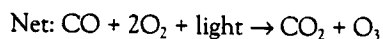
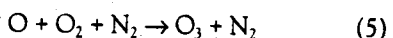
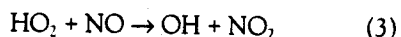
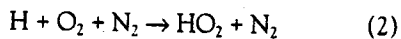
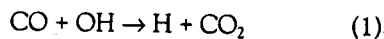


# Fires, Atmospheric Chemistry, and the Ozone Layer

Ralph J. Cicerone

Fire has long been a powerful force in nature, altering habitats, mobilizing nutrients, and driving evolution. It is also an old tool of agriculture used to clear land of trees and shrubs in preparation for planting or as pastures and to incinerate postharvest residues. Such biomass burning also represents a kind of nonindustrial pollution produced mostly by lesser developed countries (1). About 15 years ago, Crutzen *et al.* (2) realized that the potential impact of biomass burning worldwide on atmospheric chemical composition is larger than first meets the eye. One new part of that impact is discussed on page 1255 of this issue, in which Manö and Andreae report the surprisingly large amount of methyl bromide ( $\text{CH}_3\text{Br}$  or MeBr) emitted in biomass burning (3).

Looking beyond the easily visible smoke and bright flames with instruments, Crutzen *et al.* (2) saw that gases released by biomass burning could alter the air chemistry of various regions. For example, nitrogen oxides ( $\text{NO}$  and  $\text{NO}_2$ ) and carbon monoxide ( $\text{CO}$ ) can produce ozone ( $\text{O}_3$ ) in the lower atmosphere (troposphere) downwind from the burning—just as in polluted, smoggy urban air—through photochemical reaction sequences such as

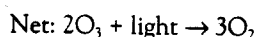
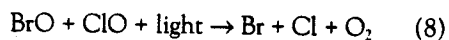
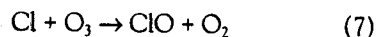
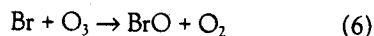


Equally dramatic is the role of  $\text{CH}_3\text{Cl}$  from burning vegetation; although most  $\text{CH}_3\text{Cl}$  is destroyed photochemically in the troposphere, a few percent survives the upward journey to the stratosphere where the ozone-destroying Cl atoms are released.

Now we learn that biomass burning also produces gaseous MeBr and that this source may account for 30% of the MeBr in the atmosphere (3). This discovery comes at a

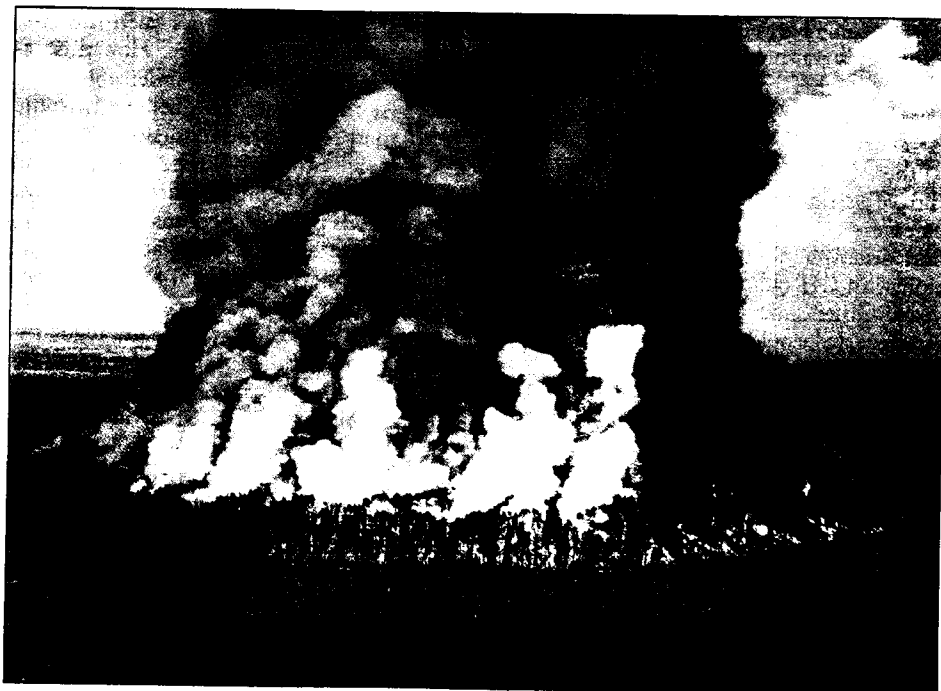
time when many researchers are trying to understand and quantify the budget of atmospheric MeBr without knowing about this source and when the atmospheric chemistry of bromine compounds has come front and center. There is much current interest because Br atoms apparently have a higher ozone-destroying efficiency (20 to 60 times) than Cl atoms. Although stratospheric ozone losses observed to date (4) are mostly attributable to Cl from chlorofluorocarbon (CFC) gases, in the Antarctic spring, up to 25% may be attributable to Br from synthetic halon compounds and  $\text{CH}_3\text{Br}$ , even though stratospheric inorganic Br amounts are less than 1% of inorganic chlorine concentrations (5).

Free Br atoms catalyze stratospheric ozone destruction mainly through the reaction sequence



The Br atoms are delivered to the stratosphere bound in relatively stable organic compounds such as halon 1301 ( $\text{CF}_3\text{Br}$ ), halon 1211 ( $\text{CF}_2\text{BrCl}$ ), and MeBr. Atmospheric lifetimes of the halons are 65 and 20 years, respectively, so that almost 100% of the halons released at Earth's surface reach the stratosphere intact. The 1990 worldwide release rates of halons imply a Br flux into the stratosphere of  $7.2 \times 10^6$  kg year<sup>-1</sup> (this number is probably known to within 10%). Methyl bromide is much more reactive than the perhalogenated halon compounds: Its atmospheric lifetime is about 2 years [if atmospheric OH is the only sink (3)], only a few percent of the MeBr emitted at the surface reaches the stratosphere, and there are natural sources as well as anthropogenic ones.

Aside from scientific curiosity, there is a practical reason to want to know the sizes of the anthropogenic source ( $S_A$ ) and the natural source ( $S_N$ ). On 30 November 1993, the U.S. Environmental Protection Agency (EPA) added MeBr to the Clean Air Act list of Class I Ozone-Depleting Substances; the EPA final rule will freeze production and importation of MeBr by the United States in 1994 at 1991 levels, with a phaseout of production and consumption by the year 2001. Some kind of regulation is needed because the worldwide synthetic production of MeBr increased by about 50% between 1984 and 1991, but we would also like to know how much atmospheric MeBr concentrations will decrease if no more MeBr is synthesized and how much less ozone depletion



**Biomass bromine.** During the burning of biomass, such as this boreal forest fire near Krasnoyarsk, Siberia, surprisingly large amounts of bromine compounds, especially methyl bromide, can be released. [Courtesy J. G. Goldammer, Max Planck Institute for Chemistry, Mainz, Germany]

The author is the Daniel G. Aldrich Professor of Earth System Science at the University of California, Irvine, CA 92717-3100, USA.

will occur. The answers, assuming that all nations cease synthesis, depend on the relative sizes of  $S_A$  and  $S_N$ , on whether other sinks beside tropospheric OH radicals are significant, and on details of stratospheric chemistry that control the chain length of the cycle comprising reactions 6 through 8. The effectiveness of BrO clearly depends on ClO amounts, and with greatly reduced emissions of CFCs as a result of international agreements and industrial actions, ClO amounts will decrease but only slowly, requiring decades for complete purging.

By introducing biomass burning as a significant source, Manö and Andreae (3) have added more questions to the puzzle. For example, although most current biomass burning is probably human-controlled, amounts of material may be known only to within about 60% (1), and temporal trends are not known well. Further, the new data (3) raise other questions. For example, why is MeBr released both during the flaming phase (along with  $CO_2$ ) and the smoldering phase of burning (along with CO), whereas  $CH_2Cl$  is released mostly during smoldering? How variable are the Br contents of plants, and how does one do a proper inventory of Br of the material burnt annually?

These new questions add to previous uncertainties about atmospheric MeBr amounts, sources, and sinks. To illustrate, in a first approximation, the total steady-state atmospheric inventory,  $B$ , is related to annual global sources,  $S$ , and the atmospheric residence time  $T$  by  $B = S \times T$  [see (6) for a more general analysis]. At present,  $B$  is probably between  $1.5$  and  $2.1 \times 10^8$  kg, although some published data suggest values 60% higher.

Individual components of  $S$  have been estimated, but only roughly in my opinion, so there is merit to estimating  $S$  as  $B/T$ . In turn,  $T$  is estimated from knowledge of elementary chemical and biological processes and atmospheric transport models; reaction with OH radicals limits  $T$ , to about 2 years. Other sinks discussed by Manö and Andreae (3) could lower  $T$ , but not to as little as 1 year, I believe. Further information can be deduced from two- or three-dimensional transport models that use the spatial distribution of atmospheric MeBr as input data, but our current knowledge of the distribution is also rough. Excesses are observed north of the equator, suggesting the dominance of anthropogenic (or at least continental) sources, but the north/south ratio is reported to be anywhere between 1.15 and 1.5, with seasonal variations of unknown origin (6). Altogether,  $S = S_A + S_N$  is not known very well. Measured stratospheric concentrations of the key inorganic Br species, BrO, are generally

consistent with BrO amounts predicted from halon and MeBr amounts (7), but these data cannot tell us how much of the BrO is from anthropogenic MeBr.

Unmentioned by Manö and Andreae (3) is another new proposal (8)—that the oceans may serve as a buffer in the global MeBr system. A decrease in anthropogenic emissions should induce a compensating flux from the ocean to the atmosphere, thus lessening the expected change in atmospheric amount (8); how much of a change depends on rates of chemical and biological consumption in oceanic surface waters. To my knowledge, there is very little research under way to address this idea quantitatively. Returning to anthropogenic MeBr, we have very little empirical evidence from which to estimate the fraction,  $F$ , that escapes to the atmosphere during and after agricultural soil fumigation, a principal target of the new regulations. The potential for fumigant MeBr to destroy stratospheric ozone has been calculated assuming that no MeBr is destroyed in the soil. Shouldn't we estimate  $F$  first and then calculate the effects of the MeBr that actu-

ally enters the atmosphere, as suggested by Ko *et al.* (9)?

The questions outlined here are intrinsically interesting to many atmospheric and oceanic scientists. We want to pursue them not only to understand how this system works, but also to provide a solid scientific basis for industrial decisions and governmental regulations concerning MeBr, and to be able to estimate how effective such actions can be.

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