

# Handbook of **ATMOSPHERIC ELECTRODYNAMICS**

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## Lightning and Atmospheric Chemistry: The Rate of Atmospheric NO Production

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### 1. INTRODUCTION

Although 80% of the atmosphere is composed of molecular nitrogen ( $N_2$ ), this element is often the limiting nutrient in both terrestrial and marine photosynthesis. The reason for this apparent paradox arises from the high chemical stability of nitrogen when it is in its molecular form. Before molecular nitrogen can be used by green plants to make proteins, it must first be converted into a less stable chemical form, often referred to in the aggregate as fixed nitrogen. Fixed nitrogen includes all nitrogen-containing compounds in which the nitrogen atom or atoms are bonded to an element other than nitrogen itself. Ammonium ions and nitrate ions found in soils and aquatic systems are fixed nitrogen compounds, as are reactive nitrogen compounds found in the atmosphere, such as the nitrogen oxides ( $NO_x = NO + NO_2$ ). Because the natural abundance of fixed nitrogen — many orders of magnitude less than molecular nitrogen — is often at a level sufficiently low to be the limiting factor in plant growth, its rate of production often plays a key role in controlling the rate of growth of ecological systems.

The fixation of nitrogen on the earth is accomplished through a variety of both anthropogenic and naturally occurring biogenic and abiogenic processes. Biogenic fixation occurs as a result of the metabolic processes of a variety of nitrogen-fixing bacteria and algae on land and in the ocean, and is estimated to occur at a rate of about 200 Tg (N) year<sup>-1</sup>; that is  $200 \times 10^{12}$  g of N per year (Schlesinger, 1991). Abiogenic nitrogen fixation occurs in processes involving the dissipation of sufficient amounts of energy to cause the dissociation of atmospheric molecular nitrogen. These processes include both naturally occurring fires and sparks and a wide range of anthropogenically

induced combustion processes, often involving the burning of fossil fuels. In total, anthropogenic nitrogen fixation is estimated to yield about 60 Tg (N) year<sup>-1</sup>, dominated by the industrial production of fertilizers such as ammonium nitrate (Delwiche, 1970). Nitrogen fixation by natural abiotic processes is dominated by the conversion of molecular nitrogen to nitric oxide (NO) by lightning, which is the subject of this chapter.

An interesting review of the early, seminal research on the fixation of nitrogen by lightning can be found in Hutchinson (1954). The first documented proposal that lightning acts as a source of fixed nitrogen is generally attributed to von Liebig, who in 1827 proposed that the nitrate found in rainwater arises from the conversion of molecular nitrogen to NO by lightning and its subsequent oxidation in the atmosphere to nitric acid. Following von Liebig's proposal, a number of investigators working in the late 19th and early 20th centuries attempted to infer the magnitude of the lightning fixation rate by determining the degree of correlation between local lightning flash rates and the concentration of nitrate in rainwater. The conclusion of these studies was generally that the lightning fixation rate was a relatively small source of fixed nitrogen when compared with biogenic and anthropogenic processes, and as a result interest in the lightning fixation rate throughout much of this period was relatively small. Interestingly, it is now recognized that these early studies were fundamentally flawed. Because of the relatively long time required to convert atmospheric NO to soluble nitrate, which can then be incorporated in rain, one would not expect to find a strong correlation between local lightning and nitrate in rainwater even if lightning were a major source of atmospheric NO (see Chameides et al., 1977).

In the 1970s, some 150 years after von Liebig's initial writings, it was realized that atmospheric NO<sub>x</sub> plays a key role in the photochemistry of the earth's lower atmosphere or troposphere by acting to control the concentrations of ozone and the OH radical, as well as the acidity of rainwater and other precipitation (Chameides and Davis, 1982; Chameides and Walker, 1973; Crutzen, 1973; Ehhalt et al., 1992; Levy, 1971; Wofsy et al., 1972). Because of the possibility that lightning might be an important source of atmospheric NO<sub>x</sub>, the magnitude of the lightning fixation rate became a critical issue in atmospheric chemistry. As a result, in the last two decades a myriad of works have attempted to determine this rate. However, in spite of all these studies, a consensus on the lightning fixation rate is not yet apparent. Illustrative of this lack of consensus is Table 8.1.1, where we list the fixation rates,  $G(\text{NO})$ , obtained by various investigators over the past 20 years. The rates vary from about 1 Tg (N) year<sup>-1</sup> to more than 200 Tg (N) year<sup>-1</sup>. That this range represents a significant uncertainty in the global budget of atmospheric NO<sub>x</sub> can be seen by inspecting Table 8.1.2, where the major sources of atmospheric NO<sub>x</sub> are listed. Depending on the actual magnitude of the lightning fixation rate, a situation could exist where lightning is the dominant source of NO<sub>x</sub> and anthropogenic emissions are relatively small, or vice versa. Clearly, a more constrained estimate of the lightning fixation rate is key to an accurate assessment of the role of anthropogenic emissions in the budget of atmospheric NO<sub>x</sub> and, by extension, the chemistry of the atmosphere. In this chapter we review the fixation rate estimates presented in Table 1 to infer a more constrained range of rates; we then discuss the implications of this estimated range for the chemistry of the troposphere.

## 2. THE MECHANISM OF NO PRODUCTION BY LIGHTNING

The intense burst of radiation visible to the naked eye from a bolt of lightning is ample evidence of the profound chemical changes of the air in and around the lightning discharge tube. More sophisticated spectroscopic measurements typically indicate strong emissions from neutral and singly ionized atomic nitrogen and oxygen, indicating the widespread dissociation of atmospheric N<sub>2</sub> and O<sub>2</sub>, as well as from CN and H, indicating the dissociation of CO<sub>2</sub> and H<sub>2</sub> (Salanave, 1961; Uman, 1969). In general, these chemical changes can be related to the high temperatures in and around the discharge tube. As illustrated in Figure 8.2.1, these high temperatures drive chemical reactions that rapidly bring the gaseous mixture into a radically altered thermochemical equilibrium. Immediately following the discharge, temperatures in the discharge tube approach 30,000

Table 8.1.1 Summary of estimates of the global nitrogen fixation rate by lightning

$P(\text{NO})$ ( $10^{16} \text{ NO J}^{-1}$ )	$E_f$ ( $10^9 \text{ J flash}^{-1}$ )	$P(\text{NO})$ ( $10^{25} \text{ NO}$ $\text{flash}^{-1}$ )	$f_f$ ( $10^2 \text{ flashes}$ $\text{s}^{-1}$ )	$G(\text{NO})$ ( $\text{Tg (N)}$ $\text{year}^{-1}$ )	Ref.
<b>FEA—Theoretical Estimates</b>					
—	—	1.1	5	4.0	Tuck (1976)
3–7	20	6–14	4	18–41	Chameides et al. (1977)
8–17	20	16–34	4	47–100	Chameides (1979a)
—	—	0.8	5	3	Dawson (1980)
—	—	1.2 <sup>a</sup>	1	0.9 <sup>a</sup>	Hill et al. (1980)
—	—	1.6	—	1.2	Bhetanabhotla et al. (1985)
<b>FEA—Laboratory-Based Estimates</b>					
6 ± 1	20	12 ± 2	4	35 ± 6	Chameides et al. (1977) Low energy sparks
8 ± 4	20	16 ± 4	4	47 ± 23	High energy sparks
5 ± 2	1	0.5	5	1.8 ± 0.7	Levine et al. (1981)
1.6	20	3.2	4	9.4	Peyrous and Lapeyre (1982)
9 ± 2	4 (1.6–10)	3.6 ± 0.8	1	2.6 ± 0.6	Borucki and Chameides (1984)
<b>FEA—Field Observation-Based Estimates</b>					
—	—	10	5	37	Noxon (1976, 1978)
—	—	10	.5	3.8	Kowalczyk and Bauer (1982) CG
—	—	1	2.5	1.9	IC
—	—	40	1	30	Drapcho et al. (1983)
—	—	(10–100)	—	—	—
—	—	300	—	220	Franzblau and Popp (1989)
<b>Thunderstorm Extrapolation-Based Estimate</b>					
—	—	—	—	7	Chameides et al. (1987)
<b>Nuclear Blast Extrapolation-Based Estimate</b>					
4	6.25	—	5	5.6	Tuck (1976)
<b>Review-Based Estimates</b>					
—	—	—	—	81	Liaw et al. (1990)
—	—	2.3 (1–7)	1 (0.7–1.5)	2 (1–8)	This work

Note: G is obtained as the product  $P(\text{NO}) \cdot f_f$  and may differ slightly from the fixation rates given in the original studies; FEA = flash extrapolation approach.

$6 \times 10^{25}$  molecule  $\text{flash}^{-1}$  and  $4.4 \text{ Tg (N) year}^{-1}$  is stated in the original Hill et al. (1980) paper; the values here include a correction factor of 5.2 for the miscalculation noted by Borucki and Chameides (1984).

K, causing the gas to be converted into a completely ionized plasma. As the gas undergoes hydrodynamic expansion and turbulent mixing, it cools and its equilibrium composition changes from a plasma to a mixture of neutral atoms and then to a mixture of molecular species. When the temperature returns to ambient, the equilibrium composition includes  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$ , much like what is found in the ambient atmosphere.

Thus if the gas around the discharge tube were always to remain in thermochemical equilibrium, the net effect of lightning on atmospheric chemistry would likely be negligible. Once the temperature of the gas returned to ambient, its composition would be similar to that of the background atmosphere and there would be no net production or destruction of chemical species. However, in the case of a few specific species (most notably NO) thermochemical equilibrium is not maintained throughout the cooling process and net production from lightning results. The mechanism by which this occurs is similar to that expounded by Zel'dovitch and Raizer (1966) for the production of NO in explosions, and invokes rapid cooling of the heated air, which in turn causes an enhanced NO concentration to be frozen into the gas. A simple physical analogy to this chemical production is that of dropping a bead through a column of rapidly cooling water

Table 8.1.2 Assessments of the global tropospheric NO<sub>x</sub> budget

Ref.	Ehhalt and Drummond (1982)	Logan (1983)	Penner et al. (1991)
	Sources		
Fossil fuel combustion	13.5 (8.2–18.5)	21 (14–28)	22.4
Biomass burning	11.2 (5.6–16.4)	12 (4–24)	5.8
Soil emissions	5.5 (1–10)	8 (4–16)	10.0
Lightning <sup>a</sup>	5 (2–8)	8 (2–20)	3.0
Other sources	4 (1.7–6.2)	6 (1.5–11.5)	1.0
Total sources	39 (19–59)	55 (26–100)	42.2
	Sinks		
Wet deposition	24 (15–33)	27 (12–42)	
Dry deposition	(0–7)	17 (12–22)	
Total sinks	24 (15–40)	44 (24–64)	

Note: All values have units of Tg (N) year<sup>-1</sup>.

<sup>a</sup> The lightning source is estimated by various previous works to range from 1–220 Tg (N) year<sup>-1</sup>, and by this work to range from 1–8 Tg (N) year<sup>-1</sup>.

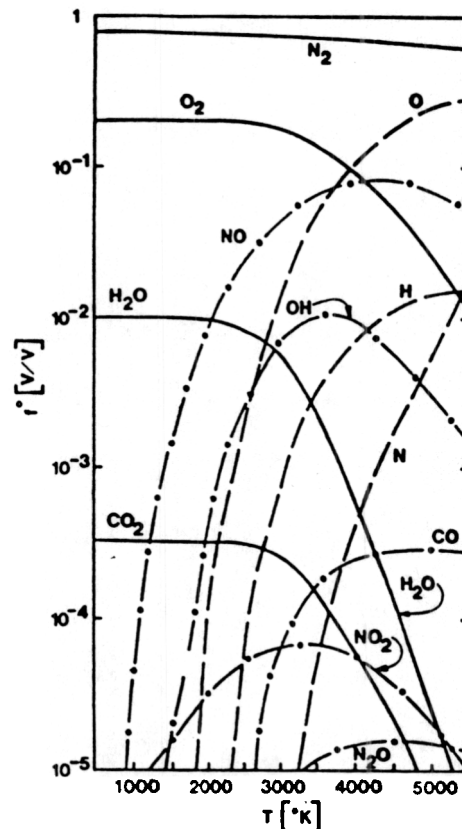
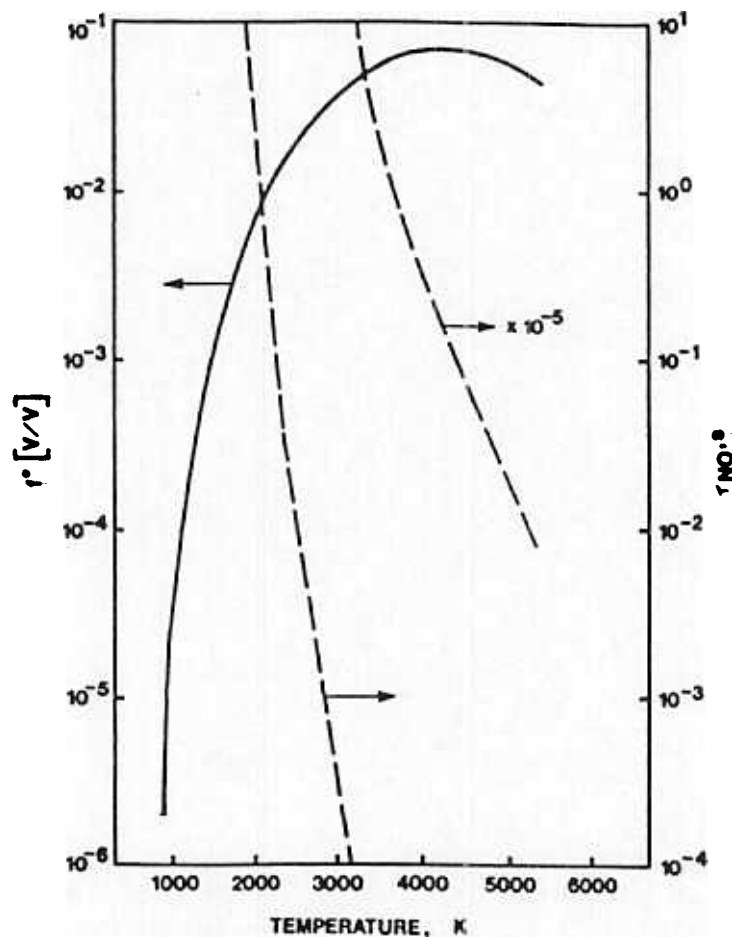


Figure 8.2.1 Temperature dependence of the equilibrium volume mixing ratio for several species in heated tropospheric air. (From Chameides, W.L. (1986). *The Earth's Electrical Environment*, National Academy Press, Washington, D.C., 70. With permission.)



**Figure 8.2.2** Temperature dependence of the equilibrium volume mixing ratio for NO,  $f_{\text{NO}}^{\circ}$  (solid line), and time constant to equilibrium,  $\tau_{\text{NO}}$  (dashed lines), in a heated tropospheric air mixture. (From Chameides, W.L. (1986). *The Earth's Electrical Environment*, National Academy Press, Washington, D.C., 70. With permission.)

in a gravitational field. Because of the bead's tendency to minimize its potential energy, it will tend to fall to the bottom of the water column. If, however, the water were to cool so rapidly that it froze before the bead reached the bottom, the bead would be frozen in the column at a position of higher potential energy and would be prevented from reaching its minimum potential energy at the bottom of the column.

In the case of NO, the high temperatures in and around the discharge channel give rise to a sequence of reactions that both produce and destroy NO. The thermochemical equilibrium concentration,  $f_{\text{NO}}^{\circ}$ , is the NO concentration at which the production and destruction reactions are in balance. As illustrated in Figure 8.2.2, this parameter is a strong function of temperature with a maximum value of about 10% at a temperature of about 4000 K. At lower temperatures the concentration is limited by the difficulty of dissociation of  $\text{N}_2$  and  $\text{O}_2$ , and at higher temperatures N and O atoms become increasingly stable. Hence, if NO were to remain in equilibrium, it would reach a maximum concentration of about 10% when the temperature in and around the discharge channel was about 4000 K and would then decrease to negligibly small concentrations as the heated air cooled to ambient temperatures. However, this does not occur because  $\tau_{\text{NO}}$ , the time required to establish thermochemical equilibrium, increases rapidly with decreasing temperature (see Figure 8.2.2). Whereas only a few microseconds are required for NO equilibrium at 4000 K, milliseconds are required at 2500 K, and about 1000 years are required at 1000 K. Thus, as

the air cools, a temperature is reached at which the rates of reactions become too slow to keep NO in equilibrium. This temperature, often referred to as the freeze-out temperature,  $T_F$ , can be crudely approximated by the relationship:

$$\tau_T(T_F) = \tau_{\text{NO}}(T_F) \quad (1)$$

where  $\tau_T$  is the characteristic cooling time of the heated air (see Zel'dovitch and Raizer, 1966). The net amount of NO produced is then computed from  $f_{\text{NO}}^o(T_F)$ , the equilibrium NO concentration at  $T_F$ , and the amount of gas heated to temperatures above  $T_F$ .

### 3. THE FLASH-EXTRAPOLATION APPROACH FOR ESTIMATING THE FIXATION RATE BY LIGHTNING

Inspection of Table 8.1.1, where we present a summary of previous estimates of the annual rate of nitrogen fixation by lightning, reveals that the vast majority of these estimates adopted the same basic approach, designated here as the flash-extrapolation approach (FEA). In this approach,  $G(\text{NO})$ , the global rate of NO production by lightning, is determined from:

$$G(\text{NO}) = P(\text{NO}) f_f \quad (2)$$

where  $P(\text{NO})$  is the molecular production of NO by a single, average flash of lightning and  $f_f$  is the global lightning flash frequency. Implicit in this approach is the assumption that the global rate of NO production by all lightning flashes can be characterized by the production of NO from a so-called average or representative flash multiplied by the number of flashes occurring globally. Suffice it to say that it is extremely difficult to prove the validity of this assumption and thus, given the widely varying properties of lightning flashes, estimates using this approach are subject to a significant degree of uncertainty. As illustrated in the discussion below, this uncertainty has resulted in a fairly wide range of estimates of the lightning fixation rate by different investigators.

#### 3.1. THE GLOBAL FLASH RATE

We begin our discussion of estimates that employ the FEA by reviewing the values typically adopted for  $f_f$ , the global flash rate. Global flash rate statistics obtained from a broad range of data types are remarkably consistent. Analysis of data from a variety of relatively simple ground-level observations to more sophisticated optical and electrical measurements from space-borne platforms generally indicate global flash rates of about  $100 \text{ s}^{-1}$  (e.g., Chalmers, 1967; Orville and Spencer, 1979; Turman, 1978; Turman, 1984; Turman and Edgar, 1982). Nevertheless, the values of  $f_f$  used in previous studies of NO production by lightning using the FEA vary from 100 to  $500 \text{ s}^{-1}$  (see Table 8.1.1). Much of the variation in these values can be attributed to confusion over the roles of two dominant lightning types, cloud-to-ground (CG) lightning and intracloud (IC) lightning. Some studies have assumed that the value of  $100 \text{ s}^{-1}$  includes both CG and IC. Others have assumed that the value of  $100 \text{ s}^{-1}$  from ground-based observations only accounted for CG, requiring the addition of IC, or that the  $100 \text{ s}^{-1}$  value from satellite data only accounted for IC, requiring the addition of CG. Those studies that adhered to the latter two assumptions generally added in IC or CG lightning using a ratio of between 3 and 5 IC for each CG (Prentice and Mackarras, 1977), and thus tended to use an  $f_f$  value significantly larger than  $100 \text{ s}^{-1}$ . The relatively large value for  $f_f$  of  $300 \text{ s}^{-1}$  used by Kowalczyk and Bauer (1982) was derived from preliminary radio data obtained from the Ionospheric Sounding Satellite. It was later found that the  $300 \text{ s}^{-1}$  value is in error, and that the data from this satellite actually indicate a global flash frequency of  $63 \text{ s}^{-1}$  (Kotaki et al., 1981), a value reasonably consistent with more commonly obtained frequencies noted above.

For our own calculations presented later in this chapter, a value of 100 (70 to 150)  $s^{-1}$  will be adopted. The high end of the uncertainty range allows for the possibility that the satellite data are missing some fraction of the CG flashes and the IC flashes that occur in the mid- to lower cloud. The low end accounts for the possibility that the lower estimates from the satellite study of Kotaki et al. (1981) are more representative of the actual total global flash frequency.

### 3.2. DETERMINATION OF NO YIELD PER FLASH: THEORETICAL AND LABORATORY

The other parameter needed to estimate  $G(\text{NO})$  from Equation 2 is  $P(\text{NO})$ , the NO yield per lightning flash. Previous estimates of  $P(\text{NO})$  can be roughly separated into three classifications: theoretical, laboratory, and field observations. The theoretical and laboratory studies have generally computed  $P(\text{NO})$  from:

$$P(\text{NO}) = p(\text{NO}) E_f \quad (3)$$

where  $p(\text{NO})$  is the yield of NO per unit energy of discharge, and  $E_f$  is the energy of a lightning flash. In the subsections below, we review the values estimated for each of these parameters.

#### 3.2.1. NO Yield per Unit Energy Discharge

Theoretical estimates of  $p(\text{NO})$ , the NO yield per unit energy of discharge, have generally been determined by invoking the Zel'dovitch freeze-out mechanism described in Section 2. The NO yield is thus approximated by an equation having the following general form:

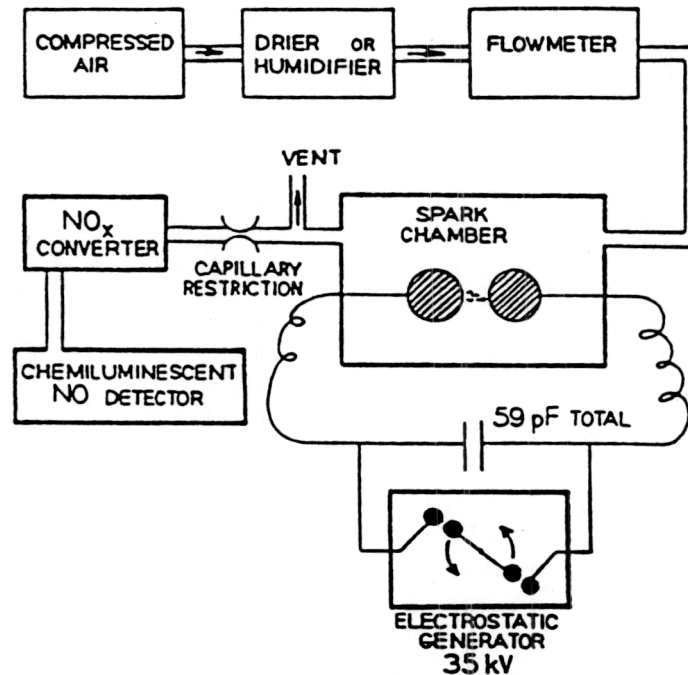
$$p(\text{NO}) = M_E(T_F) f_{\text{NO}}^{\circ}(T_F) \quad (4)$$

where  $M_E(T_F)$  is the number of molecules of air heated to temperatures above the freeze-out temperature per unit of energy of discharge, and  $T_F$  and  $f_{\text{NO}}^{\circ}$  are as previously defined. Estimates of  $M_E$  and  $T_F$  have generally been obtained using two different models for the dissipation of the discharge energy. One assumes that the energy dissipation process is dominated by the hydrodynamic rapid expansion of the discharge tube by a shock wave (see, for instance, Chameides et al., 1977 and Chameides, 1979a, 1979b). The other assumes that the energy dissipation occurs by a slower ohmic heating process using a turbulent hot channel model (see Hill et al., 1980). Values obtained for both approaches are listed in Table 8.1.1.

An interesting contrast to the theoretical calculations described above is provided by a few more empirical estimates of  $p(\text{NO})$  derived using data from laboratory experiments. These experiments employ an apparatus similar to that shown in Figure 8.3.1, in which air is allowed to pass through a simple, electrostatic spark, and the NO concentration is measured using standard chemiluminescent techniques (see Chameides et al., 1977; Levine et al., 1981; and Peyroux and Lapeyre, 1982). The value of  $p(\text{NO})$  is then related to the energy of the spark and to the change in the concentration of NO in the air before and after exposure to the spark. While these experiments have the obvious advantage of being straightforward and thus easy to interpret, they do have the potentially serious drawback of requiring an extrapolation of size and energy density from a laboratory spark to a lightning discharge. If the NO production mechanism varies nonlinearly with discharge characteristics (e.g., radius, energy), these laboratory results would not represent an appropriate surrogate for NO production by lightning.

A somewhat different approach was adopted by Borucki and Chameides (1984). These investigators used the results of the high energy discharge experiments of Picone et al. (1981) to obtain values for the cooling time constant of the hot channel, which allowed for the determination of  $T_F$  and  $f_{\text{NO}}^{\circ}(T_F)$ , and for the ratio of  $M_E(T_F)$  to  $E_f$ . These values were then used to calculate  $p(\text{NO})$  using Equation 4. Interestingly, this approach yielded a value for  $p(\text{NO})$  that is quite similar to that found in the other laboratory studies (see Table 8.3.1).





**Figure 8.3.1** Schematic diagram demonstrating the type of apparatus used in laboratory studies to determine NO<sub>x</sub> molecular production due to a spark discharge. (From Chameides, W.L. et al. (1977). *J. Atmos. Sci.*, 34, 143. With permission.)

Table 8.3.1 summarizes the  $p(\text{NO})$  values obtained by previous investigators using each of the methods described above. Note that in spite of the widely varying approaches adopted, the NO yields obtained are all generally consistent, ranging from a minimum of about  $2 \times 10^{16}$  to a maximum of about  $13 \times 10^{16}$  molecules of NO per joule of discharge energy.

### 3.2.2. Energy per Flash

The energy per flash,  $E_f$ , is essentially the sum of the energy dissipated in each of the individual strokes that make up the flash. Values used in previous studies have tended to be in the range  $(1 \text{ to } 20) \times 10^8 \text{ J flash}^{-1}$  (see Table 8.1.1). No doubt this large range of values reflects, at least in part, the large variability in the actual energy of lightning flashes in the earth's atmosphere (see Uman, 1969). Perhaps the most reliable value available for lightning flash energy dissipation is that from Borucki and Chameides (1984), derived by considering six studies of electrical measurements and six studies of optical measurements. Adjusting the values to account for 1.75 equivalent return strokes per flash, they obtain an average of  $(4 \pm 2) \times 10^8 \text{ J flash}^{-1}$  for the optical measurements, and  $(4 \pm 3) \times 10^8 \text{ J flash}^{-1}$  for the electrical measurements. An energy of  $4 \times 10^8 \text{ J flash}^{-1}$  will thus be used later in this chapter in converting from NO production per unit energy to NO production per flash.

### 3.3. DETERMINATION OF NO YIELD PER FLASH: FIELD OBSERVATIONS

Direct field observations represent a third method of estimating the lightning fixation rate of nitrogen for use in Equation 2; in these studies,  $P(\text{NO})$  is typically directly estimated, rather than its component parts  $p(\text{NO})$  and  $E_f$  (Equation 3). As indicated in Table 8.1.1, four major estimates using field observations along with the FEA have been made. The obvious advantage of this approach is that it represents a direct measurement and does not require knowledge of the flash energy, a parameter that appears to be subject to a high degree of variability and uncertainty. On

Table 8.3.1 Review of previous estimates of the NO molecular production rates:  $p(\text{NO})$  and  $P(\text{NO})$ 

	$p(\text{NO})$ ( $10^{16}$ NO J <sup>-1</sup> )	$P(\text{NO})$ ( $10^{25}$ NO flash <sup>-1</sup> )	$P(\text{NO})$ —Normalized <sup>a</sup> ( $10^{25}$ NO flash <sup>-1</sup> ) Theoretical	Ref.
	4 (bomb)	1.1 (flash)	1.6, 1.1	Tuck (1976)
	12	—	4–5.2	Griffing (1977)
	5	10	1.2–2.8	Chameides et al. (1977)
	13	26	3.2–6.8	Chameides (1979a)
	—	1.2 <sup>b</sup>	1.2	Hill et al. (1980)
	—	0.8	0.8	Dawson (1980)
	—	1.6	1.6	Bhetanabhotla et al. (1985)
Average	$8.5 \pm 4.7$	$6.7 \pm 10$	$2.1 \pm 1.4$	
			<b>Laboratory</b>	
	$6 \pm 1, 8 \pm 4$	12, 16	2.4, 3.2	Chameides et al. (1977) (low and high energy sparks, resp.)
	$5 \pm 2$	0.5	2	Levine et al. (1981)
	1.6	3.2	0.6	Peyrous and Lapeyre (1982)
	$9 \pm 2$	3.6	3.6	Borucki and Chameides (1984)
Average	$5.9 \pm 2.8$	$7.0 \pm 6.6$	$2.4 \pm 1.2$	
			<b>Field Observations</b>	
		10	—	Noxon (1976, 1978)
		2.5	—	Kowalczyk and Bauer (1982)
		10–100	—	Drapcho et al. (1983)
		300	—	Franzblau and Popp (1989)
Average		$92 \pm 122$	—	

Note: Average values given with  $\pm 1$  SD.

<sup>a</sup> Normalized  $P(\text{NO})$  calculated assuming a uniform  $E_f = 4 \times 10^8$  J flash<sup>-1</sup> (see text).

<sup>b</sup> Inferred following method of Borucki and Chameides (1984).

the other hand, the approach is not without its own set of problems. A major source of uncertainty for all field measurements of this kind relates to the representativeness of the observations; it is extremely difficult to determine whether the particular event observed is representative of events on a global scale. Moreover, as will be seen below, the interpretation of the observations generally requires the adoption of several fairly arbitrary assumptions. Given the varying nature of the field observations, a brief account of each is presented below.

The first direct observations of enhanced  $\text{NO}_x$  concentrations in the vicinity of lightning flashes were made by Noxon (1976, 1978), who used a spectrometer to measure  $\text{NO}_2$  concentrations below the cloud base of active thunderstorms. The observed increase in  $\text{NO}_2$  as the storm passed over the area of observation, along with estimates of the flash rate within the vicinity of the storm from visual observations and assumptions with regard to the volume of the storm and the relative abundances of  $\text{NO}$  and  $\text{NO}_2$ , were then used to estimate  $P(\text{NO})$ . Kowalczyk and Bauer (1982) attempted to improve upon Noxon's estimates for  $P(\text{NO})$  by correcting for the fact that Noxon's measurements primarily represented production from CG, while most flashes are actually IC. Because of their assumption that IC are some ten times less energetic than CG, Kowalczyk and

Bauer's estimate for  $P(\text{NO})$  was significantly smaller than that originally obtained by Noxon (see Table 8.1.1).

Drapcho et al. (1983) used a chemiluminescent analyzer to measure  $\text{NO}_x$  concentrations following a CG lightning flash that occurred about 700 m from the analyzer. The production of NO from this one flash was then estimated assuming that, on reaching the measurement site shortly after the flash occurrence, the NO from the flash was uniformly dispersed in a cylinder of 700 m in radius and 3 km in height. Franzblau and Popp (1989) adopted a combination of the Noxon and the Drapcho et al. approaches: they used an  $\text{NO}_2$  spectrometer, along with commercial local lightning frequency data, to compute an  $\text{NO}_x$  molecular production rate per flash from two distant storms, as well as from measurements of enhanced  $\text{NO}_2$  in the vicinity of a single CG flash. These authors' final value for  $P(\text{NO})$  was taken to be the average of the three values thus obtained.

#### 3.4. SUMMARY OF VALUES DERIVED FOR NO YIELD PER FLASH

A summary of all values obtained for  $p(\text{NO})$  and  $P(\text{NO})$ , the NO yields per unit energy or per flash, respectively, is presented in Table 8.3.1. A remarkably good agreement is seen between the theoretical and laboratory values, while a significant inconsistency appears to exist between these values and those obtained from field observations. The average theoretical and laboratory values for  $p(\text{NO})$  are seen to be  $(8.5 \pm 4.7) \times 10^{16}$  and  $(5.9 \pm 2.8) \times 10^{16}$  molecules  $\text{J}^{-1}$ . If a uniform flash energy of  $4 \times 10^8$  J  $\text{flash}^{-1}$  (see Section 3.2.3) is applied to these  $p(\text{NO})$  values, an average  $P(\text{NO})$  of  $(2.1 \pm 1.4) \times 10^{25}$  and  $(2.4 \pm 1.2) \times 10^{25}$  molecules  $\text{flash}^{-1}$  is derived from the theoretical and laboratory results, respectively. By comparison, the average  $P(\text{NO})$  from the field studies is  $(92 \pm 122) \times 10^{25}$  molecules  $\text{flash}^{-1}$ .

The high average value for  $P(\text{NO})$  from the field observations is primarily caused by the yields obtained by Franzblau and Popp (1989) and Drapcho et al. (1983). Note that the NO yield of Kowalczyk and Bauer (1982), derived from Noxon's data in conjunction with an assessment of the IC and CG differences, is in excellent agreement with the theoretical and laboratory averages. There are several reasons for being suspicious of the NO yields of the two anomalous studies. In the case of the Drapcho et al. (1983) estimate it should be kept in mind that the  $P(\text{NO})$  value was derived from a single flash, which may or may not have been very representative. Moreover, measurements were made in an urban area where background  $\text{NO}_x$  concentrations were relatively large (from 3 to 24 ppbv) and quite variable. As a result, quantitative conclusions about lightning production based on these authors' observations of elevated  $\text{NO}_x$  concentrations of about 15 ppbv should be taken with caution (Franzblau and Popp, 1989). In the case of the Franzblau and Popp (1989) estimate, there appears to be some question as to the accuracy of the local flash frequency data used. The authors themselves demonstrate that the data are likely low by about a factor of two; such an error in the flash frequency would cause an overestimate in their global production estimate. Further, lightning in New Mexico, where the measurements were made, has been found to have on an average of 6.5 return strokes (Kowalczyk and Bauer, 1982), compared to a more typical global average of 2 to 3 return strokes (Uman, 1969). Thus, the lightning discharges observed by these authors may have been more energetic than those that would be expected in most other regions of the globe. These uncertainties, along with the uncertainties implicit in deriving a  $P(\text{NO})$  value from an observed enhancement in ambient  $\text{NO}_x$  or  $\text{NO}_2$  concentrations, could easily account for over an order of magnitude uncertainty in these estimates, and perhaps explain the discrepancy between them and the other values listed in Table 8.3.1.

#### 3.5. RECALCULATION OF THE GLOBAL NO PRODUCTION RATE USING THE FLASH-EXTRAPOLATION METHOD

Discussion in the previous sections indicates that a large portion of the disparities found among the previous estimates for  $G(\text{NO})$  using the FEA can be attributed to: (1) differences in the value used for the flash rate,  $f_f$ ; (2) differences in the value used for the flash energy,  $E_f$ ; and (3) two apparently anomalous estimates of the NO yield from field observations. From the values adopted

in the preceding sections, we can now recalculate the value for  $G(\text{NO})$  using the FEA. Taking  $f_f$  to be 100 (70 to 150)  $\text{s}^{-1}$ , as per Section 3.1, and taking  $P(\text{NO})$  to be  $2.3 (1 \text{ to } 7) \times 10^{25}$  molecules  $\text{flash}^{-1}$ , based on Table 3, the resulting value for  $G(\text{NO})$  is 2 (1 to 8)  $\text{Tg (N) year}^{-1}$ . It is interesting to note that this value is more than an order of magnitude smaller than the global production rate of 81  $\text{Tg (N) year}^{-1}$  recently obtained by Liaw et al. (1990) through a similar review and normalization of previous estimates of the global nitrogen fixation rate. The difference between our value and that of Liaw et al. can be attributed primarily to the high value for  $E_f$  adopted by Liaw et al., along with their inclusion of the anomalously high values obtained by Drapcho et al. (1983) and Franzblau and Popp (1989).

#### 4. OTHER ESTIMATES OF GLOBAL FIXATION RATE BY LIGHTNING

While the discussion in the previous section indicates a fairly high degree of consistency between different estimates of the global rate of nitrogen fixation by lightning using the FEA, it is important to bear in mind that this method is not without potential flaws. As noted earlier, the method requires a fairly large extrapolation from the amount of NO produced from a single representative flash to the total production from all flashes. Such an extrapolation assumes, at the very least, a linear relationship between flash energy and channel volume and NO production, which may not be strictly correct. To address this problem, estimates of the fixation rate by lightning using different and independent approaches are needed. As indicated in Table 8.1.1 and described below, two such estimates may be found in the literature.

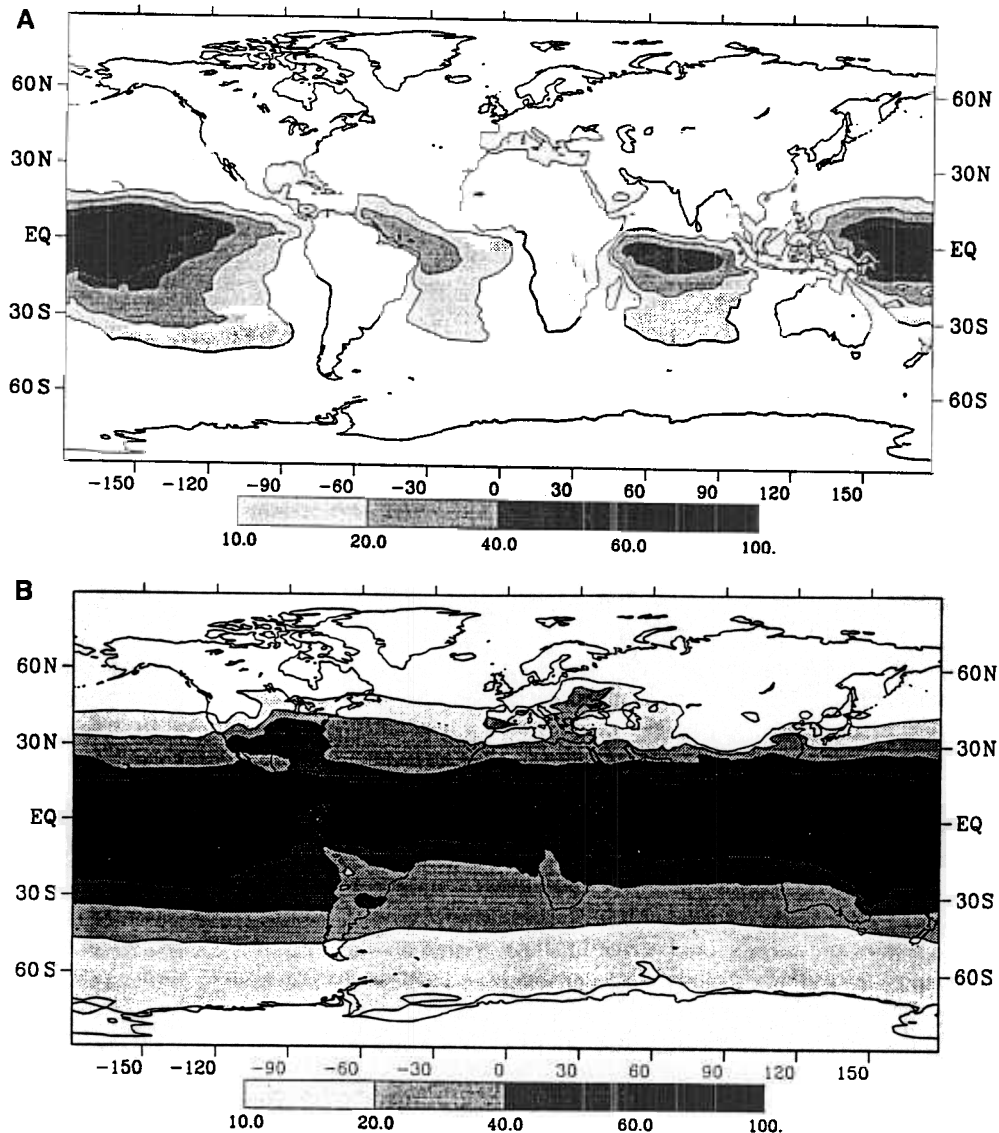
The first such estimate (by Chameides et al., 1987) was based on an extrapolation of the amount of NO produced by a single thunderstorm rather than of the amount produced by a single lightning flash. The amount of NO produced by a thunderstorm was estimated from airborne measurements of elevated NO concentrations in the anvil regions of two active cumulonimbus clouds (Davis et al., 1987), along with evaluations of the  $\text{NO}_x$  concentration from the photostationary state equations and the typical advective flow rate out of the tops of thunderclouds. This quantity was then multiplied by the number of active thunderclouds over the earth at any time to obtain a  $G(\text{NO})$  of 7  $\text{Tg (N) year}^{-1}$ , a value within the range of the bounds obtained in Section 3.5 of this study using the FEA. An interesting feature of the Chameides et al. (1987) estimate is that it does not assume *a priori* that lightning flashes are the only electrical source of NO in thunderclouds, and thus includes contributions from other discharges, such as corona that commonly occur in electrified clouds.

Another relatively independent estimate for  $G(\text{NO})$  is that obtained by Tuck (1976), who estimated the global nitrogen fixation rate by lightning via analogy to a similar value obtained from nuclear blasts determined theoretically by Taylor (1950). By comparing the heated channel of a lightning stroke to the blast area of a nuclear bomb and by arguing that because lightning involves extranuclear processes, it should be twice as efficient at producing  $\text{NO}_x$  as a nuclear blast, Tuck arrived at an estimate for  $G(\text{NO})$  of 5.6  $\text{Tg (N) year}^{-1}$ , a number also in good agreement with that obtained in Section 3.5.

In spite of the fact that these two additional estimates, like those obtained from the FEA, are subject to significant uncertainties, they are generally consistent with the FEA estimates. This overall consistency across essentially independent methods lends credence to all three methods and thus suggests that the global fixation rate by lightning is indeed of the order of 1 to 10  $\text{Tg (N) year}^{-1}$ . In the next section we discuss the probable impact of this source on the global distribution of reactive nitrogen in the earth's troposphere.

#### 5. THE ROLE OF LIGHTNING IN THE BUDGET OF TROPOSPHERIC REACTIVE NITROGEN

The total rate of production of reactive nitrogen in the troposphere is estimated to be about 20 to 100  $\text{Tg (N) year}^{-1}$  (see Table 8.1.2). On this basis it might be concluded that lightning, estimated



**Figure 8.5.1** (A) Percent of the annually averaged NO<sub>x</sub> concentration as a function of latitude and longitude calculated to arise from the production of NO by lightning at the surface (990 mbar) and (B) in the midtroposphere (500 mbar). Results based on the three-dimensional chemical transport model of Kasibhatla et al. (1993) with a 2 Tg (N) year<sup>-1</sup> source strength assumed for lightning.

here to produce some 1 to 8 Tg (N) year<sup>-1</sup>, must play a relatively minor role in controlling the abundance and concentration of reactive nitrogen in the troposphere. Such a conclusion, however, would not be strictly correct. Reactive nitrogen is relatively short-lived in the atmosphere, having a residence time against removal by rain and dry deposition of the order of days to weeks (Logan, 1983). As a result, its concentration is highly variable, being highest in urban-industrial areas where anthropogenic emissions dominate and lowest in remote locations and in the upper troposphere where the impact of surface sources such as combustion is minimal. In these regions the production of reactive nitrogen by lightning can have its greatest impact. This impact is illustrated in Figure 8.5.1, where the results of a simulation of the global atmospheric nitrogen cycle using the three-dimensional chemical transport model (CTM) of Kasibhatla et al. (1993)

are illustrated. Inspection of the figure reveals negligibly small contributions from lightning in the lower atmosphere of the continents, where production from fossil fuel burning, biomass burning, and soil emissions dominate. However, in the remote tropical marine atmosphere and the mid- to upper troposphere, lightning makes a significant and in some cases a dominant contribution.

## 6. CONCLUSIONS

The global magnitude of  $\text{NO}_x$  production by lightning is an important subject of debate among the atmospheric chemistry community. In contrast to recent indications of a dominant role for lightning in global tropospheric  $\text{NO}_x$  chemistry (Franzblau and Popp, 1989; Liaw et al., 1990), a range of 1 to 8 Tg (N) year<sup>-1</sup> — accounting for less than 20% of the global tropospheric  $\text{NO}_x$  budget — is derived using the FEA in this review. This value is in good agreement with two independent estimates of  $\text{NO}_x$  production, as well as the magnitude of the known sinks of  $\text{NO}_x$ .

Much research remains to be done before a consensus can be reached regarding the role of lightning in the global  $\text{NO}_x$  budget. Further, the role of lightning needs to be examined on a more region-specific basis, rather than simply on a coarse global budget basis, with particular attention being paid to the remote ocean and the upper troposphere. In closing, a few remarks on what appear to be the most pertinent research needs are appropriate. More field observations in regions other than the western U.S., particularly in remote tropical regions, are needed. Fieldwork-based calculations such as those of Chameides et al. (1987), which represent estimates based on thunderstorm activity rather than single lightning stroke production, are strongly encouraged. Research to obtain greater confidence in values for lightning energy dissipation and global flash frequency is also needed. A better assessment of the sinks for  $\text{NO}_x$  may allow an ostensible upper bound to production estimates to be established more rigorously. Finally, continued theoretical work may help to determine the differences in the mechanisms of lightning production by cloud-to-ground and intracloud lightning, and thus may shed light on the vertical distribution and overall global significance of lightning in tropospheric  $\text{NO}_x$  chemistry.

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## REFERENCES

- Bhetanabhoda, M. N., B. A. Crowell, A. Coucouvinos, R. D. Hill, and R. G Rinker. (1985). Simulation of the trace species production by lightning and corona discharge in moist air, *Atmos. Environ.*, 19, 1391.
- Borucki, W. J. and W. L. Chameides. (1984). Lightning: estimates of the rates of energy dissipation and nitrogen fixation. *Rev. Geophys. Space Phys.*, 22, 363.
- Chalmers, J. A. (1967). *Atmospheric Electricity*, Academic Press, New York, 515 pp.
- Chameides, W. L. (1979a). Effect of variable energy input on nitrogen fixation in instantaneous linear discharges, *Nature (London)*, 277, 123.
- Chameides, W. L. (1979b). The implications of CO production in electrical discharges, *Geophys. Res. Lett.*, 6, 287, April.
- Chameides, W. L. (1986). The role of lightning in the chemistry of the atmosphere, in *The Earth's Electrical Environment*, National Academy Press, Washington, D.C., 70.

- Chameides, W. L. and D. D. Davis. (1982). Chemistry in the troposphere, *Chem. Eng. News*, 60, 38.
- Chameides, W. L. and J. C. G. Walker. (1973). A photochemical theory of tropospheric ozone, *J. Geophys. Res.*, 78, 8751.
- Chameides, W. L., D. H. Stedman, R. R. Dickerson, D. W. Rusch, and R. J. Cicerone. (1977).  $\text{NO}_x$  production in lightning, *J. Atmos. Sci.*, 34, 143.
- Chameides, W. L., D. D. Davis, J. Bradshaw, M. Rodgers, S. Sandholm, and D. B. Bai. (1987). An estimate of the  $\text{NO}_x$  production rate in electrified clouds based on NO observations from the GTE/CITE 1 Fall 1983 field operation, *J. Geophys. Res.*, 92, 2153.
- Crutzen, P. J. (1973). A discussion of the chemistry of some minor constituents in the stratosphere and troposphere, *Pure Appl. Geophys.*, 106–108, 1385.
- Davis, D. D., J. D. Bradshaw, M. O. Rodgers, S. T. Sandholm, and S. KeSheng. (1987). Free tropospheric and boundary layer measurements of NO over the Central and Eastern North Pacific Ocean, *J. Geophys. Res.*, 92, 2049.
- Dawson, G. A. (1980). Nitrogen fixation by lightning, *J. Atmos. Sci.*, 37, 174.
- Delwiche, C. G. (1970). The Nitrogen Cycle, in *The Biosphere*, A Scientific American Book, W.H. Freeman, 69.
- Drapcho, D. L., D. Sisterson, and R. Kumar. (1983). Nitrogen fixation by lightning in a thunderstorm, *Atmos. Environ.*, 17, 729.
- Ehhalt, D. H. and J. W. Drummond. (1982). The tropospheric cycle of  $\text{NO}_x$ , in *Chemistry of the Unpolluted and Polluted Troposphere*. D. Reidel Publishing, 219.
- Ehhalt, D. H., F. Rohrer, and A. Wahner. (1992). Sources and distribution of  $\text{NO}_x$  in the upper troposphere at northern mid-latitudes, *J. Geophys. Res.*, 97, 3725.
- Franzblau, E. and C. J. Popp. (1989). Nitrogen oxides produced from lightning, *J. Geophys. Res.*, 94, 11089.
- Griffing, G. W. (1977). Ozone and oxides of nitrogen produced during thunderstorms, *J. Geophys. Res.*, 82, 943.
- Hill, R. D., R. G. Rinker, and H. Dale Wilson. (1980). Atmospheric nitrogen fixation by lightning, *J. Atmos. Sci.*, 37, 179.
- Hutchinson, G. E. (1954). The biogeochemistry of the terrestrial atmosphere, in *The Earth as a Planet*, G. P. Kuiper, Ed., University of Chicago Press, Chicago, 371.
- Kasibhatla, P. S., H. Levy, II, and W. J. Moxim. (1993). Global  $\text{NO}_x$ ,  $\text{HNO}_3$ , PAN, and  $\text{NO}_y$  distributions from fossil fuel combustion emissions: a model study, *J. Geophys. Res.*, 98, 7165.
- Kotaki, M., I. Kuriki, C. Katoh, and H. Sugiuchi. (1981). Global distribution of thunderstorm activity observed with ISS-b, *J. Rad. Res. Lab.*, 28, 49.
- Kowalczyk, M. and E. Bauer. (1982). Lightning as a source of  $\text{NO}_x$  in the troposphere, Technical Report FAA-EE-82-4, Inst. for Defense Anal., Alexandria, VA, 76 pp.
- Levine, J. S., R. S. Rogowski, G. L. Gregory, W. E. Howell, and J. Fishman. (1981). Simultaneous measurements of  $\text{NO}_x$ , NO, and  $\text{O}_3$  production in a laboratory discharge: atmospheric implications, *Geophys. Res. Lett.*, 8, 357.
- Levy, H. (1971). Normal Atmosphere: large radical and formaldehyde concentrations predicted, *Science*, 173, 141.
- Liaw, Y. P., D. L. Sisterson, and N. L. Miller. (1990). Comparison of field, laboratory, and theoretical estimates of global nitrogen fixation by lightning, *J. Geophys. Res.*, 95, 22489.
- Liebig, J. von. (1827). Une note sur la nitrification, *Ann. Chem. Phys.*, 35, 329.
- Logan, J. A. (1983). Nitrogen oxides in the troposphere: global and regional budgets, *J. Geophys. Res.*, 88, 10,785.
- Noxon, J. F. (1976). Atmospheric nitrogen fixation by lightning, *Geophys. Res. Lett.*, 3, 463.
- Noxon, J. F. (1978). Tropospheric  $\text{NO}_2$ , *J. Geophys. Res.*, 83, 3051.
- Orville, R. E. and D. W. Spencer. (1979). Global lightning flash frequency, *Mon. Weather Rev.*, 107, 934.
- Penner, J. E., C. S. Atherton, J. Dignon, S. J. Ghan, J. J. Walton, and S. Hameed. (1991). Tropospheric nitrogen: a three-dimensional study of sources, distributions, and deposition, *J. Geophys. Res.*, 96, 959.
- Peyroux, R. and R.-M. Lapeyre. (1982). Gaseous products created by electrical discharges in the atmosphere and condensation nuclei resulting from gaseous phase reactions, *Atmos. Environ.*, 16, 959.
- Picone, J. M., J. P. Boris, J. R. Grieg, M. Rayleigh, and R. F. Fernsler. (1981). Convective cooling of lightning channels, *J. Atmos. Sci.*, 38, 2056.
- Prentice, S. A. and D. Mackerras. (1977). The ratio of cloud to cloud-ground lightning flashes in thunderstorms, *J. Appl. Meteorol.*, 16, 545.
- Salanave, L. E. (1961). The optical spectrum of lightning, *Science*, 134, 1395.
- Schlesinger, W. H. (1991). *Biogeochemistry: An Analysis of Global Change*, Academic Press, San Diego.
- Taylor, G. I. (1950). The formation of a blast wave by a very intense explosion, *Proc. R. Soc.*, A201, 159.
- Tuck, A. F. (1976). Production of nitrogen oxides by lightning discharges, *Q. J. R. Meteorol. Soc.*, 102, 749.
- Turman, B. N. (1978). Analysis of lightning data from the DMSP satellite, *J. Geophys. Res.*, 83, 5019.
- Turman, B. N. (1984). Comparison of lightning flash rates from the PBE sensor streak counting from the DMSP satellite, paper presented at VII International Conference on Atmospheric Electricity, American Meteorological Society, Albany, NY, June 3–8.
- Turman, B. N. and B. C. Edgar. (1982). Global lightning distributions at dawn and dusk, *J. Geophys. Res.*, 87, 1191.
- Uman, M. A. (1969). *Lightning*, McGraw-Hill, New York, 264.
- Wofsy, S. C., J. C. McConnell, and M. B. McElroy. (1972). Atmospheric  $\text{CH}_4$ , CO, and  $\text{CO}_2$ , *J. Geophys. Res.*, 77, 4477.
- Zel'dovitch, Y. B. and Y. P. Raizer. (1966). *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena*, Academic Press, New York, 445 pp.