

to one water molecule. Figure 3c, d shows ^{27}Al DOR spectra taken 2 days and 23 days after dehydration; the sample remained inside the inner rotor of the DOR probe during this period, allowing water molecules to diffuse slowly into the material. The two sharp lines that emerge, g at 37.3 p.p.m. and h at 38.8 p.p.m., arise from Al-2 species influenced by adsorbed water molecules. Figure 3c shows that the relative intensity of peak d associated with dehydrated Al-1 sites undergoes little change as a result of partial rehydration, bearing in mind that the 1:2 ratio of Al-1 to Al-2 species must be maintained at all stages of hydration. The sensitivity of the VPI-5 framework to guest loading and packing, as indicated by these data, should yield new insight into the behaviour of molecules in confined micro-porous environments.

Both DOR and dynamic angle spinning (DAS) (recently demonstrated for ^{17}O and ^{23}Na (ref. 12)) make it possible to measure ^{27}Al quadrupole-coupling parameters and chemical shifts, allowing the study of adsorbate-host interactions in molecular sieves and subtle microstructural features in other aluminium-containing solids including catalysts, glasses, ceramics, minerals and semiconductors. □

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1. Stucky, G. D. & MacDougall, J. E. *Science* **247**, 669–678 (1990).
2. Llor, A. & Viret, J. *Chem. Phys. Lett.* **152**, 248–253 (1988).
3. Samoson, A., Lippmaa, E. & Pines, A. *Mol. Phys.* **65**, 1013–1018 (1988).
4. Chmelka, B. F. *et al. Nature* **339**, 42–43 (1989).
5. Davis, M. E., Saldarriaga, C., Garces, J. M. & Crowder, C. *Nature* **331**, 698–699 (1988).
6. Crowder, C. E., Garces, J. M. & Davis, M. E. *Adv. X-ray Analysis* **32**, 503–510 (1989).
7. Richardson, J. W. Jr, Smith, J. V. & Pluth, J. J. *J. phys. Chem.* **93**, 8212–8219 (1989).
8. Davis, M. E. *et al. J. Am. chem. Soc.* **111**, 3919–3924 (1989).
9. Wu, Y., Sun, B. Q., Pines, A., Samoson, A. & Lippmaa, E. *J. magn. Res.* (in the press).
10. Grobet, P. J. *et al. Appl. Catal.* **56**, L21–L27 (1989).
11. Blackwell, C. S. & Patton R. L. *J. phys. Chem.* **88**, 6135–6139 (1984).
12. Mueller, K. T. *et al. J. magn. Res.* **86**, 470–487 (1990).

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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 chemistry^{1–6}. 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 CH_3CN 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, N_2 , leading to an estimated annual loss of $12\text{--}28 \times 10^{12}$ g of biomass nitrogen ('pyrodenitrification'), equal to $\sim 9\text{--}20\%$ of the estimated global rate of terrestrial nitrogen fixation.

According to recent estimates³, $\sim 3\text{--}6 \times 10^{15}$ g of biomass carbon is burned annually, corresponding to $24\text{--}57 \times 10^{12}$ g of biomass nitrogen. This burning produces mostly CO_2 , but also 10% CO and $\sim 2\%$ CH_4 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 CO_2 , CO, non-methane hydrocarbons (NMHC) and CH_4 as well as the most important nitrogen-containing species: NO_x (NO and NO_2), ammonia (NH_3), some cyanogen compounds such as hydrogen cyanide (HCN) and acetonitrile (CH_3CN), and nitrous oxide (N_2O). 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 CO_2 , NO_x and N_2O , 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 CO_2 emission at ~ 96 s.

Our data show that on average $\sim 90\%$ 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 CO_2 , CO, hydrocarbons and in the ash. By contrast, only $\sim 32\%$ of the nitrogen could be regained by the above mentioned nitrogen-containing compounds and the nitrogen content of the ash (Table 1).

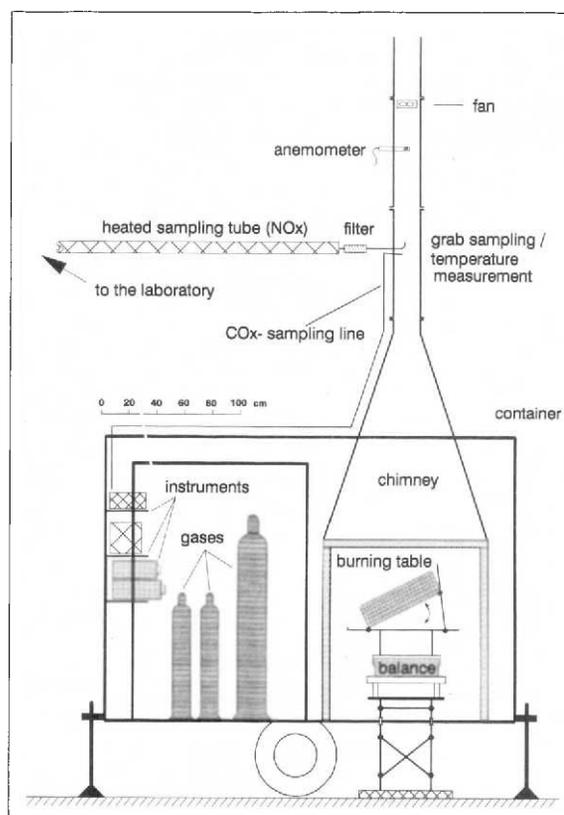


FIG. 1 Burning apparatus for an experimental simulation of open biomass burning⁶.

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.

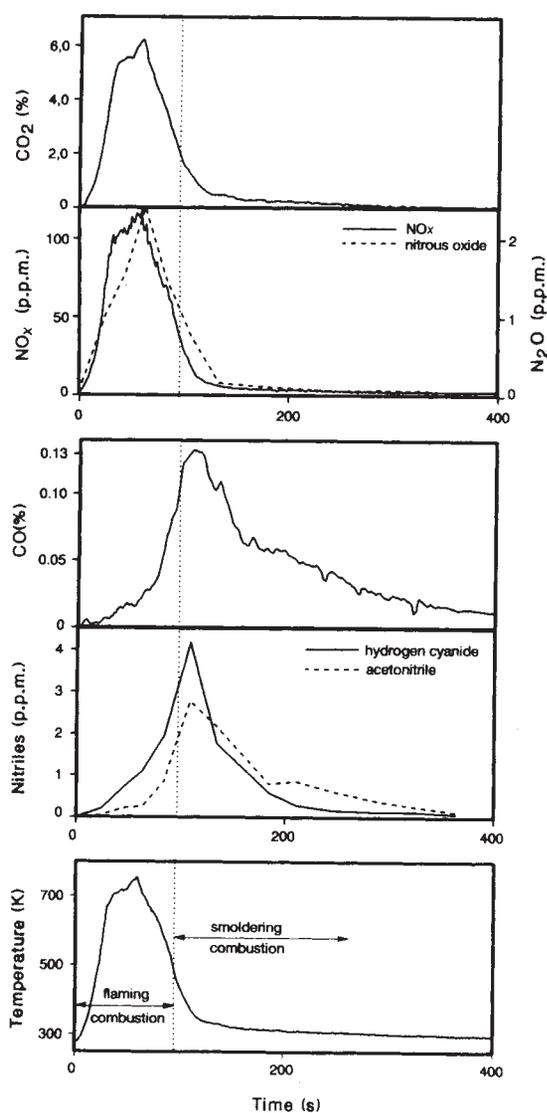


FIG. 2 Mixing ratios of some gases in the fire exhaust, and the stack-gas temperature of a burning experiment, as a function of time. The dotted vertical line represents the transition between flaming and smoldering stages⁶.

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 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 0.17×10^{12} and 0.40×10^{12} 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 $12\text{--}28 \times 10^{12}$ 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 (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. □

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1. Crutzen, P. J., Heidt, L. E., Krasnec, J. P., Pollock, W. H. & Seiler, W. *Nature* **282**, 253–256 (1979).
2. Crutzen, P. J. et al. *J. Atmos. Chem.* **2**, 233–256 (1985).
3. Crutzen, P. J. & Andreae, M. O. *Science* (in the press).
4. Andreae, M. O. et al. *J. geophys. Res.* **93**, 1509–1527 (1988).
5. Cofer, W. R. *J. geophys. Res.* **94**, 2255–2259 (1989).
6. Lobert, J. M. thesis, Max-Planck-Institut für Chemie (Mainz) (1990).
7. Seuwen, R. thesis, Max-Planck-Institut für Chemie (Mainz) (1989).
8. Hamm, S. & Warneck, P. *J. geophys. Res.* (in the press).
9. Neurath, G. *Beitr. Tabakforsch.* **5**, 115–133 (1969).
10. Soderlund, R. & Svensson, B. *H. Ecol. Bull., Stockholm* **22**, 33–73 (1976).
11. Logan, J. *J. geophys. Res.* **88**, 10785–10807 (1983).
12. World Health Organization *Global Ozone Research and Monitoring Proj.* Rep. 16 (WHO, Geneva, 1985).

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An ice-core record of atmospheric response to anthropogenic sulphate and nitrate

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RECORDS of sulphate and nitrate concentrations in ice cores show that these concentrations have increased recently because of the long-range transport of pollution from middle latitudes^{1–5}. But these records have been neither complete enough nor long enough to allow an assessment of their sensitivity to variations in the emissions of sulphate and nitrate precursors. We have now analysed sections from an ice core in South Greenland which have allowed us to extend its sulphate and nitrate record back from 1869 to 1767. This longer record has enabled us to determine the pre-industrial natural interannual variability of non-sea-salt sulphate and nitrate. We find that the background concentration in the remote atmosphere over South Greenland is sensitive to changes in the anthropogenic emissions of sulphate and nitrate, and responds to these variations on a timescale of the order of decades.

The highest resolution, continuous glaciochemical time-series available for Greenland¹ (site 20D; located 40 km southwest of

Dye 3 to avoid any local pollution effects⁶) previously covered the period 1869–1984. Analysis of the remainder of the core has now provided a detailed record extending back to 1767 (Fig. 1).

For south Greenland the most probable sources of sulphate are: sea-salt aerosol (for which Fig. 1 has been corrected) oxidation of the dimethylsulphide (DMS) produced by phytoplankton and emitted from the oceans; natural stratospheric aerosols; volcanic emissions via SO₂; and anthropogenic emissions via SO₂ (primarily stationary-source fuel combustion⁷).

The principal source of nitrate to the site is anthropogenic activity (mainly stationary-source fuel combustion and transportation-related emissions⁷ in addition to biomass burning). Other sources include lightning, NH₃ oxidation and NO exhalation⁸. Biomass burning is probably a more effective source of NO_x for the Southern Hemisphere free troposphere.

Probability plots (Fig. 2) verify the major trends indicated in the extended time-series for non-sea-salt (n.s.s.) sulphate and nitrate (Fig. 1). For n.s.s. sulphate the following time periods can be differentiated: 1767–1903, 1903–1960 and 1960–1984 during which the ranges in concentration are 10–154, 28–77 and 41–93 ng g⁻¹, respectively. An estimate of the concentration range in n.s.s. sulphate, corrected for volcanic input (from identifiable discrete events and not including volcanic background) can be determined from the probability plots by subtracting the number of years affected by volcanic activity per period⁹ from the upper end of the probability plot (8% for 1960–84, 31% for 1903–60; 25% for 1767–1903, estimated from the total 1869–1984 record). The concentration ranges for non-volcanic n.s.s. sulphate then become 10–28, 28–51 and 41–84 ng g⁻¹.

Measurements of methanesulphonic acid, an atmospheric oxidation product of dimethylsulphide (DMS), provide an estimate of the general strength of the biogenic sulphur signal at site 20D (decadal mean values < 4.5 ng g⁻¹ and highs < 10 ng g⁻¹; E. Saltzman, personal communication). Thus, for the period 1767–1903 two-thirds or more of the n.s.s. non-volcanic (discrete

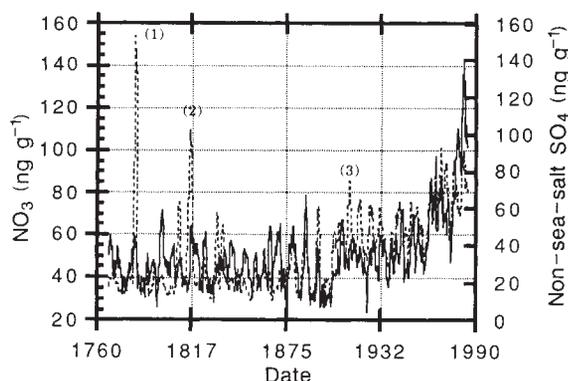


FIG. 1 Time-series of the non-sea-salt sulphate (dashed line) and nitrate (solid line) concentrations at site 20D. Data have been smoothed (using a gaussian function) to 1–2 years from the original ~5.8 samples per year, to remove seasonal signals not discussed here. Examples of volcanic events recorded by n.s.s. sulphate spikes are: (1) Laki (1783); (2) Tambora (1815); (3) Katmai (1912).

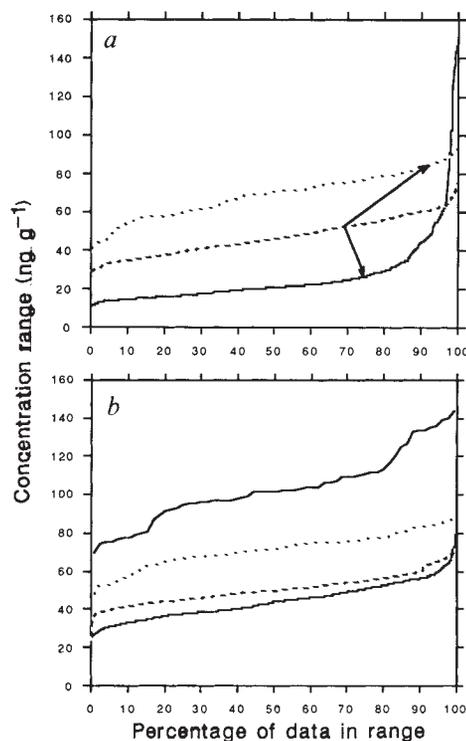


FIG. 2 *a*, Probability plot for n.s.s. sulphate (solid line, 1767–1903; dashed line, 1903–1960; dotted line, 1960–1984). *b*, Probability plot of nitrate (upper solid line, 1767–1903; dotted line, 1960–1976; dashed line, 1903–1960; lower solid line, 1976–1984). Both plots were produced using a normalized linear probability (percentage) distribution.