon (OC), and strong absorption by “brown carbon”) and the best way to represent LAC in models is an area of active research (Andreae and Gelencsér, 2006; Magi, 2009; Chakrabarty et al., 2010). Most of the high molecular mass NMOC in both the gas and condensed phases are still unidentified, making it difficult to model their atmospheric impact. Moving from the current common mass resolution of ~ 200 to ~ 5000 and scanning at higher masses will allow more of these compounds to be identified. However, compounds with different structural formulas can have the same molecular mass at any resolution (e.g. acetic acid and glycolaldehyde) (Jordan et al., 2009). Species with identical mass can sometimes be quantified based on their different tendencies to form clusters, pre-separation, or MS-MS techniques, but all these approaches have limitations and many of the unknown species are semi-volatile and thus difficult to sample (Crouse et al., 2006; Karl et al., 2007). However, improved knowledge of the chemical formula of the emissions present at higher masses should enable an improved assessment of the physical properties of these emissions (e.g. vapor pressure, reactivity, etc.).

Limitations exist for all platforms used to study BB. Each offers well-documented advantages, but here we mention some key limitations and ideas for overcoming them. In laboratory studies many fire-types are hard to replicate and the different products of flaming and smoldering combustion may not mix the same way as in real fires. Wall losses limit aging studies to a few hours. Careful comparison/synthesis of laboratory results with field results for similar fuels (discussed at length in Yokelson et al., 2008) should maintain a key role for laboratory studies in future BB research.

Airborne studies sample real fires, but the lofted and unlofted emissions can have different chemistry and post-emission transport. Simultaneous ground-based and airborne EF measurements have been made on the same fire (Yokelson et al., 2008), but more measurements of the biomass consumption contributing to the lofted and unlofted emissions are needed, as noted above. Airborne platforms can study aging on long time scales, but real world smoke is often a complex mixture of young and old plumes and non-BB sources. The use of multiple tracers helps deconvolute mixtures of urban and BB emissions (Crouse et al., 2009).

Remote sensing provides numerous products to drive and validate models, but the global loss of information due to cloud coverage and lack of daily coverage by MODIS in the tropics are serious limitations. Detection efficiency of fires as hot-spots or burn scars is poor for small fires, which may comprise the majority of tropical fires (Hawbaker et al., 2008; Chang and Song, 2010a; Giglio et al., 2006). Comparison of burned area or hotspot products often reveals factor of ten or larger disagreements (e.g. Al-Saadi et al., 2008; Tables 5–7 in Chang and Song, 2010a, b). The latter authors noted that GFED2.1-based estimates of CO emissions from tropical Asia were 5–7 times higher than their estimates based on MODIS or L3JRC burned area products. On the other hand, Kopacz et al. (2010) concluded that GFED2.1 significantly underestimated CO from biomass burning in this region and globally. Better characterization of remote sensing products could improve their incorporation into models and possibly inform the development of new sensors.

The most serious measurement limitations from the standpoint of model accuracy may be as follows. At the plume scale, there is a large fraction of unidentified, reactive NMOC and few measurements of plume aging that constrain/validate chemical mechanisms. At regional-global scales there is uncertainty in biomass consumption, plume injection heights, and model parameterizations for processes that occur on spatial scales much smaller than the model grid (Alvarado et al., 2009, 2010; Fast et al., 2009). Additional measurements and improvements in computing power and parameterization of fast processes could increase model performance (Alvarado et al., 2009, 2010).

4 Conclusions

In the past ten years significant progress has been made in characterizing the initial emissions of trace gases and particles from biomass burning and their post-emission evolution. New instruments better quantify particle species, useful BB tracers, and light oxygenated NMOC, which account for much of the gas-phase NMOC emitted by fires. The detailed chemical evolution of several individual BB plumes has now been measured in the field. This new information has improved model performance for several biomass burning fuel types. In this work, recent studies are used to derive emission factors that characterize the nascent emissions from 14 types of biomass burning. Biomass burning terminology, biomass consumption, and plume aging are also summarized. Large uncertainties still exist for fire types (e.g. biofuels) and smoke-processing scenarios (e.g. clouds, night-time) that have been sampled only minimally with currently available instruments. Thus, significant advances could be achieved in the near future by deploying existing technology more extensively and we plan to update the EF data as warranted.

Supplementary material related to this article is available online at:
<http://www.atmos-chem-phys.net/11/4039/2011/acp-11-4039-2011-supplement.zip>.

Acknowledgements. We thank Isobel Simpson, Don Blake, Andy Weinheimer, Armin Wisthaler, Guido van der Werf, Thijs van Leeuwen, Ian Burling, Tami Bond, Christoph Roden, and Ted Christian for advance data. We thank Jennifer Logan, Ed Hyer, Jim Reardon, John Graham, Mark Carroll, Angelika Heil, and Ben Foster, for helpful discussions. SKA thanks Paulette Middleton and GEIA for financial support. Akagi and Yokelson were supported by NSF grants ATM-0513055 and ATM-0936321.

Edited by: C. Granier

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