



Importance of biomass burning in the atmospheric budgets of nitrogen-containing gases

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BIOMASS burning is a primary source of many trace substances that are important in atmospheric chemistry¹⁻⁶. More than 80% of the world's biomass burning takes place in the tropics³ as a result of savanna fires, forest-clearing activity, and the burning of agricultural waste and wood. Here we report results from laboratory studies on the emission of nitrogen-containing compounds from the burning of dry vegetation. We find that the emission rates of NO_x, HCN and CH₃CN are sufficient to contribute significantly to the global atmospheric budget of the compounds. Furthermore, possibly up to half of the biomass nitrogen can be converted to molecular nitrogen, N₂, leading to an estimated annual loss of 12-28 × 10¹² g of biomass nitrogen ('pyrodenitrification'), equal to ~9-20% of the estimated global rate of terrestrial nitrogen fixation.

According to recent estimates³, ~3-6 × 10¹⁵ g of biomass carbon is burned annually, corresponding to 24-57 × 10¹² g of biomass nitrogen. This burning produces mostly CO₂, but also 10% CO and ~2% CH₄ and other hydrocarbons. Many other gases and particulate matter are also emitted. Here we consider the emissions of nitrogen-containing compounds.

Our results have been obtained using a small-scale burning apparatus built to simulate open fires (Fig. 1). The details of this apparatus are described elsewhere⁶. Because most of the biomass burning takes place in the tropics, we burned mostly tropical grasses from savanna regions and also agricultural wastes, in a total of 41 burning experiments.

Our analytical system was designed to determine CO₂, CO, non-methane hydrocarbons (NMHC) and CH₄ as well as the most important nitrogen-containing species: NO_x (NO and NO₂), ammonia (NH₃), some cyanogen compounds such as hydrogen cyanide (HCN) and acetonitrile (CH₃CN), and nitrous oxide (N₂O). Determination of the flow rate in the stack, the weight loss of the fuel, and the elemental content of both biomass and ash, as well as the concentrations of gaseous emissions, enabled us to carry out a mass balance for each experiment.

Our apparatus also allows us to observe the different burning stages separately. A burn can be divided into a hot flaming phase emitting oxidized compounds such as CO₂, NO_x and N₂O, and a colder, incompletely combusting smouldering phase producing much more smoke and less oxidized substances such as CO, hydrocarbons, ammonia and nitriles⁶. Figure 2 shows some of the compounds emitted during one of our experiments, and the corresponding stack-gas temperature. The transition between flaming and smouldering combustion is clearly observable in our experiments and corresponds to a large increase in the CO concentration and a decrease in CO₂ emission at ~96 s.

Our data show that on average ~90% of the biomass nitrogen and 95% of the carbon were volatilized during the burn, with a mean weight loss of 75% in the flaming and 25% in the smouldering stage. Almost all of the carbon was recovered in the measured emissions of CO₂, CO, hydrocarbons and in the ash. By contrast, only ~32% of the nitrogen could be regained by the above mentioned nitrogen-containing compounds and the nitrogen content of the ash (Table 1).

The most important emissions in terms of the original nitrogen content of the fuel were NO_x (~13%), ammonia (~4%), HCN (2.4%) and acetonitrile (~1%). Minor contributions were made by N₂O, other nitriles, C₁ to C₅ amines⁷ and other nitrogen

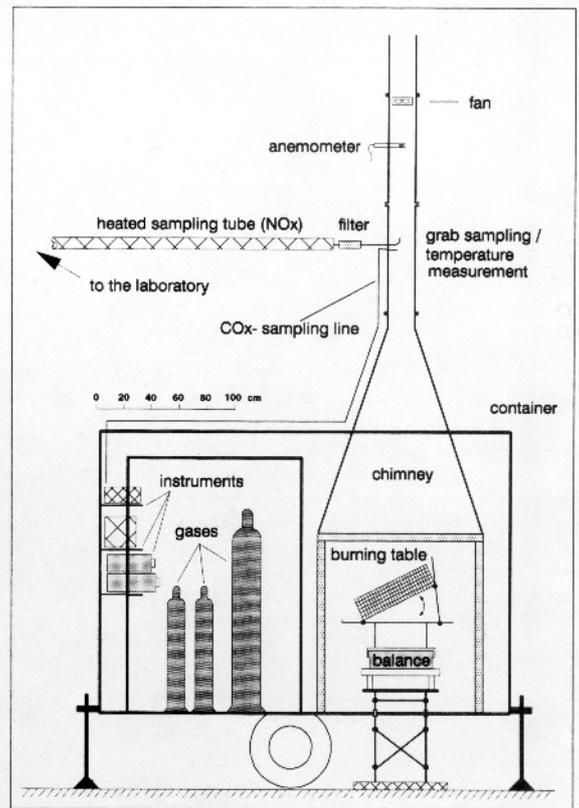


FIG. 1 Burning apparatus for an experimental simulation of open biomass burning⁶.

oxides (mainly HNO₃).

The NO_x emissions from tropical biomass burning account for ~20% of the global budget¹¹ whereas ammonia emissions could represent ~10% of the global source⁴. What is remarkable is the high amount of nitriles emitted during biomass burning. These emissions may dominate the atmospheric inputs of hydrogen cyanide and acetonitrile, being much greater than automotive and industrial emissions. Therefore, HCN and CH₃CN may well serve as global tracers for biomass burning emissions. The most important atmospheric sink for these gases, the reaction with OH[•] radicals (which consumes about 0.17 × 10¹² and 0.40 × 10¹² N yr⁻¹ for HCN and CH₃CN respectively), is much smaller than their biomass-burning source, implying that other important sinks must exist; these probably include uptake in the ocean⁸ and in plants⁶. Our results also show that biomass burning does not contribute significantly to the global budget of nitrous oxide.

Our measurements do not include all organic nitrogen compounds produced by incomplete combustion. As an indication of their relative importance, we may consider the product distribution in tobacco smoke, which contains mainly aliphatic and aromatic amines and heterocyclic constituents as well as the compounds considered here⁹. Using this distribution we estimate that such compounds can account for only another 20% of the plant nitrogen.

This implies that up to 50% of the original fuel nitrogen was emitted in a form that neither was detected during our own experiments nor can be deduced from analyses of tobacco effluents. Thus molecular nitrogen, which cannot be measured in open fires, is a likely candidate for the missing nitrogen. Some preliminary burning experiments in a closed apparatus supplied with a helium/oxygen mixture indeed show that a significant fraction of N₂ is formed (T. A. Kuhlbusch, personal communication). If the missing 50% does indeed consist of N₂, this represents an annual loss of 12-28 × 10¹² g N from tropical ecosystems. Such a rate of loss in plant nitrogen equals ~9-20% of the estimated annual, global, terrestrial nitrogen fixation rate

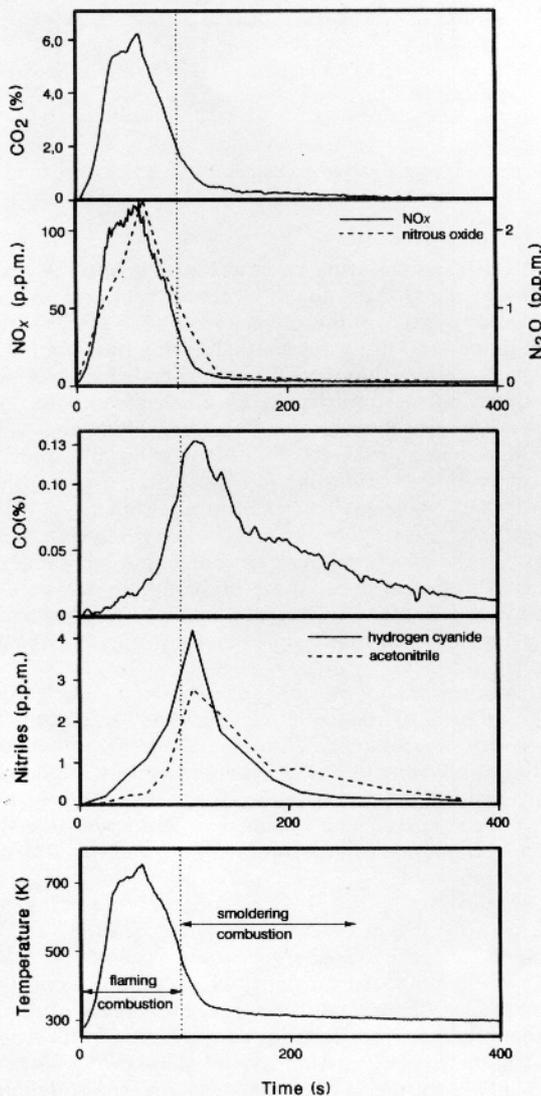
TABLE 1 Nitrogen balance of burning experiments

Compound	Percentage of biomass nitrogen	Number of experiments	Source* (10^{12} g N yr $^{-1}$)	Global† (10^{12} g N yr $^{-1}$)	Ref.
NO $_x$	12.7 ± 4.94	22	2.46–8.65	25–99	11
NH $_3$	4.00 ± 3.05	15	0.59–3.15	20–80	4
HCN	2.42 ± 1.79	12	0.37–1.89	?	
CH $_3$ CN	0.95 ± 0.74	11	0.14–0.75	?	
Other nitriles	0.21 ± 0.21	10	0.03–0.18	?	
N $_2$ O	0.77 ± 0.21	12	0.16–0.50	14	12
Amines ⁷	0.24 ± 0.21	5	0.03–0.20	?	
HNO $_3$	≈1	2	0.24–0.57	?	
Residue (ash)	9.89 ± 0.95	41	2.26–5.91		
Sum	32.2				
Unknown	67.8				
Higher N-compounds	20?		5–11		9
N $_2$	50?		12–28	139‡	10

* Annual source strength for the compounds using our emission ratios and the global biomass-burning nitrogen volatilization of $24\text{--}57 \times 10^{12}$ g N yr $^{-1}$ (ref. 3). In estimating the final range we multiplied the mean value ± half of the standard deviation with the range of nitrogen release. For example, source of NO $_x$ = $(12.7 \pm 2.47) \times (24\text{--}57)$.

† Global budgets of the gases and reference for these estimates.

‡ Global terrestrial nitrogen fixation rate.



(139×10^{12} g N yr $^{-1}$)¹⁰ and an even higher proportion from tropical ecosystems, especially savannas and agricultural lands.

Thus biomass burning is important not only to atmospheric chemistry but, because of nitrogen gas release and pyrodenitrification, also to the biogeochemical nitrogen cycle of tropical savannas and agricultural ecosystems. Because most biomass burning takes place as a result of human activity³, its long-term effect on the functioning of these ecosystems is an important issue that warrants further exploration. □

FIG. 2 Mixing ratios of some gases in the fire exhaust, and the stack-gas temperature of a burning experiment, as a function of time. The dotted vertical line represents the transition between flaming and smoldering stages⁶.

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