Experimental Evaluation of Biomass Burning Emissions: Nitrogen and Carbon Containing Compounds

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Today biomass burning is accepted to be an important source of many trace gases affecting atmospheric chemistry (Crutzen et al., 1979; Cofer et al., 1988a; Radke et al., 1988; Crutzen et al., 1990). Despite its global significance and in contrast to fossil fuel use, where detailed investigations on global amounts and their distributions are available, still little quantitative information is known about the emissions of some of the compounds emitted and the global amounts consumed by biomass burning. Estimates of these global quantities are difficult to derive because of a very uncertain data base. The most recent values published by Crutzen et al. (1990) indicate that 1900 to 5000 teragrams (Tg) biomass carbon is released annually.

In order to obtain more reliable emission data, improvement of measurement techniques as well as methods for calculating emission data are required. A growing number of measurements on biomass burning emissions have been published since the first estimates (Crutzen et al., 1979), but some of the trace gas emissions are still very uncertain or even unknown as, for example, in the case of some nitrogen-containing species.

Most of the data on biomass burning emissions were derived from airborne measurements above large-scale fires. An experimental system, on the other hand, is advantageous in cases when information cannot be derived from open fires or when field measurements are inappropriate. In this chapter we describe results obtained by the latter technique. An important advantage of the apparatus described is the possibility of learning about burning behavior and burning stages, and thus clarifying relationships between combustion processes and emissions, finally leading to new methods for estimating emissions.

To extend our knowledge of the inventory of nitrogen and carbon in biomass burning, we took a close look at the most important emissions, trying to identify the major fractions which complete the mass balance. Such a balance cannot be achieved from natural fires due to the impossibility of exactly determining the absolute mass of burned and unburned plants.

Experimental Section

Burning Apparatus

The apparatus which was used for conducting open fires is shown in Figure 36.1. A more detailed description of this system is given by Lobert (1990a). The main parts of the apparatus include a hood in the form of an inverted funnel and a burning table of 60 × 60 centimeters (cm), which is placed on a high-resolution balance (E1210 and EB60; Mettler). The balance itself is placed on a frame which stands on the ground outside to avoid vibrations. A simple mechanism allows the raising of the burning table to an angle of 45° in order to simulate different wind directions, i.e., heading and backing fires. All the major parts are made of stainless steel and are mounted in a mobile trailer (Fladafi), which also contains most of the equipment required for carrying out the experiments.

A fanwheel-anemometer (Höntzsch) was used to measure the flow rate of stack gases; more recently, the device was replaced by a differential pressure sensor due to a high dirt sensitivity of the mechanical fan wheel. An electrical fan was built into the top of the chimney in order to provide a minimum draft during low-temperature combustion and to prevent the reaction gases from leaving the funnel from the bottom. Temperature sensors (Ni/Cr-Ni, TICON) were used to determine both stack gas and fuel temperatures, and two optical monitors were built in for the determination of CO and CO_2 concentrations. Several heated sampling tubes (stainless steel and teflon; Heraeus) allowed the exhaust gases to enter instruments in an adjacent laboratory to determine NO_x or for the on-line injection of the compounds mentioned above.

All the continuous measurements were recorded with a data logger (WES) at a frequency of 1 to 0.2 sec^{-1} and stored online on a personal computer for further calculations. The duration of an experiment was typically 15 to 20 minutes from ignition until the fuel bed cooled. Two switches connected to this data logger enabled us to send signals to the computer for synchronizing experiment and sampling procedures.

Figure 1

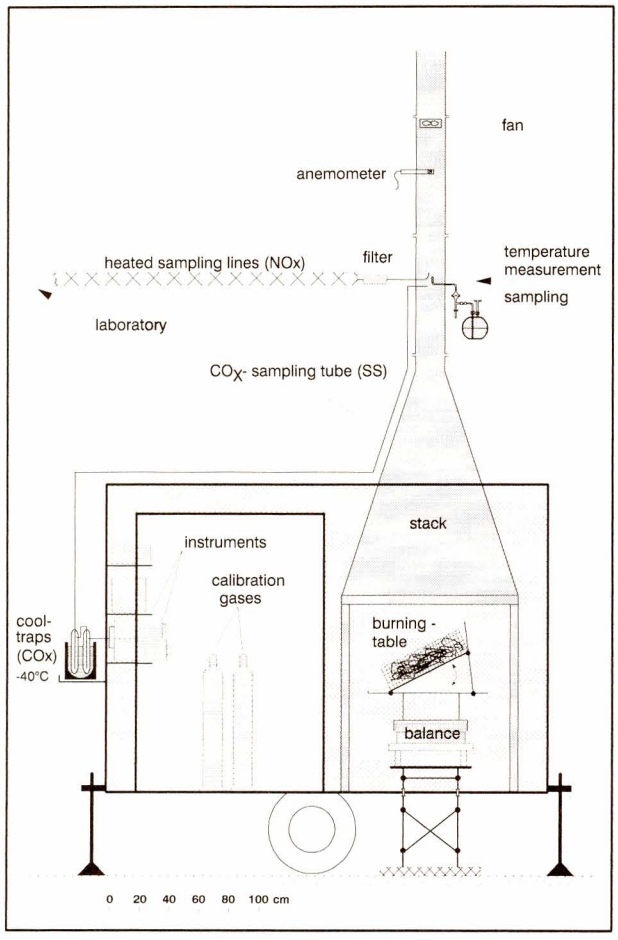

Figure 36.1 Burning apparatus for simulating open fires. The trailer is made of galvanized steel; all other parts are stainless steel or aluminum. Power and data transfer cables are connected to the adjacent laboratory.

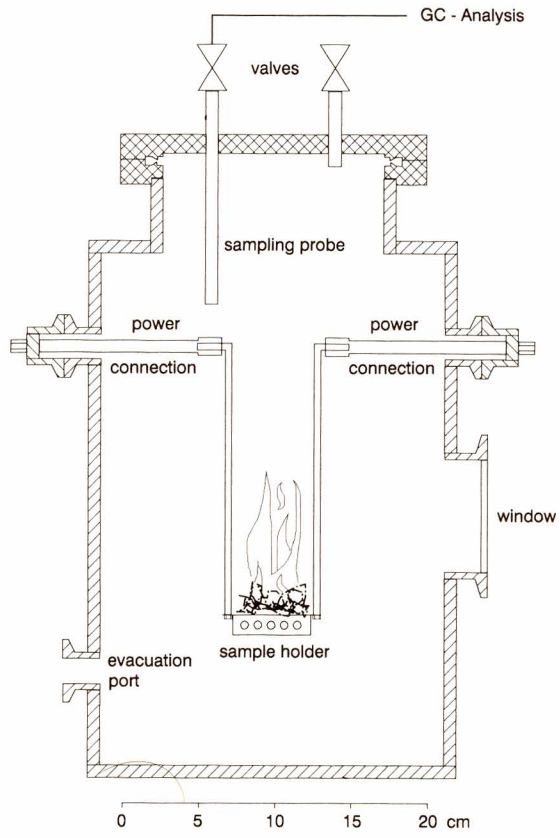

Figure 36.2 Apparatus for conducting uncontrolled burning experiments in an artificial atmosphere. The system is made of stainless steel and sealed with Small and ConFlat flanges.

A detailed description of sampling and analytical methods is given below.

Apparatus for N_2 Measurements

For the determination of molecular nitrogen emission we constructed a closed apparatus which enabled us to carry out burning experiments excluding atmospheric nitrogen (Kuhlbusch, 1990). This apparatus is shown in Figure 36.2 and consists of a stainless steel cylinder equipped with several sampling and supply valves in the top as well as two windows for observing the inside. The cylinder further contains a sample holder which is loaded with 0.5 to 1.0 gram (g) of biomass sample prior to the experiment and which is connected to the electrodes of a power supply. An additional port for evacuating the system is located at the bottom of the apparatus. After reaching the final vacuum, which is determined with a Pirani pressure gauge ($1–10^{-4}$ hectopascals, or hPa) and a high-accuracy gauge (0–1400 hPa), the cylinder is flushed with a mixture of very high-purity helium or argon and oxygen (79% : 21%) and pumped out several times in order to remove traces of nitrogen which might be adsorbed on the (electropolished and very smooth) inside surfaces. Helium leak tests were carried out in order to ensure the tightness of the system.

Following several blank tests, the sample is ignited by resistance heating of the stainless steel or tantal sample holder. The duration of such an experiment (ignition and self-sustaining combustion) lasts for about one to two minutes. Afterwards, the combustion gases are allowed to spread and disperse homogeneously inside the cylinder for one hour, followed by direct injection GC-analysis using a valve with two sample loops.

Sampling Procedures

As shown in Figure 36.1, there are several ways of sampling the stack-gas continuously. For the analysis of CO and CO_2, gases are pumped through the analyzers using a stainless steel tube (1/4″ × 5 m), connected to several flow controllers and passing three different filter units including a cold trap (−40°C), a glass fiber filter, and a stainless steel sinter-filter in order to remove water vapor, particles, and tar, which otherwise condense on the surface of the analyzer's optical parts. A dynamic on-line dilution of these gases is included due to the fixed concentration ranges of the analyzers. NO_x is determined by pumping the exhaust gases through the analyzers connected to a heated 1/4″ Teflon tube of 8 m length passing a Teflon filter (0.5 μm) and a cold trap at −20°C to remove big particles and water vapor.

The grab-sampling system which is used to determine most of the gases studied is shown in a cross-sectional view in Figure 36.3. Stack gas samples are taken from the middle of the chimney (see Figure 36.1) by sucking them into the evacuated 1 liter (L) stainless steel canisters. The canisters were electron beam welded and electropolished inside to ensure a smooth surface without diffusion-traps such as scratches and holes. They are equipped with two metal bellows valves (Nupro SS 4H). The biomass burning gases are pumped through the filter holder carrying glass fiber filters. After sampling, prior to the analysis, a dilution with high purity helium is performed in order to slow down possible reactions and to get a slight overpressure inside the canisters. Analysis starts about 10 minutes after taking the first of about 12 to 14 samples obtained during an experiment. After analysis, the canisters were evacuated and flushed several times at about 100°C for cleaning, and thereafter stored evacuated at about 10^{-2} hPa.

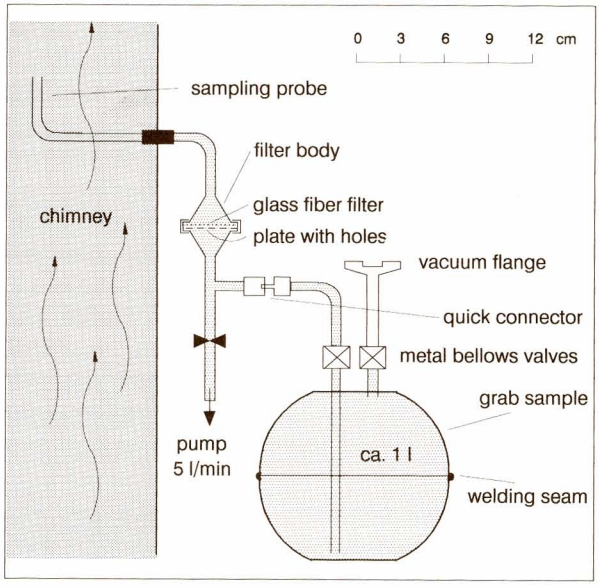

Figure 36.3 Cross-section of the grab sampling system. The 1 liter stainless steel samples are electropolished inside and electron beam welded. A pump connected to the filter holder provides a flow rate of 5 L/min.

The sampling of ammonia and the aliphatic amines was carried out using several scrubber methods. While ammonia was sampled by bubbling the gases through a solution of 30 milliliter (ml) 0.1 N sulfuric acid in polyethylene bottles with a flow rate of 8.5 L/min, the amines and, in recent experiments, also ammonia were sampled using an advanced scrubber method, which is described by Cofer et al. (1985) and modified for our use by Hartmann et al. (1990). The efficiency for sampling ammonia and amines with these methods was determined to be 99%; there was no significant observable difference in the results using the different scrubber methods for ammonia. Teflon filters of 0.5 μm pore size in the front of the 1/4″ Teflon sampling tube were used to remove particles from the emitted gases. Ammonia on the filters was ultrasonically desorbed into an H_2SO_4 solution before analysis.

Analytical Methods

Carbon monoxide and carbon dioxide were determined by using two BINOS nondispersive infrared analyzers (Heraeus), which operate at two different concentration ranges. The CO instrument contains one cell which is electronically split into ranges of 0 to 100 parts per million by volume (ppmv) and 0 to 2000 ppmv, while the CO_2 instrument contains two separate cells with ranges of 0 to 1500 ppmv and 0 to 6% by volume, respectively. The detection limits for these instruments are a few ppmv (noise level is 1 ppmv). Calibration of the instruments is carried out with commercial standard gas mixtures of CO and CO_2 (Steininger).

Methane analysis was carried out with a Shimadzu gas chromatograph (GC) Mini-3 equipped with a flame ionization detector (FID) and a stainless steel 3 m × 1/8″ OD column packed with 60/80 mesh molecular sieve 10 Å and supplied with high-purity nitrogen carrier gas at a flow rate of 25 ml/min; the column temperature was maintained at 110°C isothermally. Two ml of gaseous sample were injected with a valve allowing a detection limit of about 9 ppbv (three

times noise level) of methane, equal to 9 picograms (pg) C. For the calibration of methane measurements commercial standard gases of 1.5 to 1000 ppmv are used (Steininger).

To determine nonmethane hydrocarbons, a Siemens double oven GC L402 equipped with FID and WCOT fused silica capillary column 50 m × 0.32 mm ID coated with CP SIL 5 CB (1.19 μm) was used. Carrier gas flow rate (very high purity helium) was maintained at 1 bar inlet pressure equal to a linear gas velocity of 27 cm/sec. The method originally described by Matuska et al. (1986) was used for analyzing preconcentrated samples. An air sample of 0.4 ml is injected onto the first 10 cm of the column which is cooled to 77°K causing a cryofocussing of the sample, rendering sharp signals and enhancing detection limits. Injection of this sample is executed by removing the cryotrap followed by a temperature programmed heating (−40°C for 2 min; 15°C/min to +40°C; 10°C/min to +210°C; 10 min at 210°C). The detection limit (three times noise level) for this procedure is about 7 pg C or 18 ppbv for C_3 compounds. For compound identification, the absolute retention time method was used. Relative response factors (Dietz, 1967) were used for individual compounds and a response factor of 1.0 relative to CH_4 was used for the determination of $\Sigma(C_2–C_8)$. The absolute detector response was determined with a standard gas mixture of 10 ppmv propane in helium (AGA).

The sum of the nitrogen oxides NO and NO_2 (NO_x) is determined by using a Thermo Electron chemoluminescence NO_x analyzer type 14 A equipped with a stainless steel converter. The converter temperature was maintained at 600°C in order to minimize interference by other nitrogen-containing compounds. At this temperature there is no interference of, for example, acetonitrile, while at 800°C about 80% of an acetonitrile calibration gas is recorded with this detector. According to our experiments, fresh biomass burning NO_x emissions consist of about 90% NO and only 10% NO_2. For calibration of the instrument, standards of NO and NO_2 are used. The detection limit of this instrument for NO_x is around several ppbv in air.

Nitrous oxide was analyzed by taking 2 ml of gas sample from the canisters described above with gastight syringes and injecting them into a Dani GC equipped with Carlo Erba Electron Capture Detector (ECD). Gas samples first pass through a cold trap at −30°C to remove water, then through a precolumn (20 cm × 1/4″) packed with NaOH coated asbestos to remove CO_2 followed by a 1.5 m × 1/8″ OD stainless steel column packed with 60/80 mesh Porapak N for separation. The flow rate of the carrier gas N_2 was maintained at 25 ml/min, adding 3 ml/min of makeup gas (N_2/5%CH_4); oven temperature was held constant at 55°C. For calibration purposes gas mixtures containing from 310 ppbv to 360 ppmv were used. For further details see Hao et al. (1991a).

A new method for the sensitive determination of volatile C_1 to C_3 nitriles in one step was evaluated by Lobert (1990a, 1991b). A Delsi GC DI 200 equipped with a nitrogen specific Thermal Ionization Detector (TID) enables determining small amounts of nitrogen-containing compounds over a background of large quantities of hydrocarbons which are suppressed with a factor of 10^4 relative to the nitrogen substances. This detection method, described several times by other authors, was modified using a 30 m × 0.53 mm OD megabore column GS-Q of J&W (Porapak Q-like) and outlines for the first time a very good separation of cyanogen (NCCN), hydrogen cyanide (HCN), acetonitrile (CH_3CN), acrylonitrile (CH_2CHCN), and propionitrile (CH_3CH_2CN) in a single analysis. Even butyronitrile (C_3H_7CN) and higher compounds can be detected with this method, but were not determined during this work because they are only produced in small quantities. The parameters used were: 5 ml/min of helium-carrier gas, 3.5 ml/min of hydrogen, and 180 ml/min of synthetic air for the detector. Detector-bead temperature was maintained at 680° to 720°C with an electrode voltage of + 10V. An air sample of 0.5 ml was injected by a valve directly on column resulting in a detection limit (three times noise level) of about 2 pg N, which equals 10 ppbv of acetonitrile in air. Changing the detector parameters enables lowering the detection limit to a minimum of about 0.8 ppbv of acetonitrile in air. Calibration of the nitriles was realized by using gaseous cyanogen diluted by static dilution, solutions of KCN which are converted to HCN on an acidic precolumn, and solutions of the liquids in methanol (other nitriles). Gaseous standards were not used because they are very unstable and therefore require recalibration by the mentioned methods at least once a week.

The ammonia contents in the H_2SO_4 and HCl scrubber solutions were mostly determined by using an NH_3 sensitive electrode (Orion model 95-10) with a sensitivity of 10^{-5} mole/liter; in recent experiments ion chromatography was used. The sum of gaseous and particulate NH_3 are reported in this article. Detection limit for the electrode method is about 0.9 ppmv or 5.1 mg N for the integrated sample. The

detection limit with ion chromatography is dependent on the sampling time at several pptv in air (Ernst, 1990).

For the determination of volatile aliphatic amines a method was developed by Seuwen (1990) using a nitrogen specific TID mounted on a Delsi GC DI 200. For separation of the amines, a glass column (2.3 m × 2 mm ID) packed with 60/80 mesh Carbopack B/4% Carbowax 20 M/0.8% KOH was used. A carrier gas flow rate of 20 ml/min He was maintained in addition to 4 ml/min of hydrogen for the detector. Several capillary columns proposed for the separation of amines had been tested and found to be unsuitable because of a very poor resolution for the low molecular amines. Six amines could be determined in biomass burning emissions and separated with the described method: methylamine, dimethylamine, ethylamine, trimethylamine, methylbutylamine and n-pentylamine, together referred to as "amines" in this paper. Calibration of the amines was carried out by using the amino hydrochlorides in water which had been converted on an alkaline precolumn (15 cm × 1/4" OD) packed with 0.8 to 1.6 mm NaOH on asbestos. Stable and certified gaseous amine standards are not available.

For the determination of N_2 emissions, combustion gases from the closed apparatus described above were directly injected into a Delsi GC DI 700 equipped with a Thermal Conductivity Detector (TCD) using an 8-port-valve with two 250 μl sample loops. The lower detection limit is about 10 ppmv of N_2 in air equal to 3.6 ng N in the sample loop. The 600 μl TCD was operated at 285 mA constant current (84% of maximum), 3.5 ml/min carrier gas, and 17 ml/min of makeup gas (both very high-purity helium), using a Chrompack 30 m × 0.32 mm OD 5Å/30 μm molecular sieve fused silica column at 30°C isothermally. Calibration of the N_2 measurement is realized by using a standard of 1000 ppmv N_2 in He followed by a series of static dilutions.

Elemental analysis of both biomass and ash samples was carried out using a Heraeus Rapid C/H/N analyzer (Dindorf, 1990). Samples were pulverized with a mill to an average particle size of about 60 μm, dried in an oven at 105°C for 24 hours, and allowed to cool in a desiccator prior to the analysis. Two to four single analyses were done on one ash or biomass sample, the detection limit is about 2 to 5 μg N which is equal to about 0.1% of nitrogen content in the sample.

Fuel

The fuels which were used for the open burning experiments were chosen to be as representative as possible of natural fires. Thus we burned two types of savanna grass as well as wood, hay, and straw representing agricultural wastes and forest-type fuels like pine needles and partially decomposed needle litter. Table 36.1 shows the fuel types, their carbon and nitrogen content as well as their molar N/C ratio and average moisture. Some of these fuels were also used for the N_2 measurements to compare open and closed burning. Also included in the table are some of the ash data, where all analyses are put together to give an average number which does not distinguish between different fuel types.

Table 36.1 Elemental composition of biomass burning fuels and ashes of our experiments

	C-content (%)	N-content (%)	Moisture (%)	N/C molar (%)
Savanna grass (Australian)	45.7 ± 0.1 (3)	0.15 ± 0.02 (3)	2.0 (1)	0.29 ± 0.04 (3)
Straw	45.0 ± 0.4 (15)	0.19 ± 0.08 (15)	4.1 ± 2.1 (5)	0.35 ± 0.15 (15)
Deciduous wood	48.3 ± 0.1 (3)	0.23 ± 0.02 (3)	3.4 (1)	0.47 ± 0.04 (3)
Savanna grass (Venezuelan)	44.1 ± 0.6 (24)	0.48 ± 0.06 (24)	5.2 ± 1.9 (7)	0.94 ± 0.12 (24)
Needle litter	48.1 ± 2.8 (9)	1.24 ± 0.46 (9)	8.7 ± 0.8 (2)	2.18 ± 0.69 (9)
Hay	42.0 ± 1.1 (18)	1.12 ± 0.14 (18)	6.7 ± 1.6 (4)	2.29 ± 0.29 (18)
Pine needles	49.5 ± 0.5 (24)	1.33 ± 0.22 (24)	8.7 ± 4.1 (3)	2.31 ± 0.38 (24)
Green grass	37.2 ± 0.1 (3)	2.13 ± 0.04 (3)	n.b.	4.92 ± 0.10 (3)
Tobacco	40.6 ± 0.0 (3)	2.37 ± 0.05 (3)	11.0 (1)	5.01 ± 0.09 (3)
Total average, fuels without tobacco	45.5 ± 3.3 (99)	0.86 ± 0.54 (99)	5.8 ± 2.7 (23)	1.63 ± 1.06 (99)
Total average, ashes	19.7 ± 13.8 (162)	0.58 ± 0.47 (162)	2.8 ± 1.4 (162)	2.73 ± 1.55 (162)

Note: Average ± standard deviation is followed by number of observations in parentheses.

Results and Discussion

Terminology

The term *volume mixing ratio* represents the volumetric fraction of a gaseous compound in the surrounding atmosphere.

Emission ratios are used for a relative comparison of different emissions and are defined as the above background mixing ratio of the compound studied, divided by the above background mixing ratio of a reference compound. In biomass burning calculations carbon dioxide is mostly taken to be the reference compound. The emission ratio of, e.g., nitrogen oxide to carbon dioxide is defined as

$$\Delta\mu_{NO} / \Delta\mu_{CO2}$$

where $\Delta\mu$ indicates the mixing ratio of the compound reduced by its ambient air level.

The calculation of the emission ratios of our experiments is based on a mass determination of the emissions. For that reason the mass flux of the compounds was determined during each experiment. Integration of this mass flux over one of the burning stages, or the whole fire, results in a total mass emitted during a fire, or during one of the burning stages, respectively, expressed in grams (g) carbon or g nitrogen. The ratio of the emitted mass of compound to the emitted mass of CO_2 gives the emission ratio of the compound relative to CO_2. All emission ratios presented here are expressed as *molar* ratios (mole compound per mole of CO_2).

Calculating the amounts relative to the fuel nitrogen or to the fuel carbon is an alternative way of expressing emission factors. This method is known as the carbon balance method, described by Radke et al. (1988). A balance of the nitrogen-containing compounds has not been presented previously. While Radke et al. use an approximate average percentage for the carbon content of 49.7%, we are able to use the elemental contents of both biomass and ash, which we measured and which, in the case of nitrogen, differ widely (Table 36.1).

Observations

Figure 36.4 shows mixing ratios of different compounds during the course of a typical biomass burning experiment. The abscissa shows the first 400 of about 900 to 1200 seconds of a complete fire, while the ordinate shows the volume mixing ratios of various gases. Curve 36.4g shows the temperature about 2 meters (m) above the fire, where gas samples are taken. The dotted, vertical line at 96 seconds represents the transition between flaming and smoldering combustion. These two burning stages are characterized by hot combustion with open flames, involving oxidation of pyrolysis products in the flame, and a colder, incomplete combustion without, or maybe with only small flames where the pyrolytic, oxygen-free fuel conversion predominates. In order to get a reproducible reference, the transition point was calculated from the first derivative of the CO mixing ratio versus time (Figure 36.4h). The maximum of the first derivative was defined to be the transition between flaming and smoldering stages. Indeed, this coincides closely with the cessation of the flames.

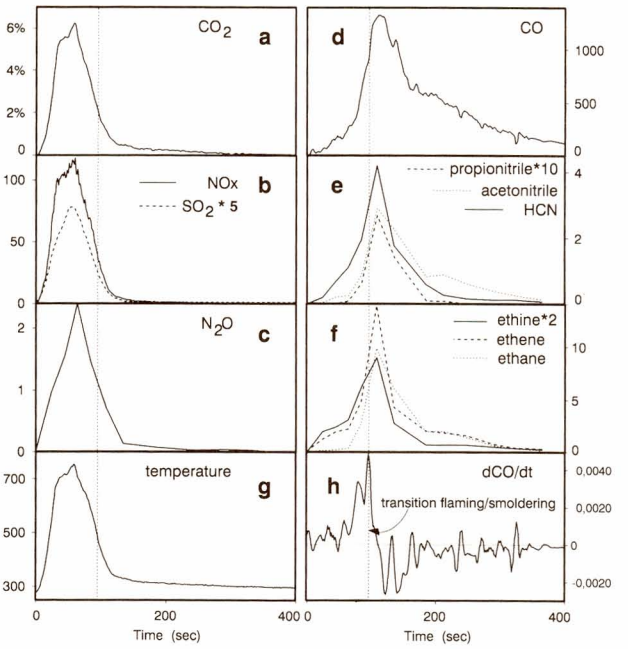

Figure 36.4 Mixing ratios above background in % for CO_2 and ppmv for the other gases, stack-gas temperature in °K, and the first derivative of the CO-curve during the first 400 seconds of a typical experiment. The maximum in dCO/dt is taken to define the transition between flaming and smoldering combustion.

Some of the gaseous emissions are closely related to the temperature during a fire. The rapid increase in stack-gas temperature coincides with a similar increase in CO_2, NO_x, SO_2, and N_2O mixing ratios. These gases are shown in parts a to c of Figure 36.4. Parts d to f give examples of some gases with maximum mixing ratio during the smoldering stage of a burn. Substances matching this behaviour are defined to be *smoldering stage compounds* while those which are mostly emitted during the flaming stage are called *flaming stage compounds*. The latter are substances in a comparatively high oxidation state, while the for-

mer are less oxidized compounds, products of incomplete combustion such as carbon monoxide, hydrocarbons, ammonia, and the nitriles.

Gaseous emissions are basically a product of the pyrolytic cracking of the fuel. Additionally, depending on the presence or absence of flames, the pyrolysis gases are more or less oxidized. HCN, for example, with up to 90% of the fuel nitrogen, is one of the major products of pyrolytic (oxygen free) protein decomposition (Johnston et al., 1971; Lobert, 1990a), but during open fires it is emitted at a total of just several percent of the fuel nitrogen. This is a result of its oxidation to NO_x and CO_x in the flame. The flaming stage is supplied with plenty of oxygen by thermally induced *convection*. The smoldering stage produces much lower temperatures, which result in a low oxygen supply by *diffusion* into the fuel bed. If gases in this phase leave the fuel bed, they are no longer converted. Table 36.2 gives typical, maximum mixing ratios of the compounds during our experiments and the corresponding combustion phase.

Knowledge about the types of flaming stage and smoldering stage emissions allows correlation between compounds and gives insight into the use of different reference compounds for the calculation of emission ratios. Figure 36.5 shows graphs of the emissions of some compounds versus those of CO or CO_2. Part a shows a very good linear correlation between NO_x and CO_2 emissions, since both compounds are mostly produced in the flaming stage, while NO_x shows *no* correlation to CO (b). Acetonitrile, on the other hand, shows a good correlation only with CO (d); both of them belong to the smoldering stage class of compounds. A linear regression with CO_2 (c) would be negative in this case. As CO_2 is used as a reference compound for biomass burning emissions, this finding shows that single measurements of smoldering stage compounds correlated to CO_2 are not useful for a comparison with other samples without information about the burning stage in which the sample was taken. If samples are taken from above large-scale, open fires, where a mixture of both burning stages exist, an emission ratio derived from regression analysis is only meaningful if both compounds belong to the same class.

Table 36.2 Typical maximum mixing ratios of several compounds during our experiments

Compound	Maximum mixing ratio during fire (ppmv)	Corresponding burning stage
CO_2	60,000–100,000	Flaming
CO	1500–3000	Smoldering
CH_4	43–350	Smoldering
$HC{\equiv}CH$	4–36	Flaming
$H_2C{=}CH_2$	11–46	Smoldering
$H_3C\text{-}CH_3$	5–36	Smoldering
NO_X	100–160	Flaming
N_2O	2–19	Flaming
NH_3	Avg ~5	Smoldering
HCN	4–30	Smoldering
CH_3CN	2–10	Smoldering
SO_2	20–30	Flaming

For that reason we propose calculating emission ratios, depending on the type of compounds, relative to either CO_2 *or* CO, whichever gives a better linear correlation. There are only a few compounds which belong to the flaming stage class, such as CO_2, NO_x, N_2O, and SO_2. Most of the compounds emitted by biomass burning are produced mainly in the smoldering stage and therefore belong to the smoldering stage class. Taking carbon monoxide as a reference for emission ratios also has a practical advantage for aircraft measurements. The ambient air background mixing ratio of CO_2 is very high at about 350 ppmv, while an enhancement through biomass burning emissions seldom exceeds 50 ppmv and is often much lower. Because of the natural variability in CO_2 mixing ratios and measurement uncertainties, calculations of emission ratios to CO_2 may thus become very uncertain. For the smoldering stage compounds, on the other hand, which represent the majority of the emissions, it is much more reliable to use CO as the reference gas, since its background mixing ratio is only 50 to 150 ppbv and the fire plume excess can be up to several ppmv.

The procedure of taking both CO_2 and CO as reference compounds works well for most of the emissions, although some transition between flaming stage and smoldering stage type is observable. The C_2 hydrocarbons and the nitriles illustrate such a transition. Figure 36.4e shows the mixing ratios of three nitriles versus time. It can be seen that the amount which was produced in the flaming stage (area under the curve) increases from propionitrile over acetonitrile to hydrogen cyanide. The same effect is observable with CH_3CH_3, $CH_2{=}CH_2$, and $HC{\equiv}CH$ (Figure 36.4f). It is interesting to note that, on average, more than 50% of both HCCH and NCCN are—probably because of their thermal stability—produced during the flaming phase (see Table 36.4) although, due to their rela-

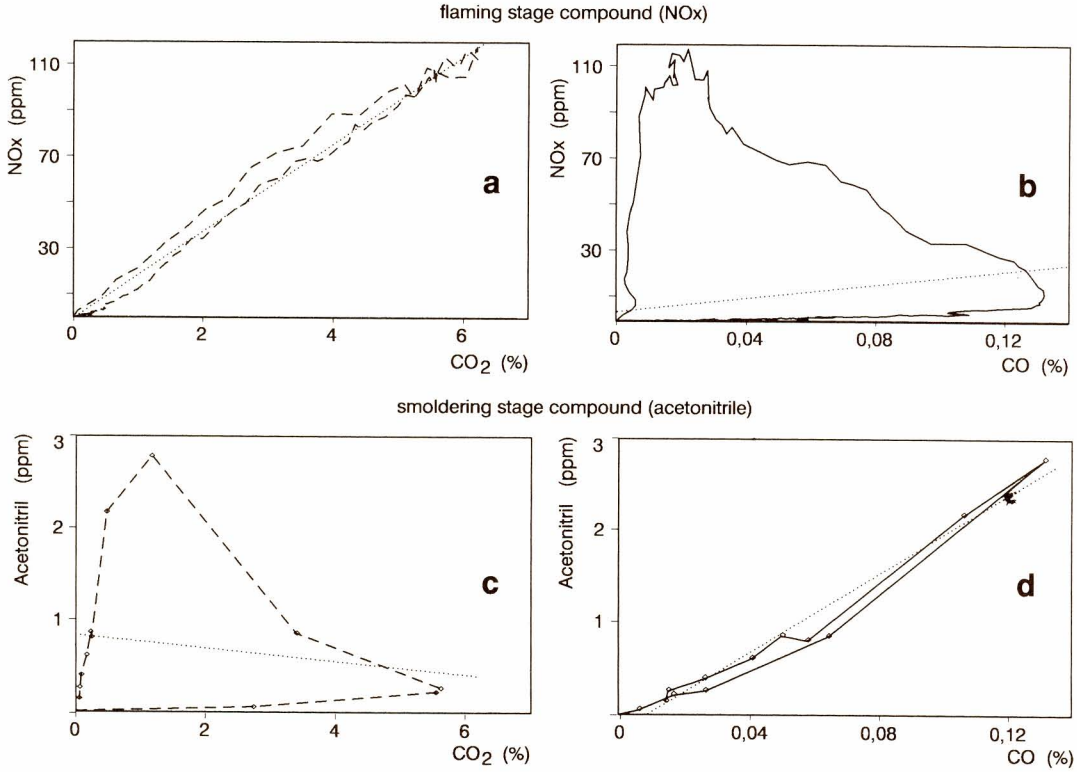

Figure 36.5 If compounds are produced in the same combustion stage, they show a good, linear correlation (a and d), otherwise a significant anti-correlation is observable (b and c). Emission ratios should be derived only from regression analysis, if a positive, linear correlation is given.

tively low oxidation state, one would expect them to be smoldering stage compounds.

Influences on Emissions

There are several factors influencing biomass burning emissions. The most important effect has been identified to be the kind and duration of the burning stage. The relative importance and distribution of the burning stages, on the other hand, is dependent on the type of fuel, the fuel moisture and density, and the wind direction during a burn. Since CO/CO_2 is an indicator of the quality of combustion, we took this ratio to show different influences on the emissions of CO during hay and savanna grass burns in Table 36.3. As can be seen, this ratio can vary between flaming and smoldering combustion by a factor of 20 to 30. The effect of moisture is demonstrated in the first two lines of this table. The much higher moisture of burn 2 (16%) causes an overall CO/CO_2 ratio which is twice as high as for the dry fire (5% moisture) due to the virtual absence of a flaming stage. On the other hand, there are no significant differences observable for a moisture content of under 10%. In order to be able to study the different burning stages, we burned fuels with an average water content of 5%, which is typical of tropical savannas during the dry season.

The direction of the wind produces a further effect. We simulate different wind directions by raising the burning table to an angle of 30° to 45° and igniting the fuel either at the top or the bottom of the table. Since the wind is always moving into the chimney, ignition at the top forces the flames to burn against the air stream, thus simulating a *backing fire*. Ignition at the bottom of the table, on the other hand, results in a burn moving with the wind, a *heading fire*. Heading fires normally burn faster and less efficiently than backing fires, resulting in higher amounts of smoldering stage compounds. This can be confirmed from the last lines of Table 36.3, where the CO/CO_2 ratio increases by 40% from backing to heading fire. It is obvious that the effect of varying wind direction on the emissions is substantial, but much smaller than the differences between flaming and smoldering combustion, which are controlled by fuel moisture and fuel density.

One of the major influences on nitrogen emissions

Table 36.3 Examples of the influence of different burning factors on the emission ratios of compounds

Fuel	Moisture (%)	CO/CO_2 (%)			Wind direction
		Total	Flaming	Smoldering	
Hay	5%	7.1%	2.4%	11.9%	Backing
Hay	16	15.6	15.7	15.6	Backing
Savanna grass	4	5.0	0.7	20.0	Backing
Savanna grass	6	7.2	1.5	18.2	Heading

is the nitrogen content of the fuel. We found that most of the emission ratios of nitrogen-containing gases are significantly correlated to the N/C ratio of the fuel. Figure 36.6 shows emission ratios of CH_2CHCN, N_2O, and NO_x plotted versus the molar N/C ratio as well as the corresponding regression line. Due to this strong influence it is necessary to take into consideration the nitrogen content of biomass burning fuels when estimating global source strengths.

Owing to the design of our burning apparatus we can reduce variations in emissions to a minimum by using similar fuels and fire conditions during any experiment, and we can observe and separate the variations due to different burning stages with a high degree of control. Thus we are able to give emission ratios for any kind of fire behavior and any fuel variation. In this article, we present only overall mean values from our experiments, without distinguishing between different fuels and different fire types. Such values will be presented elsewhere (Lobert et al., 1991a).

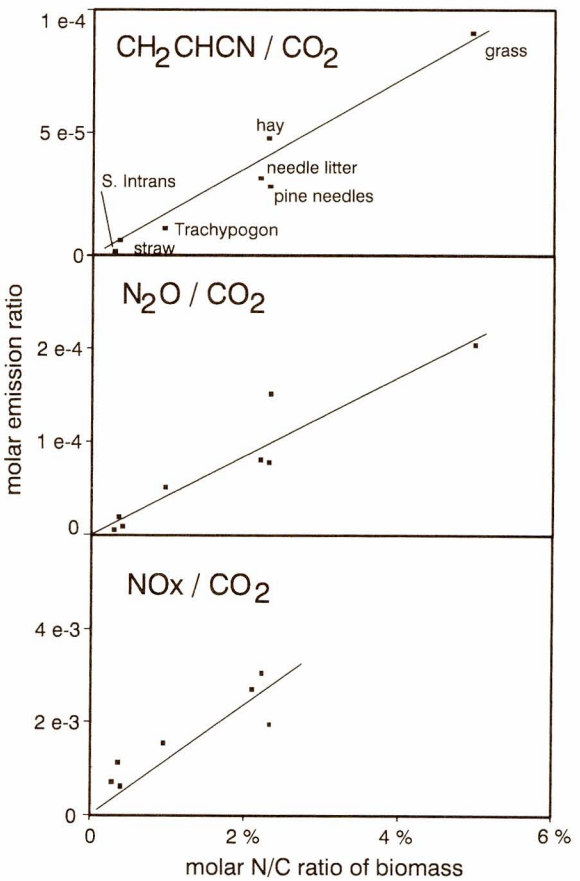

Figure 36.6 Influence of the N/C ratio of the fuels on the emissions of nitrogen containing compounds. The line represents the linear regression forced to zero, R^2 values are 0.95, 0.52, and 0.62, respectively. The scattering of the data shows clearly that the nitrogen content is just *one* important influence.

Emission Ratios

Based on the above discussion, Table 36.4 gives an overview of the determined emission ratios of the carbon and nitrogen-containing compounds relative to CO or CO_2. Also included are the emission factors relative to the fuel nitrogen and carbon discussed below.

The table lists all mean values and the number of experiments for each compound, as well as the range of minimum and maximum values observed. The last columns give values for the distribution of the compounds to the burning stages. The bigger these numbers are, the more the compound belongs to the burning class indicated. The distribution values for RNO_x and NH_3 are results of one and two experiments only.

A maximum uncertainty of 20% for an emission ratio for a single fire is estimated for our measurements. As can be seen from our results, the variations

Table 36.4 Emission ratios of the described compounds relative to CO_2, CO, the carbon and the nitrogen content of the fuel

		Molar emission ratio relative to CO (%) or CO_2 (exponential)			Emission factor relative to the fuel C or N (%)			Fraction in burning stage (%)	
Compound	Formula	Mean	Number of experiments	Observed range (min–max)	Mean	Number of experiments	Observed range (min–max)	Flaming	Smoldering
Carbon dioxide	CO_2	13.8			82.58	24	49.17–98.95	63	37
Carbon monoxide	CO	7.3E-02	24	3.2E-02–1.6E-01	5.73	24	2.83–11.19	16	84
Methane	CH_4	9.11	12	5.21–12.17	0.424	13	0.14–0.94	27	73
Ethane	CH_3CH_3	0.68	10	0.16–1.05	0.061	11	0.008–0.143	27	73
Ethene	$CH_2 = CH_2$	1.21	10	0.40–2.08	0.123	11	0.021–0.420	43	57
Ethine	$CH \equiv CH$	4.2E-04	10	6.9E-05–1.7E-03	0.056	11	0.010–0.237	56	44
Propane	C_3H_8	0.15	10	0.021–0.319	0.019	11	0.002–0.042	22	78
Propene	C_3H_6	0.49	10	0.132–0.696	0.066	11	0.010–0.160	33	67
n-butane	C_4H_{10}	0.03	10	0.006–0.078	0.005	11	0.0006–0.010	21	79
2-butene (cis)	C_4H_8	0.02	10	0.003–0.032	0.004	11	0.0003–0.008	30	70
2-butene (trans)	C_4H_8	0.03	10	0.004–0.041	0.005	11	0.0005–0.011	28	72
i-butene, 1-butene	$C_4H_8 + C_4H_8$	0.19	10	0.025–0.398	0.033	11	0.003–0.082	28	72
1,3-butadiene	C_4H_6	0.11	10	0.039–0.185	0.021	11	0.004–0.056	31	69
n-pentane	C_5H_{12}	0.03	10	0.008–0.064	0.007	11	0.0012–0.024	44	56
Isoprene	C_5H_8	0.05	10	0.014–0.093	0.008	11	0.002–0.016	21	79
Benzene	C_6H_6	0.21	10	0.106–0.401	0.064	11	0.018–0.214	45	55
Toluene	C_7H_8	0.12	10	0.027–0.233	0.037	11	0.005–0.103	32	68
m-, p-xylene	C_8H_{10}	0.03	10	0.006–0.060	0.011	11	0.0012–0.025	29	71
o-xylene	C_8H_{10}	0.02	10	0.001–0.045	0.006	11	0.0003–0.015	27	73
Methyl chloride	CH_3Cl	0.16	9	0.018–0.437	0.010	10	0.0006–0.025	28	72
NMHC (as C)	C_2 to C_8	25.41	10	5.39–41.66	1.18	11	0.14–3.19	33	67
Ash (as C)					5.00	41	0.66–22.28		
Total sum C	C_1 to C_8				94.92 (including ash)				
Nitrogen oxides	NO_2O	2.0E-03	21	8.8E-04–7.7E-03	13.55	21	5.27–21.69	66	34
Ammonia	NH_3	1.55	15	0.118–4.89	4.15	15	1.04–11.74	15	85
Hydrogen cyanide	HCN	1.13	11	0.049–5.81	2.64	11	0.31–6.75	33	67
Acetonitrile	CH_3CN	0.25	10	0.013–0.53	1.00	10	0.079–2.323	14	86
Cyanogen	NCCN (as N)	4.1E-06	9	2.0E-08–2.3E-05	0.023	10	0–0.133	56	44
Acrylonitrile	CH_2CHCN	0.05	10	0.008–0.135	0.135	10	0.030–0.343	32	68
Propionitrile	CH_3CH_2CN	0.02	9	0.006–0.055	0.071	10	0–0.188	17	83
Nitrous oxide	N_2O	9.2E-05	12	1.2E-05–2.8E-04	0.772	13	0.336–1.200	74	26
Methylamine	CH_3NH_2	0.08	5	0.040–0.131	0.047	5	0.025–0.076	27	73
Dimethylamine	$(CH_3)_2NH$	0.06	5	0.016–0.118	0.030	5	0.013–0.061	39	61
Ethylamine	$CH_3CH_2NH_2$	0.01	2	0.006–0.006	0.005	2	0.004–0.006	60	40
Trimethylamine	$(CH_3)_3N$	0.03	3	0.021–0.047	0.020	3	0.013–0.024	41	59
2-methyl-1-butylamine	$C_5H_{11}NH_2$	0.07	3	0.032–0.094	0.040	3	0.032–0.052	15	85
n-pentylamine	$n\text{-}C_5H_{11}NH_2$	0.22	4	0.132–0.329	0.137	4	0.039–0.238	32	68
Nitrates (70% HNO_3)	RNO_X	0.38	1		1.10	1		f	<s
Ash (as N)					9.94	41	1.75–45.98		
Total sum N (as N)					33.66 (including ash)				
Molecular nitrogen	N_2	4.7E-03	10	8.1E-04–9.9E-03	21.60	17	4.33–41.20	f	>s
Higher HC and particles					20				

Note: Presented are the mean values, number of experiments, and the range of minimum to maximum values ever observed as well as the distribution of the emissions to the burning stages. Emission ratios relative to CO are expressed in percent; those relative to CO_2 are given as exponential numbers. Emission factors are presented in percent of the fuel nitrogen or carbon.

between minimum and maximum emission ratios are fairly high, as observed by most other authors, and are to be explained by the high variability of the biomass burning process.

Mass Balance

On average, the carbon compound measurements account for nearly 95% of the carbon initially present in the fuel. CO_2 is the major emission (82.6%), followed by CO (5.7%) and CH_4 (0.42%). Nonmethane hydrocarbons contribute together 1.2%. Including the carbon found in the ash, the balance adds up to 94.9%, leaving only 5.1% unidentified. This is most likely hydrocarbons higher than C_8 emitted in gaseous or particulate form and also includes emissions of oxygenated or nitrogen-containing gases with low FID detector response. Table 36.4 also shows that the nitrogen-containing compounds determined in our work add up to only one third of the fuel nitrogen, including about 1% of nitrates ($R\text{-}NO_X$, mostly HNO_3) (Flocke, 1989). This leaves an unknown fraction of nearly 70% (Lobert et al., 1990b) and there are several candidates for this missing nitrogen.

First, the emission of molecular nitrogen contributes a significant amount to the nitrogen inventory. This emission is not detectable in natural fires due to the high nitrogen content of the atmosphere. Preliminary results obtained with the apparatus described above (Figure 36.2) show that during these experiments, on average, 22% of the fuel nitrogen was emitted as molecular nitrogen. Much larger N_2 emissions have been observed in our experiments during more intense combustion. Work is still in progress on this question. Detailed results are reported by Kuhlbusch (1990) and Kuhlbusch et al. (1991). See also the discussion below.

Second, we did not measure the many high molecular weight compounds containing substantial amounts of nitrogen. To estimate this fraction, we considered the compounds found in tobacco smoke listed by Neurath (1969). We added all the reported compounds (as far as amounts had been given, excluding the compounds we measured) and found that, at most, 20% of the fuel nitrogen (tobacco) could be contained in these emissions. These are mainly aliphatic and aromatic amines and heterocyclic constituents with a high N/C ratio. Thus, tar and particulates may account for a substantial part of the nitrogen balance. This estimate, however, is uncertain until measurements on this subject are carried out.

Source Strengths

As described previously, the calculation of global emissions requires information on the amount of biomass that is burned worldwide. Unfortunately, such estimates are very uncertain because of a lack of information. The most recent estimate on global biomass burning emissions is given by Crutzen et al. (1990) and is used for our calculations. Table 36.5 summarizes the emissions from different types of ecosystems due to biomass burning.

Annual global source strengths of single compounds can be determined in several ways. The most common is by multiplying their emission ratios relative to CO_2 with the total CO_2 emissions from biomass burning per year. Again, this method is only reliable when the compound correlates with CO_2 (and there-

Table 36.5 Global amounts of biomass burned in different ecosystems expressed in terms of carbon and nitrogen

Source or activity	Carbon exposed (Tg C/yr)	Carbon released (Tg C/yr)	Molar (N/C ratio)	Nitrogen released (Tg N/yr)
Shifting agriculture	1000–2000	500–1000	1	5.0–10.0
Permanent deforestation	500–1400	200–700	1	2.0–7.0
Savanna fires	400–2000	300–1600	0.6	1.8–9.6
Firewood	300–600	300–600	0.5	1.5–3.0
Agricultural wastes	500–800	500–800	1–2	5.0–16.0
Prescribed + wild fires	150–300	120–250	1–2	1.2–5.0
Total	2900–7100	1900–5000	1.24[a]	17–51
			1.46[b]	28–72[c]
Quartile ranges		2700–4200		39–61[c]

Note: Amounts are expressed in terms of teragrams of carbon per year (10^{12} g C/yr). Corresponding nitrogen amounts are taken from Crutzen et al. (1990).

a. Average value of the table.

b. Average value of our 41 burning experiments.

c. Calculated from (1900–5000) × 1.455 and used for our estimates.

fore is nearly constant, not dependent on the burning stages), or when the emission factors are calculated on a mass basis for a complete fire, giving a true average, as in our measurements. If no correlation to CO_2 is given, global amounts should be calculated using emission ratios relative to CO multiplied by the corresponding ratio of CO/CO_2 and the global CO_2 amount. This method is proposed for use in field measurements of smoldering stage compounds, thus allowing comparison of emission ratios and source strengths from different fires.

In this article, we use a third way of estimating the global sources using our emission factors relative to the fuel carbon or nitrogen. The global sources which are presented in Table 36.6 are derived by dividing the emission factors relative to the fuel C or N by 0.95 or 0.90, which represent, respectively, the *emitted* fraction of C or N (total C or N minus ash content), and multiplying with the globally released carbon and an average N/C ratio of 1.455% (for the nitrogen compounds only) derived from our 46 experiments. Our N/C ratio is higher than the average value of 1.24% used by Crutzen et al. (1990). It must be noted that the global estimates for nitrogen compounds based on the emission factors relative to the fuel N show lower values than the same estimates based on the emission ratios relative to CO or CO_2, whereas the two computing methods give similar results in the case of carbon compounds. This might be due to a nonrepresentative N/C ratio used in our calculations, although higher sources would require an even higher N/C ratio.

For calculating the final range of global, annual emissions, we multiplied half the range of the estimated global carbon emissions with half the range of the emission factors. These *quartile ranges* were derived from the minimum and maximum values and the overall arithmetic mean:

$$\text{Mean} - \tfrac{1}{2}(\text{mean} - \text{minimum}) \text{ or}$$
$$\text{Mean} + \tfrac{1}{2}(\text{maximum} - \text{mean})$$

The range of possible CO emissions then is given by

$$2700 \text{ Tg C} \times 4.28\% / 0.95 \text{ to } 4200 \text{ Tg C} \times 8.46\% / 0.95 = 121 \text{ to } 373 \text{ Tg C / yr}$$

This generates a narrower range for the global emission estimates and was used instead of the standard deviations which require a normally distributed data base. Due to the high variations in the emissions, we feel that this calculation provides more useful ranges.

Carbon Emissions

Our emission factors show that CO_2 is the major carbon compound which is emitted by biomass burning, at a rate of 1.9 to 4.0 Pg C/yr. It should be noted that these emissions represent the prompt release of CO_2 to the atmosphere; the net release is about one third to one half of the former (Crutzen et al., 1990) due to the uptake by plants covering the postburned areas. According to estimates of Andreae (1990) the amounts of carbon dioxide from biomass burning could contribute some 25% to the greenhouse effect produced by the global CO_2.

The range of our CO/CO_2 emission ratios covers most of the previously published results except for a few high values greater than 15% (Crutzen et al., 1979; Greenberg et al., 1984). Even such high values are observable in our experiments if we consider the pure smoldering stage values, which demonstrates clearly the importance of information about the burning stage when CO/CO_2 values are compared. Most authors present values between 4% and 15% (Andreae et al., 1988; Cofer et al., 1988a; Hegg et al., 1990), so our mean value of 7.3%, which was derived from complete fires, is a good working value. This CO/CO_2 ratio is close to the value presented by Andreae et al. (1988), who took integrated samples over a large volume and thus also considered an average of different burning stages. Our results show that carbon monoxide is the second but most important carbon emission with 121 to 373 Tg C/yr, which accounts for about 22% (16% to 34%) of the total CO source reported by Logan et al. (1981). Thus, pyrogenic CO is as important as fossil fuel emission, which, according to Logan, is in the order of 200 Tg C/yr.

For the hydrocarbons, which are discussed in more detail elsewhere (Hao et al., 1991b), the most important compound emitted from biomass burning is methane. CH_4/CO ratios average about 9.1%, in fairly good agreement with the values of 7.8% calculated from results of Greenberg et al. (1984) but substantially higher than the 3% determined by Hegg et al. (1990). The remaining hydrocarbons are also listed in Table 36.4. The highest emission ratios were measured for ethene (1.2%) and for C_3 and C_4 alkanes and alkenes as well as for benzene and toluene (0.1% to 0.5% each). Methane contributes strongly to the atmospheric greenhouse effect and also to global atmospheric chemistry. Our estimate results in a contribution to the global methane budget of 3% (2% to 4%) based on global source estimates by the WMO (1985).

Table 36.6 Global, annual source strengths of the compounds and the significance of biomass burning to their global budgets

Compound	Formula	Biomass burning source range (as C or N) (Giga-g/yr)			Total source range (as C or N) (Tg/yr)	Reference	Contribution to global source	
		Mean	Minimum	Maximum			Mean	Range
Carbon dioxide	CO_2	2,990,000	1,860,000	4,010,000				
Carbon monoxide	CO	207,000	120,000	370,000	610–1270	Logan, 1981	22%	16%–34%
Methane	CH_4	15,300	7,900	30,100	390–765	WMO, 1985	3%	2%–4%
Ethane	CH_3CH_3	2,190	972	4,495				
Ethene	$CH_2=CH_2$	4,460	2,030	12,000				
Ethine	$CH\equiv CH$	2,020	928	6,465				
Propane	C_3H_8	670	284	1,334	C_2–C_4			
Propene	C_3H_6	2,380	1,070	4,980	100	Greenberg, 1984	14%	6%–34%
n-butane	C_4H_{10}	169	75	327				
2-butene (cis)	C_4H_8	134	56	261				
2-butene (trans)	C_4H_8	171	73	338				
i-butene, 1-butene	$C_4H_8 + C_4H_8$	1,190	500	2,531				
1,3-butadiene	C_4H_6	754	352	1,707				
n-pentane	C_5H_{12}	266	121	701				
Isoprene	C_5H_8	302	139	548				
Benzene	C_6H_6	2,310	1,150	6,140				
Toluene	C_7H_8	1,340	594	3,098				
m-, p-xylene	C_8H_{10}	402	174	807				
o-xylene	C_8H_{10}	213	87	471				
Methyl chloride	CH_3Cl	357	147	780	0.55–1.2	WMO, 1985	41%	21%–75%
NMHC (as C)	C_2 to C_8	42,664	18,630	96,390				
Ash (as C)		180,866	79,770	602,070				
Total sum C	C_1 to C_8	3,432,000	2,004,000	4,506,000				
Nitrogen oxides	NO_x	7,520	4,070	11,930	25–99	Logan, 1983	12%	9%–15%
Ammonia	NH_3	2,310	1,120	5,380	20–80	Andreae, 1989	5%	3%–8%
Hydrogen cyanide	HCN	1,460	640	3,180				
Acetonitrile	CH_3CN	554	230	1,130				
Cyanogen	NCCN (as N)	13	5	53				
Acrylonitrile	CH_2CHCN	75	36	162				
Propionitrile	CH_3CH_2CN	39	15	88				
Nitrous oxide	N_2O	428	240	668	12–14	WMO, 1985	3%	2%–5%
Methylamine	CH_3NH_2	26	16	42				
Dimethylamine	$(CH_3)_2NH$	17	9	31				
Ethylamine	$CH_3CH_2NH_2$	3	2	4				
Trimethylamine	$(CH_3)_3N$	11	7	15				
2-methyl-1-butylamine	$C_5H_{11}NH^2$	22	15	31				
n-pentylamine	$n\text{-}C_5H_{11}NH_2$	76	38	127				
Nitrates (70% HNO_3)	RNO_x	610	476	745				
Ash (as N)		5,520	2,530	18,940				
Subtotal sum N		18,700	9,400	42,500				
Molecular nitrogen	N_2	11,990	5,610	21,270	100–170	Söderlund, 1976	9%	5%–14%

Note: The biomass burning source range is given in 10^9 g (gigagram) carbon or nitrogen per year, whereas the total source range is expressed in terms of 10^{12} g C/yr or g N/yr.

We also determined methyl chloride emissions and found an emission ratio of 1.64×10^{-3} relative to CO, which is much higher than values found by Crutzen et al. (1979) of 1.14×10^{-4}, but agrees reasonably well with the values by Tassios et al. (1985) which show a mean CH_3Cl/CO ratio of about 3×10^{-3} (assuming a CO/CO_2 ratio of 10%, not reported in that publication). The atmospheric input of methyl chloride has been reported to be 0.55 to 1.2 Tg C/yr (WMO, 1985). Adopting these amounts, biomass burning then could be the single most important source for CH_3Cl with 357×10^9 g C/yr, corresponding to a contribution of 41% (21% to 75%) to the global budget.

Nitrogen Emissions

Our values for NO_x/CO_2 lie well within the range of 0.3 to 3.5×10^{-3} published by other authors (Evans et al., 1974; Crutzen et al., 1979; Andreae et al., 1988). NO_x/CO_2 ratios do not change significantly during the different combustion stages, so *intra*fire variations are small and *inter*fire variations are due to varying fire and fuel properties. In nearly all of our experiments, NO_x is the most important reactive nitrogen emission. In a few fires, however, ammonia and hydrogen cyanide showed amounts comparable to NO_x. Calculation of the source strength yields a value of about 7.5 Tg N/yr, which can contribute 12% (9% to 15%) to the global budget of 25 to 99 Tg N/yr estimated by Logan (1983) and therefore represents an important source of atmospheric NO_x.

For N_2O, on the other hand, we estimate only minor emissions of about 0.4 Tg N/yr, contributing 3% (2% to 5%) to the global source of 12 to 14 Tg N/yr (WMO, 1985). The values for N_2O/CO_2 ratios presented in this paper are substantially lower than most other published data (Crutzen et al., 1979, 1985; Cofer et al., 1988a). Values of Crutzen et al. (1985) of 2×10^{-4} are much higher than our mean value of 9.2×10^{-5}. The reduction of published N_2O emission ratios is due to an artifact N_2O production in sample canisters of earlier measurements caused by an aqueous chemistry involving NO and SO_2, first determined by Muzio and Kramlich in 1988. We, too, observe this artifact production in our grab samples (Hao et al., 1991a), but since our SO_2 levels are fairly low (maximum mixing ratios of 20 to 30 ppmv during the flaming stage, see Table 36.2) and our samples were analyzed within 20 hours after sampling, we estimate, from repeated measurements on stored samples, a maximum artifact error in our values of +20%, so that our data on N_2O may still be a factor of 1.2 too high. Recent measurements of Griffith et al. (1990) with an FTIR method (which avoids such an artifact) show values around 8×10^{-5} in good agreement with our data. In fact, there is only one publication reporting even lower values for N_2O/CO_2 of about (0.4 to 1.4) $\times 10^{-5}$ (Elkins et al., 1990). These values had been derived from burning wood, which has a very low nitrogen content; thus, these emission ratios are probably lower than in natural fires.

There are only a few published values for the biomass burning emission of ammonia. Our ammonia emissions are represented by a value of 1.55% relative to CO, which is slightly higher than the ratio derived by Andreae et al. (1988) for particulate NH_4^+ in aged plumes and the value given by Hegg et al. (1990) for seven forest fires in North America (both around 1%). Recent FTIR measurements over prescribed fires by Griffith et al. (1990), on the other hand, show average values of NH_3/CO which are a factor of 2 higher than ours in a range of (1.2 to 5.3) $\times 10^{-2}$. Their NH_3/NO_x ratio is also very high at 5:1, while our ratio is significantly lower at about 5:15. Thus, further measurements on ammonia emissions should be carried out. Information on the atmospheric budget of ammonia is very poor; the global source has been reported to be 20 to 80 Tg N/yr (Andreae et al., 1989), most of which is due to microbial and animal release. Our estimate shows that biomass burning, representing an amount of 2.3 Tg N/yr, on average accounts for about 5% (3% to 8%) of the total ammonia source.

Our emission ratios of total C_1 to C_5 amines are around 0.5% relative to CO. A comparison to other data is not possible, since they are published for the first time. Also there are no data on their atmospheric amounts. Cadle et al. (1980) determined the concentrations of amines in automobile exhausts and Seuwen (1990) estimated from this only negligible amounts of 1×10^6 g N/yr being emitted to the atmosphere. Nevertheless, when our emission factors from biomass burning are considered, the sum of these compounds may be in the order of 0.8 Tg N/yr; thus, further investigation might be worthwhile.

An interesting outcome of our experiments was the large amounts of nitriles, especially hydrogen cyanide and acetonitrile (Lobert, 1990a; Lobert et al., 1990b). Emission ratios for these compounds were determined for the first time and lie in a range comparable to ammonia emissions. Therefore, HCN and CH_3CN are two of the most important nitrogen-containing gases emitted by biomass burning, together releasing some 3.6% of the fuel nitrogen (Table 36.4). In some experiments, HCN emissions can be as high

as NO_x emissions when incomplete combustion was predominant. The emission ratios for the remaining three nitriles—cyanogen, acrylonitrile, and propionitrile—lie a factor of 10 to 100 below those of HCN and CH_3CN. A few measurements over prescribed fires in Australia (Lobert, 1990a) show emission ratios of HCN/CO and CH_3CN/CO of 1.5×10^{-2} and 3.8×10^{-3}, respectively, which are in fairly good agreement with our experimental data of 1.1×10^{-2} and 2.5×10^{-3}. Recent measurements by Griffith et al. (1990) yield values for HCN which are ten times lower than our results. The reasons for these diverging data need to be investigated and may partially be explained by the low N/C ratio of only 1% in the burning fuels observed by Griffith et al.

Data on the global sources of nitriles are not available, but can be derived from their background mixing ratio and their lifetime against the reaction with OH radicals. The average mixing ratio in the free troposphere is about 170 parts per trillion by volume (pptv) for HCN (Cicerone et al., 1983) and about 80 pptv for CH_3CN (Hamm et al., 1990). Reaction with OH would remove 0.17 and 0.40 Tg N/yr of HCN and CH_3CN, respectively (Lobert, 1990a). The lifetimes were taken from Cicerone et al. (1983) and Harris et al. (1981). The computed amounts of 0.17 and 0.40 Tg N/yr are the required sources, which can explain the atmospheric background mixing ratio, assuming that the reaction with OH is the only important sink. In Table 36.6 we report values which are much higher than these estimates. This implies that other sinks for these gases must exist. Hamm et al. (1990) supposed the ocean to be a major sink for acetonitrile. However, it is conceivable that hydrogen cyanide can be consumed by plants (Lobert, 1990a; Selmar et al., 1988) and microorganisms (Postgate, 1982). Inherent in larger sinks, on the other hand, is a shorter atmospheric lifetime of these compounds, which causes a nonuniform distribution in the troposphere and therefore allows their use as tracer compounds for biomass burning emissions. Indeed, Hamm observed a strong acetonitrile increase in marine, equatorial latitudes during ship measurements in the dry season. Other important sources for HCN and CH_3CN are not known. Arijs et al. (1986) estimated the automotive and industrial exhausts for acetonitrile to be at most 0.02 Tg N/yr. A similar value of 0.04 Tg N/yr was derived from estimates by Lobert (1990a) for hydrogen cyanide. Thus biomass burning may well be the major source for the release of these gases into the atmosphere.

As stated above, molecular nitrogen could be an important emission of biomass burning, causing a *pyro-denitrification* of ecosystems (Lobert et al., 1990b), since N_2 is not deposited by dry or wet processes and is therefore removed from the soil irreversibly. The 17 experiments for determination of N_2 presently conducted yielded an average fraction of 22% of the fuel nitrogen. Most of these experiments showed a CO/CO_2 ratio of about 25%, which is an indicator for pure smoldering combustion or even pyrolysis. The most recent experiments were conducted to burn more efficiently with CO/CO_2 values of around 5%, emitting 41% to 46% of the fuel nitrogen in form of N_2. Thus, N_2 seems to belong to the flaming stage rather than to the smoldering stage. Based on our preliminary average of 22%, we calculate a minimum pyro-denitrification rate of 5.6 to 21.3 Tg N/yr, which equals 9% (5% to 14%) of the global, terrestrial nitrogen fixation rate of 100 to 170 Tg N/yr (Söderlund et al., 1976). Assuming N_2 emissions to be 50% of the nitrogen balance, which then is the upper estimate (Lobert et al., 1990b), it could equal 17% to 20% of the fixation rate. In either case, biomass burning has a significant effect upon the biogeochemical cycle and nutrient budget of tropical ecosystems. For detailed results see Kuhlbusch et al. (1991).

Conclusions

We presented data on the nitrogen and carbon emissions of biomass burning. The results of our experiments enable us to calculate new source strengths for many compounds, considering different burning stages and fire conditions on the one hand, and different fuel types and properties, on the other hand. We also presented a method for balancing elemental budgets of fires, which had already been described for carbon compounds by other authors but which is new for the nitrogen inventory. We feel that this is an important tool for estimating global amounts of nitrogen-containing gases. Measurements on quantifying the high molecular weight nitrogen compounds and particulate matter, which complete our balance, must be carried out in order to improve the rough estimate given in this chapter.

Based on our measurements we show that biomass burning contributes significantly to the global budgets of HCN, CH_3CN (possibly the major source), NO_x (12%), CO (22%), C_2 to C_4 hydrocarbons (14%), CH_3Cl (41%), and probably also to the global source of C_1-C_5 aliphatic amines. Further, pyrogenic CO_2 amounts are likely to represent a substantial contribution to the global greenhouse warming. An important

result from our study is the identification of N_2 emissions, which causes a significant loss of fixed nitrogen (pyro-denitrification) in tropical ecosystems in the order of 5% to 20% of the global nitrogen fixation rate. Because of an interesting interplay between an enhanced postfire nitrogen fixation (Eisele et al., 1989) and an enhanced postfire N_2O emission (Levine et al., 1988), it is not yet known if losses due to pyro-denitrification are balanced by nitrogen fixation. Therefore, the potential ecological significance of N_2 emissions presents an interesting focus for further study.

Since our experiments had been conducted in an experimental system, we need to improve our data and analytical methods by measuring the same compounds over natural fires. In order to obtain more precise source strengths, on the other hand, an improvement of estimates or, even better, an experimental attempt in quantifying the amounts of globally burned biomass is of exceeding importance. Also, a reliable determination of average N/C ratios for the burned ecosystems is essential, since a lack of such information is one of the major problems connected to global source estimates.

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