

AMMONIA EMISSIONS FROM BIOMASS BURNING

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Abstract. Measurements in the plumes from seven forest fires show that the concentrations of NH₃ were considerably in excess of ambient values. Calculation of NH₃ emissions from the fires, based on the ratio of NH₃/CO in the plumes and emissions of CO from biomass burning, suggest that biomass burning may be a significant source of atmospheric NH₃.

1984; Buijsman et al., 1987]. Of these, the dominant source, by far, has been considered to be animal wastes [Harriss and Michaels, 1982; Buijsman et al., 1987].

A recent study of the cycling of nitrogen species through a forest ecosystem has suggested that the volatilization of nitrogen compounds during forest fires could be a significant source of NH₃ [Riggan et al., 1985]. We present here data on the emissions of NH₃ from seven forest fires in the Western United States that support this conjecture.

Introduction

Ammonia (NH₃) is the primary basic gas in the earth's atmosphere. As such, it is of considerable importance in a number of atmospheric chemical processes and cycles. For example, it partially neutralizes sulfuric and nitric acid in precipitation. Despite this importance, surprisingly little quantitative data is available on the sinks and sources of atmospheric NH₃.

The assumption is generally made that wet deposition is the major sink of NH₃ [e.g., Lenhard and Gravenhorst, 1980; Harriss and Michaels, 1982], but the lack of data on dry deposition of NH₃ prevents accurate quantification of the relative magnitude of the sinks. The source strengths of NH₃ are even more uncertain, particularly over large spatial scales. Animal waste, emissions from soils, volatilization of ammonia-based fertilizers, and industrial emissions have been suggested as significant sources of NH₃ [Liu and Cicerone,

Experiment Description

The location, approximate size, and the nature of the fuel for each of the seven forest fires investigated are listed in Table 1.

Measurements were obtained from the University of Washington's C-131A research aircraft. The instrumentation package and general sampling procedures for plumes employed on this aircraft have been described by Hegg and Hobbs [1980] and Radke et al. [1978], respectively.

Measurements of the concentrations of NH₃ and CO were made in the plumes from the fires and in the adjacent ambient air. When the plume from a fire was penetrated, continuous measurements of the particle scattering coefficient and NO_x concentration were monitored to determine when the aircraft

TABLE 1. Fires Examined in Study

| Fire Designation | Location | Size (ha) | Fuel |
|-------------------|----------------------------|-----------|--------------------------------|
| Lodi 1 | Los Angeles Basin | 40 | chaparral |
| Lodi 2 | Los Angeles Basin | 150 | chaparral |
| Myrtle/Fall Creek | Roseburg, Oregon | 2,000 | pine, brush, Douglas fir |
| Silver | Grants Pass, Oregon | 20,000 | Douglas fir, true fir, Hemlock |
| Satsop | Satsop, Washington | 40 | Douglas fir, Hemlock |
| Troy | Troy, Montana | 70 | pine, Douglas fir, true fir |
| Hardiman | Chapleau, Ontario (Canada) | 325 | pine |

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was well within the plume. Close to the center of the plume, a large (1.5 m^{-3}) polyethylene bag was filled by ram air. Air was then drawn out of this bag, through sequential filters of stretched Teflon (Teflo) and oxalic acid impregnated cellulose (Whatman 41 with 5% oxalic acid). Simultaneously, the air in the bag was analyzed for CO with a TECO Model 48 gas filter correlation spectrometer (detection limit ≈ 100 ppb). The exposed filters were subsequently extracted in distilled water in the laboratory and the cellulose filters analyzed for NH_3 using a Technicon Model 2 autoanalyzer. The detection limit for NH_3 was determined from the standard error of the concentrations of NH_3 detected on multiple "blank" (i.e., unexposed) filter extracts; the value was $4 \mu\text{mol L}^{-1}$. The corresponding uncertainty in the NH_3 measurements varied with the volume of air pulled through the filters, but it was ~ 3 ppbv.

Results and Discussion

The concentrations of NH_3 and CO measured in the plumes from the seven fires and in the ambient air are listed in Table 2. The concentrations of NH_3 in the plumes ranged from 7 to 130 ppb, and those of CO from 920 to 15400 ppb.

The ambient concentrations of NH_3 were generally at or below ~ 6 ppb outside of the plumes. This concentration is in agreement with previous ambient NH_3 measurements [e.g., Lenhard and Gravenhorst, 1980; Cadle et al., 1982; Harward et al., 1982], including numerous measurements at ground level. Clearly, the fires were generally substantial emitters of NH_3 .

To evaluate the significance of forest fires as a source of atmospheric NH_3 on a continental or global scale, we first determine the ratio of NH_3 to CO in the plumes from the fires listed in Table 2. After subtracting the ambient concentrations from the plume concentrations, these ratios range from 0.002 to 0.038 (Table 2), and have a mean value of 0.012 with a standard error of ± 0.005 . This mean value is roughly comparable to the NH_3/CO emission ratio suggested by studies of wood combustion in stoves [National Research Council, 1979]. Indeed, if one combines the NH_3 emission factor from such studies ($\sim 1 \text{ kg NH}_3$ per ton of wood) with the CO emission factor for biomass burning from Logan et al. [1981] ($\sim 100 \text{ kg ton}^{-1}$), one arrives at an NH_3/CO ratio of 0.016.

One extraordinary fact shown in Table 2 must be briefly discussed. The plumes from Lodi 1 and Lodi 2, which had

TABLE 2. Concentrations of NH_3 and CO in the Plumes from the Fires and in the Ambient Air

| Fire | NH_3 (ppb) | CO (ppb) | NH_3/CO^* | Mean Value of NH_3/CO^* |
|---------------------------|------------------------|-------------|---------------------------|-----------------------------------------|
| Lodi 1 (plume) | 130 | 3400 | 0.038 | 0.038 |
| Lodi 1 (ambient) | 6 | 130 | ... | |
| Lodi 2 (plume) | 17 | 7600 | 0.002 | } 0.002 |
| Lodi 2 (plume) | 23 | 8900 | 0.002 | |
| Lodi 2 (ambient) | 0 | 100 | ... | ... |
| Myrtle/Fall Creek (plume) | 50 | 3800 | 0.013 | } 0.014 |
| Myrtle/Fall Creek (plume) | 81 | 5600 | 0.014 | |
| Myrtle/Fall Creek (plume) | 100 | 6300 | 0.016 | |
| Silver (plume) | 16 | 920 | 0.017 | } 0.011 |
| Silver (plume) | 15 | 1300 | 0.011 | |
| Silver (plume) | 7 | 970 | 0.006 | |
| Silver (ambient) | ... | 70 | ... | ... |
| Satsop (plume) | 110 | 15400 | 0.007 | 0.007 |
| Troy (plume) | 91 | 8200 | 0.011 | } 0.010 |
| Troy (plume) | 37 | 4100 | 0.009 | |
| Troy (ambient) | 0 | 120 | ... | ... |
| Hardiman (plume) | 13 | 4800 | 0.002 | 0.002 |
| Hardiman (ambient) | 3 | 100 | ... | ... |

* Ambient values have been subtracted.

essentially identical fuels, have NH_3/CO ratios that differ by a factor of 19. This contrast is interpretable in terms of differences in fire environment. The Lodi 1 fire (December) was ignited 6 days after 14 mm of rainfall. It could be sustained only on the most xeric slopes where it spread slowly. Similar fuel on similar slopes burned rapidly during Lodi 2 (June) with flame lengths exceeding 15-20 m. The lower energy release rates and higher soil moisture during December no doubt moderated soil heating. (Soil and leaf litter can account for as much as 90% of nitrogen volatilized during Chaparral fires [DeBano and Conrad, 1978]. Moderate soil heating produces NH_4^+ from pyrolysis of organic matter. At higher temperatures more organic nitrogen is volatilized but less nitrogen accumulates as NH_4^+ since the NH_4^+ and subsequent NH_3 are oxidized to NO_x [Dunn and DeBano, 1977]. Thus, some of the variability in NH_3/CO shown in Table 2 may be due to differing fire environments rather than different fuels.

We now use our measurements of the NH_3/CO ratio for smokes from forest fires, together with estimates of CO emissions from biomass burning, to estimate large-scale NH_3 emissions from biomass burning. Logan et al. [1981] estimated the emissions of CO from biomass burning (including agricultural, savanna fires and forest fires) in the northern hemisphere, to be $\sim 380 \text{ Tg yr}^{-1}$, with an uncertainty of perhaps a factor of three. On the global scale, Crutzen [1983] estimated $\sim 1000 \text{ Tg yr}^{-1}$ of CO from biomass burning. Utilizing the value of 380 Tg yr^{-1} , and assuming that the mean value of the molar emission ratio of NH_3 to CO derived from our measurements on forest fires is applicable to all biomass burning in the northern hemisphere, we arrive at an NH_3 emission rate from biomass burning in the northern hemisphere of $\sim 3 \text{ Tg yr}^{-1}$. However, the uncertainty of $\sim 40\%$ in our mean value for the NH_3/CO ratio, coupled with about a factor of three uncertainty in hemispheric CO emissions, yield a possible range for NH_3 emissions in the northern hemisphere of 0.5 to 12 Tg yr^{-1} .

The NH_3 emission rate derived above can now be compared to estimates of the strengths of other large-scale sources of NH_3 . For example, Harriss and Michaels [1982] consider domestic livestock, fossil fuel combustion and fertilizer volatilization to be the major sources of atmospheric NH_3 in the United States, and they estimated that the total emissions from these sources in the United States to be 3.4 Tg yr^{-1} . Buijsman et al. [1987] considered essentially the same sources and arrived at an emission value for Europe of 6.4 Tg yr^{-1} . These recent, and quite detailed, analyses are consistent with the earlier study of Böttger et al. [1981], in which total emissions of NH_3 in the northern hemisphere were estimated to be $\sim 20 \text{ Tg yr}^{-1}$.

Our best estimate for NH_3 emissions from biomass burning in the northern hemisphere ($\sim 3 \text{ Tg yr}^{-1}$) is $\sim 15\%$ of Böttger et al.'s estimate for the total emissions of NH_3 in the northern hemisphere. Considering the seasonality of biomass burning, this percentage may be even higher during various portions of the year. Furthermore, while our lower-bound estimate for NH_3 emissions from biomass burning (0.5 Tg yr^{-1}) would render this source of minor importance, our upper-bound estimate (12 Tg yr^{-1}) would make biomass burning a source for atmospheric ammonia comparable to the most important source previously suggested (animal wastes). These comparisons suggest that biomass burning may contribute significantly to NH_3 in the atmosphere.

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