CHAPTER 10

Exchanges between the Forest and the Atmosphere

J. W. MUNGER, C. BARFORD, and S. WOFSY

In this chapter we move beyond the forest and terrestrial ecosystems to consider the interactions between the landscape and the atmosphere. The atmosphere provides major constituents of the physical environment for forest vegetation, including climatic variables (wind, temperature, humidity), nutrients, and toxins. In turn, the atmosphere is continuously altered and modified in many ways by the vegetation and physical features of the landscape. For example, the dark foliage of a forest absorbs considerably more solar radiation than the light-colored surface of a dry grain field or snowy hillside, thereby providing more energy to heat the atmosphere, evaporate water, or support thermal convection. Evaporation of water from the surface of vegetation and through transpiration cools and humidifies the atmosphere, which leads to an observable increase in cloudiness. The dense and rough canopy of a forest slows the wind and increases surface turbulence, enhancing the removal of pollutants and aerosols, whereas soils and vegetation are themselves significant sources of many of the trace gases occurring in the atmosphere.

Human activity has fundamentally altered essential characteristics of both the land surface and the atmosphere in New England over a period of several centuries. The change from forested to intensely agricultural (eighteenth century) to reforested (nineteenth century) to urbanized (twentieth century) implies significant shifts in the structure of the land surface presented to the atmosphere and therefore important changes in the efficiency of chemical deposition and energy transfer between the two. Changes in the biomass, species composition, and soil chemistry through time in regrowing forests have resulted in major storage of carbon in forest ecosystems over the past century and have significantly altered balances of important trace gases. At the same time, unprecedented emissions of CO$_2$, nitrogen oxides, and a wide variety of pollutants from industrial sources across the eastern United States and beyond affect regional atmospheric chemistry and the biological function of forests. Understanding the interaction between the forest and the
atmosphere and the roles played by human activities on local to broad scales to alter these processes provides critical insights into both the functions of forest ecosystems and a host of global environmental issues linked through the dynamics of the atmosphere.

Global CO₂ and the Carbon Balance of Forests in Central New England

Atmospheric CO₂ is a globally important gas closely linked to forest dynamics. Carbon dioxide is a major greenhouse gas and a primary product of the combustion of fossil fuels. In the 1990s, about 25 percent of the CO₂ from fossil fuel combustion was absorbed by the ocean and roughly 40 percent stayed in the atmosphere. The remainder was taken up by terrestrial vegetation. Analyses of ¹³C/¹²C isotopic ratios in CO₂ and concentrations of oxygen in the atmosphere, along with patterns of CO₂ distribution over the globe and data from forest inventories, point to significant storage of carbon in forest vegetation and soils. According to the analysis of air retrieved from polar ice and snow cores, the process of major storage of carbon by the global terrestrial biosphere has been important only over the past few decades. Before that, the biosphere was neutral, or possibly a source of CO₂ to the atmosphere.

Many attempts have been made to explain why the biosphere is currently a net carbon sink, including

- Fertilization by increasing concentrations of CO₂ in the atmosphere and nitrogen deposition to forests, both resulting from human activities
- Longer growing seasons and northward forest expansion due to climate warming
- Reforestation of former agricultural lands in the eastern United States, Canada, and Europe; most of these regrowing forests are still increasing in wood volume

Deciding among these three major causes for increased carbon storage in temperate forests has important geopolitical implications. Fertilization by CO₂ might be expected to continue indefinitely, but nitrogen deposition can eventually lead to negative as well as positive effects on tree growth (see Chapter 12). Whether global warming results in increased uptake or release of CO₂ depends on whether photosynthesis or respiration is most sensitive to changes in temperature and the length of the growing season, as well as how each response is affected by changes in the availability of water. On the other hand, reforestation may represent only a temporary potential for storage, since forests reach a balance between growth and decay as they mature; but management options can strongly influence how, or even if, this balance is attained. Harvesting of timber could truncate increases in carbon storage in forests or could enhance forest growth and storage. The fate of products derived from forest harvesting (for example, rapidly decomposed paper versus long-term
usage in construction) and the methods and rotation pattern of harvesting are important components of this calculation of net balance.

**Motivation for Long-Term Atmospheric Measurements at the Harvard Forest**

Understanding forest carbon dynamics requires a combination of models and observations of net forest exchange at timescales appropriate to the instantaneous response of plants to temperature and light as well as the longer-term consequences of climatic variations and successional change. Similarly, atmospheric chemistry responds to short-term factors as well as long-term changes driven by emissions control regulations, urban development, technological changes, and climate variability. At the Harvard Forest we set out to answer the following questions with a comprehensive suite of observations that cover all of these timescales:

- **Carbon balance**: How much carbon is being sequestered in the aggregating, actively growing forests of the northeastern United States? What factors regulate the magnitude of this uptake? How is this uptake (amount and timing) related to the effects of land-use history; forest composition; climate variations on seasonal, annual, and decadal timescales; nutrient deposition; and pollution?
- **Atmospheric chemistry**: How is the chemistry of the atmosphere affected by emissions from, and deposition to, the forest? What influence does the forest have on the long-range transport of pollutants from the industrial Northeast and Midwest? How does this transport and deposition of pollutants affect the growth and health of the forest?

These questions have been addressed at the Harvard Forest by a comprehensive suite of observations carried out continuously since 1989 at the Harvard Forest Environmental Measurement Site (EMS, Figure 10.1). The core measurements of atmosphere-biosphere exchange have been made using the relatively new eddy covariance method and have been augmented by a set of field observations, process studies, and modeling. The first five years of the Harvard Forest project were largely devoted to developing the eddy covariance method and establishing its reliability so that it could be applied elsewhere. We have applied the technique in parallel studies in Manitoba, Canada, and Brazil. An even broader context is provided by the AmeriFlux, Euroflux, and other networks that support more than 100 flux-tower sites worldwide.

**The Harvard Forest Environmental Measurement Site**

The Harvard Forest EMS provides a long-term record at a rural continental site of trace-gas concentrations and surface-exchange fluxes, along with supporting measurements of physical environment.
Figure 10.1. Installation of the gas sampling lines on the Environmental Measurement Site (EMS) tower. The facility was established by hand with minimal site disturbance. Branches and other vegetation near the tower were left intact. Photograph by J. W. Munger.
Table 10.1. Measurements Made Routinely at the Environmental Measurement Site

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Inlet/Instrument Height</th>
<th>Determined Quantity</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sonic anemometer</td>
<td>30 m</td>
<td>Horizontal and vertical wind</td>
<td>( u, v, w, T )</td>
</tr>
<tr>
<td>( \text{NO}_x ) (catalyst→NO)</td>
<td>30 m</td>
<td>Flux of momentum and heat</td>
<td>( F_{\text{MOM}} ), ( F_{\text{HEAT}} )</td>
</tr>
<tr>
<td>High-speed ( \text{CO}_2 \cdot \text{H}_2\text{O} )</td>
<td>30 m</td>
<td>( \text{CO}_2 ) flux</td>
<td>( F_{\text{NO}_x \cdot \text{CO}_2} )</td>
</tr>
<tr>
<td>IR absorbance</td>
<td>30 m</td>
<td>( \text{H}_2\text{O} ) flux and concentration</td>
<td>( F_{\text{NO}_x \cdot \text{H}_2\text{O}} )</td>
</tr>
<tr>
<td>High-speed ( \text{O}_3 \cdot \text{C}_x \cdot \text{H}_4 ) chemiluminescence</td>
<td>30 m</td>
<td>( \text{O}_3 ) flux and concentration</td>
<td>( F_{\text{O}_3} )</td>
</tr>
<tr>
<td>Slow ( \text{CO}_2 ) absorbance</td>
<td>30, 24, 18, 12, 6, 3, 1, 0.05 m</td>
<td>( \text{CO}_2 ) vertical profile</td>
<td></td>
</tr>
<tr>
<td>Slow ( \text{O}_3 ) absorbance</td>
<td>30, 24, 18, 12, 6, 3, 1, 0.05 m</td>
<td>( \text{O}_3 ) vertical profile</td>
<td></td>
</tr>
<tr>
<td>Slow ( \text{NO}_x ) absorbance</td>
<td>30, 24, 18, 12, 6, 3, 1, 0.05 m</td>
<td>NO, ( \text{NO}_x ) vertical profile</td>
<td></td>
</tr>
<tr>
<td>Thermostat, thin-film capacitor</td>
<td>30, 22, 12, 6, 3 m</td>
<td>Temperature and relative humidity profiles</td>
<td></td>
</tr>
<tr>
<td>Thermistors</td>
<td>Surface (6 reps), 20 cm, 50 cm</td>
<td>Soil temperatures</td>
<td></td>
</tr>
<tr>
<td>Quantum sensor</td>
<td>30,12 m</td>
<td>Photosynthetically active photon-flux density</td>
<td>( P_{\text{PPFD}} )</td>
</tr>
<tr>
<td>Net radiometer</td>
<td>30 m</td>
<td>Net radiative heat flux</td>
<td>( R_{\text{net}} )</td>
</tr>
<tr>
<td>CO gas–filter correlation IR absorbance</td>
<td>30 m</td>
<td>CO concentrations</td>
<td></td>
</tr>
<tr>
<td>Gas chromatograph–Flame ionization detector (GC-FID)</td>
<td>30 m</td>
<td>CH(_4) concentrations(^*)</td>
<td></td>
</tr>
<tr>
<td>Two-channel GC-FID</td>
<td>29, 24 m</td>
<td>( \text{C}_x \cdot \text{C}_y ) hydrocarbon concentrations and gradients</td>
<td></td>
</tr>
<tr>
<td>Four-channel GC–electron-capture detector</td>
<td>29 m</td>
<td>Halocarbons, ( \text{N}_2\text{O} ), ( \text{CO} ), ( \text{CH}_4 ), ( \text{SF}_6 ) concentrations(^\dagger)</td>
<td></td>
</tr>
</tbody>
</table>

*Note: Numerous other measurements are made with specialized equipment that is installed for shorter durations. The tower and analytical equipment are inspected and serviced routinely every two to three days.
*Measurements by P. Crill, University of New Hampshire.
\(^\dagger\)Installed September 1995; official station in the NOAA halocarbon-monitoring network.

and biological processes (see Table 10.1 for a complete list of measurements). The EMS is located near the eastern boundary of the Prospect Hill tract, surrounded by Harvard Forest and private lands covered by typical upland forest dominated by mixed hardwoods, especially red oak and red maple, with scattered hemlock and pine (see Figure 2.8).

Atmospheric composition and trace-gas exchanges on a local scale in a forest are modified by the regional surroundings in prevailing upwind directions, primarily to the northwest and southwest in New England. Within 100 kilometers of Petersham, the surrounding area is largely rural, with a mixture of mostly small (population up to 10,000) and a few medium-sized (population less than 100,000) towns surrounded by forested lands. However, extensive urban areas to the southwest have relatively high pollutant emitters (Figure 10.2). Forested remnants and low population density are common northwest. As we will see in densely urbanized to rural landscapes, the EMS is reflected clearly in data through time. In general, the continental air when winds blow away, and air when the winds are southerly is generally positioned for determining forest and of the forest on policy.

The central facility of the area's sensors and sampling inlets in approximately 24-meter canopy electrical instruments and data-acquisition lines to the site. The woods road extending back to the remote forested site in order to...
relatively high pollutant emissions densities within 100 to 500 kilometers (Figure 10.2). Forested regions with interspersed local agriculture and low population density extend for hundreds of kilometers to the northwest. As we will see in the following sections, the variation from densely urbanized to rural landscapes at different directions from the EMS is reflected clearly in variations in atmospheric measurements through time. In general, the Harvard Forest receives extremely clean continental air when winds blow from the northwest and quite polluted air when the winds are southwesterly. This variation makes the site ideally positioned for determination of the influence of pollution on the forest and of the forest on pollution.

The central facility of the EMS is a 30-meter tower mounted with sensors and sampling inlets located above, within, and below the approximately 24-meter canopy. A small companion building shelters instruments and data-acquisition equipment. Electrical power and communication lines to the site are buried beneath the 1.5 kilometers of woods road extending back to Shaler Hall. The EMS was placed at this remote forested site in order to be distant from paved roads or other cul-

\[\text{Population Density of Northeastern U.S.}\]

\[\text{People/Square Mile:} \]
- 0 - 1000
- 1001 - 10000
- 10001 - 40000

\[\text{Figure 10.2.} \text{ Population density in the northeastern United States illustrating the sharp gradient between the densely populated urban-industrial zone along the coast and the mostly rural interior. As a consequence of this pattern, northwesterly winds bring relatively clean air from extensively forested areas to the Harvard Forest, whereas southwesterly winds bring air that is affected by recent industrial and automotive emissions. Sampling and discriminating these two prevailing wind directions provide insights into human influences on atmospheric composition. Population data from the U.S. Census.}\]
tural activity. To minimize disturbance, all site installation activities, including the digging of tower foundations, were done by hand, and only small limbs that directly obstructed the tower and its guy wires were cut during installation.

**Eddy Covariance and Net Flux Measurements at the EMS Tower**

We measure the fluxes or exchanges of trace gases between the atmosphere and the forest using the eddy covariance method, in which the differences in concentration and vertical velocity between updrafts and downdrafts above the forest are measured and are then used to calculate the overall direction and magnitude of fluxes (Figure 10.3). Updrafts bring to the sensor air that has just been in contact with the forest understory and canopy and hence is depleted relative to downdrafts in substances that are taken up by or deposited in the forest (for example, CO₂ during the day). They are enriched in substances emitted by or produced in the forest (for example, CO₂ at night).

Turbulence in air movement is an important regulator of the forest environment and flux rates and is often described in terms of the frequency in oscillation between updrafts and downdrafts. For instance, shifts between updrafts and downdrafts at 1-second intervals would have a frequency of 1 cycle per second (also denoted in hertz). The length of turbulent eddies is determined by frequency and wind speed; a 1-hertz eddy in a 1-meter-per-second wind would be 1 meter in length. In actual practice, turbulence at the top of the forest canopy exhibits a wide range of variation, from the rapid fluctuations (0.1 to 10 cycles per second) imparted by fast winds moving across the rough surface of the canopy, to very large eddies with slow frequencies (0.01 cycles per second) associated with convective weather cells and clouds in the planetary boundary layer. For typical wind speeds, the horizontal extent of turbulent eddies that affect the transport of materials and energy to forest canopies ranges from a few meters to several hundred meters.

In order to distinguish updrafts and downdrafts at the finest scales and to determine accurate fluxes, many tower instruments take readings of chemical concentrations and wind speed and direction at least once per second. A long-term or running average is subtracted from the instantaneous values of concentration and vertical wind speed to determine the fluctuations. The product of the fluctuations is averaged over an interval long enough (typically approximately 30 minutes for forests) to provide a valid sample of updrafts and downdrafts. An important assumption of the eddy covariance method is that averages over time at the sensor location are equivalent to spatial averages across the surrounding landscape in the upwind direction; that is, the concentrations and winds measured at the tower are typical of a larger area upwind. Determining the validity of this assumption requires identifying good data periods.

In addition to measuring the fluxes of CO₂, H₂O, and ozone (O₃), eddy covariance also measures the fluxes of sensible heat (the product of vertical temperature gradients and wind speed) and momentum (the product of vertical wind speed gradients and wind speed). Sensible heat flux is the heat exchanged between the canopy and air. The sensible heat flux is the heat exchanged, divided by the magnitude of the wind speed. It depends on the surface conditions (leaf density) and the strength of vertical mixing. The term friction velocity (denoted by the symbol $$u'$$) is a measure of the wind speed that is the momentum flux (denoted by the symbol $$F$$) divided by the density of air ($$\rho$$). The friction velocity is often written as: $u' = \sqrt{\frac{1}{\rho} \frac{F}{g}}$

![Figure 10.3](image.png)
Figure 10.3. Drawing of the eddy covariance measurement of atmosphere-biosphere exchange fluxes at the Harvard Forest. The sonic anemometer, which measures wind velocity in three dimensions, and inlets for gas measurements sit atop a 30-meter tower above the 22- to 24-meter canopy and make high-frequency (four to eight times per second) measurements of the wind, air density, and concentrations of CO₂, ozone, total oxidized nitrogen (NOₓ), and other gases. These measurements allow the direct determination of fluxes between the forest and the atmosphere. Eddy covariance was originally developed to measure CO₂, water, and energy fluxes over crops; in the early 1980s it was extended to tall vegetation where it was used for periods of a few days or weeks and was very labor intensive. In collaboration with colleagues at SUNY-Albany, we developed fully automated instrumentation that could define net ecosystem growth over a year by summing hourly data without prohibitive accumulation of error.

determining the validity of this assumption is an important criterion for identifying good data periods before making further analyses.

In addition to measuring the fluxes of trace gases such as CO₂, water (H₂O), and ozone (O₃), eddy covariance provides the fluxes of sensible heat (the product of vertical wind speed and temperature variations) and momentum (the product of vertical and horizontal wind speed fluctuations). Sensible heat flux is the exchange of warmer (or cooler) air between the canopy and air. The sum of sensible heat flux and latent heat flux, which is the heat exchanged by evaporation of water, should balance the energy gained (or lost) from the system by radiation. Momentum flux measures the influence of friction at the canopy surface to slow the wind speed. It depends on both the vertical gradient in wind speed and the strength of vertical mixing. Micrometeorologists frequently use the term friction velocity (denoted by the symbol u*, the square root of [-1 × momentum flux]). When friction velocity is large, turbulent ex-
change of air between the canopy and the atmosphere is efficient and accounts for most of the canopy-atmosphere exchanges. When friction velocity is low, turbulent mixing is weak and canopy-atmosphere exchange may occur by other processes that are not easy to measure. We will use friction velocity throughout this chapter to distinguish periods when the air at the canopy interface is thoroughly mixed from periods when it is poorly mixed.

The flux measured just above the canopy at 30 meters may not account for all of the CO₂ taken up or released by the forest; some additional CO₂ may stay in the air spaces of the canopy and contribute to changes in concentrations there that we also need to measure. Consequently, the true net ecosystem exchange of carbon (NEE) is the measured flux at the top of the tower plus the change in CO₂ mass contained in the 30-meter column of air below the flux sensor (that is, the change in mean concentration of CO₂ multiplied by the height).

Net ecosystem exchange is the sum of gross ecosystem exchange (GEE, equivalent to gross photosynthesis) by autotrophs (plants) minus the total respiration efflux (R) by both autotrophs and heterotrophs (for example, microbes, soil invertebrates, and other animals) and is generally expressed in units of mass per unit time and area (for example, micromoles of CO₂ per square meter per second, or kilograms carbon per hectare per year). Atmospheric measurements are referenced to a vertical scale with zero at the ground and increasing positively with height. By this convention, GEE is a negative flux (that is, CO₂ is moving “downward” from the atmosphere into the forest), and R is positive.

At the Harvard Forest we use the nighttime measurement of NEE to determine R because at night photosynthesis or production by plants is zero in the absence of sunlight whereas respiration activity by both plants and heterotrophs continues. Daytime R is estimated from the ambient temperature on the basis of the relationship between nighttime NEE (which is the same as R) and temperature. GEE may then be calculated from NEE (measured by eddy covariance) and R calculated by the simple relationship with temperature (Figure 10.4).

The NEE measurements have inherent uncertainties, attributable to the nature of the instruments and their occasional failure due to lightning strikes, power outages, and other events and to a variety of measurement artifacts caused by the nature of air movement under different environmental conditions over complex terrain such as occurs in central Massachusetts. We have critically evaluated the sources of uncertainty and their effect on annual carbon balances and have divided them into three types: (1) uniform systematic error, associated with equipment, calibration gas mixtures, and data processing; (2) selective systematic error, due to the inability of the tower/sensor system to sample the forest adequately under certain conditions or in certain wind directions; and (3) sampling uncertainty, associated with periods of missing data. Discussion of these uncertainties and how to address them provides important insights into the scientific process.

CO₂ Exchange and Net Seasonal and Daily Cycle
During the growing season, net exchange is a function of when respiration is the dominant process (when photosynthesis is small) and when photosynthesis increases, as in Figure 10.5). Because the vertical mixing is induced by solar heating, the boundary layer deepens from dawn to midday and then is lost in the early morning as vertical mixing decreases (Figure 10.5). Because of the influence of clear air on the canopy (FCO₂ in Figure 10.5), the forest is a net sink of carbon production or consumption.

Interestingly, the quantum flux of light energy changes during the morning for a given
**Figure 10.4.** The mean course of measured respiration (RESP), net ecosystem exchange (NEE), and gross ecosystem exchange (GEE) for 1992 through 1999 at the Harvard Forest. Respiration is derived from the relationship between nighttime temperatures and NEE. Gross ecosystem exchange is calculated by subtracting RESP from NEE. Negative values represent downward fluxes of carbon into the forest ecosystem, and positive values represent releases from the forest into the atmosphere. Measurable GEE is observed in early April because of the scattered conifers and understory vegetation that greens up early at the Harvard Forest, but respiration continues to dominate until the full forest canopy develops in late May.

data. Discussion of these uncertainties and the manner in which we address them provides important, though frequently underappreciated, insights into the scientific process (Box 10.1).

**CO₂ Exchange and Net Ecosystem Production**

**Seasonal and Daily Cycles**

During the growing season, NEE is positive during nighttime hours when respiration is the dominant process, becomes negative at dawn as photosynthesis increases, and then is positive again at dusk (Figure 10.5). Because the vertical mixing of air depends on thermal convection induced by solar heating, the friction velocity (u*) also rises abruptly at dawn and drops sharply at dusk. Net storage of CO₂ within the canopy air spaces occurs during still periods at night, and this stored carbon is lost in the early morning as wind speed and frictional velocity increase (Figure 10.5). Because of this, the flux of CO₂ across the top of the canopy (F CO₂ in Figure 10.5) varies slightly from the actual rate of carbon production or consumption by the forest (NEE, Figure 10.5).

Interestingly, the quantum yield or amount of carbon fixed per amount of incident radiation is slightly lower in the late afternoon than during the morning for a given light level because of mild water stress.
Box 10.1.
Analysis of Error in Eddy Covariance Measurements

Uniform systematic errors in the EMS measurements are caused by underestimation of the total CO₂ mass flux by the eddy covariance measurement method. We uncovered and quantified this bias by making comparisons between the CO₂ flux and latent heat flux, which is measured by the same instrument using eddy covariance. The frequency characteristics of our measurements of latent heat flux suggested that the high-frequency signals were being damped, thus masking part of the heat flux. Analysis of the total energy budget, of which latent heat is a part, supported the notion that latent heat flux was being underestimated. By analogy, the same high-frequency damping and resultant underestimation occurs in the measurement of CO₂ flux. To avoid this systematic error, we have developed and applied a correction factor based on sensible heat flux data.

Selective systematic errors occur particularly on still nights, when the EMS underestimates respiration fluxes. This bias develops especially under calm conditions, with friction velocities less than 0.2 meters per second. Without large energetic eddies driven by surface heating, other processes—including small high-frequency eddies induced by the rough canopy, cold-air drainage flows, and intermittent gusts, which are usually relatively unimportant—become the dominant mixing processes. All of these secondary processes are extremely difficult to measure accurately. Because of the relatively calm conditions and lack of vertical air movement, CO₂ storage in and beneath the canopy increases and fluxes above the canopy at 30 meters decrease. However, comparison of NEE and calculated R for calm nights indicates that CO₂ storage fails to compensate for the reduced upward flux, leaving “missing” CO₂. The morning efflux of CO₂ from the forest to the atmosphere due to resumed atmospheric mixing is also smaller than expected. This conundrum is addressed by replacing NEE data from calm nights with estimates based on regression relationships between

soil temperature and respiration. This correction has been established at this site, because nighttime turbulence above this value is important as it reduces our TKE of the Harvard Forest by 0.5 times, for example, the differences between 1996a).

Sampling uncertainty is assumed to find the total annual CO₂ in covariance data result from maintenance, and data transmitted summation technique accounted for short segments (each generally environmental conditions at each segment, missing CO₂ flux relationships between CO₂ fluxes are then averaged for and the hourly fluxes are summed to yield annual canopies). embedded in this approach is 1994 using a Monte Carlo simulation interval for sampling error was applied to the overall balance of -2.1
test that replacing missing data is an alternative approach of assuming representative. Not surprising, a long data gap creates discrepancies in the number of short data gaps during the year.

The sampling uncertainty of soil nitrogen (NO₃⁻) because of also test rates; more than 50 percent was due to extreme events that are not captured. Because of this excessive skew, subsamples containing less than
soil temperature and respiration. A friction velocity of 0.17 meters per second has been established as the threshold between windy and calm at this site, because nighttime CO₂ efflux becomes independent of air turbulence above this value. Correction for this systematic error is very important as it reduces our estimates for annual carbon sequestration at the Harvard Forest by 0.5 to 1.0 tons of carbon per hectare (see, for example, the differences between Wofsy et al. 1993 and Goulden et al. 1996a).

Sampling uncertainty arises when incomplete data sets must be summed to find the total annual carbon balance. Gaps in eddy covariance data result from interruptions for routine calibration, maintenance, and data transfer as well as equipment malfunction. Our summation technique accommodates gaps by first dividing the year into short segments (each generally about four days long) in which environmental conditions are relatively well correlated. Within each segment, missing CO₂ flux data are replaced using empirical relationships between CO₂ exchange and climate variables. Calculated fluxes are then averaged for each hour of the day within the segment, and the hourly fluxes are summed. Finally, the short segments are summed to yield annual carbon balance. The sampling uncertainty embedded in this approach was evaluated for the carbon balance in 1994 using a Monte Carlo simulation. The 90 percent confidence interval for sampling error was +0.3 tons per hectare compared with the overall balance of −2.1 tons per hectare. The analyses indicated that replacing missing data introduces less uncertainty than the alternative approach of assuming that the days with valid data are representative. Not surprisingly, simulations also showed that a single long data gap creates disproportionately more uncertainty than do a number of short data gaps of the same total duration spread through the year.

The sampling uncertainty of CO₂ flux is smaller than for oxides of nitrogen (NOₓ) because of the skewed distribution of daily deposition rates; more than 50 percent of the summer NOₓ input is deposited during extreme events that occur on only 20 percent of the days. Because of this excessive skewness, simulations with random subsamples containing less than 50 percent of possible data yielded
Box 10.1. continued

highly variable NO$_x$ deposition estimates; however, the variability between random subsamples of the data dropped below 15 percent when more than 50 percent of the available data were included. These results corroborate the uncertainty analysis of the carbon measurements. They also confirm the value of continuous, unattended monitoring combined with prompt correction of all system malfunctions.

Figure 10.5. Mean daily course of carbon exchange and light (photosynthetic photon flux density; shading) is shown in the top panel. Separate lines show the measured CO$_2$ flux ($F_{CO2}$), the storage term, and their sum, net ecosystem exchange (NEE). The monthly average light levels are shown by the stippled line. Friction velocity, a measure of the vertical mixing intensity of air, is shown in the middle panel. Energy exchange by radiation (Rnet) and the sum of sensible (H) and latent (LE) heat flux is shown in the bottom panel. The data illustrate average values from July 1998 at the Harvard Forest.

Table 10.2. Annual Net Ecosystem Exchange of CO$_2$ at the Harvard Forest as Measured at the Environmental Exchange Station.

<table>
<thead>
<tr>
<th>Growing Year</th>
<th>Carbon Gain to Forest (ton C/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1991–1992</td>
<td>0.75</td>
</tr>
<tr>
<td>1992–1993</td>
<td>0.82</td>
</tr>
<tr>
<td>1993–1994</td>
<td>0.90</td>
</tr>
<tr>
<td>1994–1995</td>
<td>0.87</td>
</tr>
<tr>
<td>1995–1996</td>
<td>0.95</td>
</tr>
<tr>
<td>1996–1997</td>
<td>0.98</td>
</tr>
<tr>
<td>1997–1998</td>
<td>0.93</td>
</tr>
<tr>
<td>1998–1999</td>
<td>0.91</td>
</tr>
<tr>
<td>1999–2000</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Note: Values are for metric ton carbon per hectare. The growing season (June to September) includes the period from May 1 to October 1 of each year. Positive values indicate a net carbon gain to the forest; negative values indicate a net carbon loss to the forest.

and decreased ambient CO$_2$ concentration, and increased soil respiration. A smaller drop in quotient was expected during the summer, presumably on account of the decreasing efficiency of the aging leaf. During a typical summer day (August), the light intensity was 3000 lux, whereas fractional conversion was 3 to 5 moles per second, whereas fractional conversion was 3 to 5 moles per second, whereas fractional conversion was 3 to 5 moles per second, whereas fractional conversion was 3 to 5 moles per second. Summation for the entire year results in a net carbon gain of about 11 and 14 tons carbon per hectare in May and late September. Thus, the Harvard Forest biological net exchange cycle is visible in the growth patterns of leaves and their contribution to the ecosystem exchange cycle (Figure 10.5). Summation for the growing season (June to September) is shown in the middle panel. GEE exceeded 30 to 60 kilogrammes of carbon per hectare, yielding the largely dormant month of October. During this period, the forest loses 10 to 20 kilogrammes of carbon per hectare, an effect of high atmospheric CO$_2$ concentration in late winter, which make up approximately 5 to 10 percent of annual photosynthesis.
and decreased ambient CO₂ concentration, which decrease photosynthesis, and increased soil and air temperatures, which increase respiration. A smaller drop in quantum yield occurs between early and late summer, presumably on account of the changing chemistry and declining efficiency of the aging leaves. Net uptake of carbon by the forest during a typical summer day (in 1992) was −14 to −19 moles per square meter per second, whereas flux out of the forest due to nighttime respiration was 3 to 5 moles per square meter per second. During the leaves-off period between October and April, carbon effluxes ranged from 0 to 5 moles per square meter per second during both night and day.

Summed for the entire year (Table 10.2), GEE has ranged between −11 and −14 tons carbon per hectare and occurred largely between late May and late September. The magnitude and timing of the carbon and ecosystem exchange cycle each year have depended closely on the timing of leaf emergence in the spring and leaf senescence and fall in the autumn (see below). GEE exceeds R throughout the growing season, when the forest gains 30 to 60 kilograms of carbon per hectare each day. During the largely dormant months when deciduous species are leafless, the forest loses 10 to 20 kilograms carbon per hectare each day, even though low soil and air temperatures reduce respiration. During warm sunny periods in winter, we can detect some CO₂ uptake by evergreen conifers, which make up approximately 25 percent of the tree basal area around the tower.

The net result of these seasonal differences in production and respiration processes has been annual carbon sequestration (net ecosystem production, or NEP) of −1 to −3 tons of carbon per hectare, which is 10 to 30 percent of annual photosynthesis (GEE, Table 10.2). This uptake

---

Table 10.2. Annual Net Ecosystem Exchange (NEE), Gross Ecosystem Exchange (GEE), and Ecosystem Respiration (R) at the Harvard Forest as Measured by Eddy Covariance Methods at the Environmental Measurement Site

<table>
<thead>
<tr>
<th>Growing Year</th>
<th>NEE</th>
<th>GEE</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1991–1992</td>
<td>−2.0</td>
<td>−11.4</td>
<td>9.4</td>
</tr>
<tr>
<td>1992–1993</td>
<td>−1.9</td>
<td>−13.3</td>
<td>11.4</td>
</tr>
<tr>
<td>1993–1994</td>
<td>−2.0</td>
<td>−12.3</td>
<td>10.3</td>
</tr>
<tr>
<td>1994–1995</td>
<td>−2.5</td>
<td>−12.3</td>
<td>9.9</td>
</tr>
<tr>
<td>1995–1996</td>
<td>−2.0</td>
<td>−13.2</td>
<td>11.3</td>
</tr>
<tr>
<td>1996–1997</td>
<td>−2.1</td>
<td>−13.9</td>
<td>11.8</td>
</tr>
<tr>
<td>1997–1998</td>
<td>−1.2</td>
<td>−12.1</td>
<td>10.9</td>
</tr>
<tr>
<td>1998–1999</td>
<td>−2.3</td>
<td>−13.9</td>
<td>11.6</td>
</tr>
<tr>
<td>1999–2000</td>
<td>−2.1</td>
<td>−14.3</td>
<td>12.2</td>
</tr>
</tbody>
</table>

Note: Values are for metric tons of carbon per hectare per year on a growing year basis that starts on October 28 and runs to the following October 27. By examining the carbon budgets over growing years, we avoid splitting up the winter dormant season. Positive values denote emissions from the forest.
can be attributed largely to the developmental age of the forest; namely, it is maturing and growing actively after a history of intensive cutting and agriculture. More than half of the organic matter fixed during the past few years (about 60 percent) was stored in the trunks and larger branches and roots of live trees (1.5 of 2.2 tons of carbon per hectare per year). Red oak, which constitutes half of the aboveground woody biomass, made the largest contribution to this carbon storage. Examination of growth by oaks in 1998 to 2000 suggests consistent carbon sequestration between large- and small-NEP years. In contrast, carbon sequestration by the other dominant species in the forest, red maple, was much smaller and more variable. Further study of tree growth will help define the relationship between NEP and ongoing changes in species composition at the Harvard Forest and enable better predictions of future sequestration.

In addition to providing net annual carbon fluxes, the high-frequency information obtained by eddy covariance methods provides a totally new kind of data on whole-canopy physiology that is valuable for either parameterizing or validating existing models of canopy processes. A number of models have been used in this way, including Jeff Amthor’s “big-leaf” physiologically based model of deciduous canopies that predicts hourly CO₂ and O₂ uptake; Richard Waring’s “quantum efficiency” model for mixed-conifer and deciduous hardwood canopies that predicts monthly gross ecosystem productivity; and John Aber’s PnET II, a whole-forest model that predicts monthly GEE, NEE, and carbon allocation. After validating a model with data from a particular site, such as the Harvard Forest, the model can be extended and further evaluated across larger regions, as for example the application of PnET-II to our entire New York/New England study region (see Chapter 17).

CARBON BALANCE MODULATED BY ENVIRONMENTAL CONDITIONS AND CLIMATE VARIATION

Some of the most interesting features of the long-term measurements for GEE, NEE, and R at the EMS are the shorter-term responses to variations in climate. Overall, annual uptake of carbon varied by up to a factor of two over the nine-year period of observations (Table 10.2). Analysis of this variation provides important information on the factors that regulate the rate of carbon sequestration in this maturing and actively growing forest. Because CO₂ is the currency of both carbon fixation and oxidation, control of carbon exchange between the forest and the atmosphere involves all the environmental regulators of photosynthesis and respiration, notably light, soil and air temperatures, wind, humidity, and soil moisture. The number of these physical and chemical factors, their potential to compensate or interact with one another, and the importance of their timing with respect to daily and seasonal cycles all contribute to the natural variability and complexity of forest ecosystems. Continuous monitoring over nearly a decade has allowed us to untangle the factors regulating carbon exchange, and to observe interannual variations in NEP.

In nine complete years of data, conditions included cold and moist, hot and cool summers, and changing conditions, NEE varied from 850 g C m⁻² per year, with a total range from -500 to 1600 g C m⁻² per year (Table 10.2). However, the effects of climate anomalies on NEP were particularly sensitive, rather than consistent. For example, GEE was 48% higher in 1992 and 1995 compared with 1991 and 1993. GEE corresponded with short periods of six to ten days in spring leaf growth, delayed leaf senescence and nighttime respiration boosted gross production by 12% per hectare per year. Summer cloudiness also affected NEP, with the most deficit during the growing season, as opposed to the growing season, as opposed to the growing season, as opposed to the growing season, as opposed to the growing season, as opposed to the growing season.

Water relations provide another explanation for this effect. The trees were sampled during a severe drought in late 1992, with SWC below 10% at the time. This may account for carbon storage. Soil carbon storage and the microbial pool of carbon in the roots, the microbially dominated surface conditions and drainage. This contrast in susceptibility to drought makes the role of grasslands, savannas, and forests particularly relevant.

Closely examined the functional features of the relationship of temperature, rainfall. The seasonal growth of extension forest respiration, what is termed a “Q₁₀” value...
monitoring over nearly a decade has yielded the data required to begin untangling the factors regulating carbon exchange on a forest level and to observe interannual variation in NEE.

In nine complete years of measurement (1992 to 2000), climate conditions included cold and mild winters, snowy and snowless winters, hot and cool summers, and wet and dry summers. In response to these changing conditions, NEE varied up to 40 percent between successive years, with a total range from 1.2 to 2.5 tons of carbon per hectare per year (Table 10.2). However, these shifts in annual NEE resulted from the major effects of climate anomalies during specific intervals when the forest was particularly sensitive, rather than differences in annual mean conditions. For example, GEE was 10 percent less on average for 1992, 1994, and 1995 compared with 1993, 1997, and 1999–2000. These decreases in GEE corresponded with shorter growing seasons, resulting from delays of six to ten days in spring leaf emergence. In contrast, in 1992 and 1993, delayed leaf senescence and leaf fall due to relatively warm autumn nights boosted gross production by about 500 kilograms of carbon per hectare per year (12 percent) compared with other years. Given the importance of intercepted light for carbon uptake, it is not surprising that summer cloudiness also affects GEE. This effect is seen in mid-July 1992, mid-August 1992, and August 1994, when cloudy periods reduced gross production by around 400 kilograms of carbon per year. These results reflect the disproportional influence on annual NEE of weather during the growing season, as opposed to the dormant months.

Water relations provide an example of compensating effects on NEE that were unexpected at the initiation of the study. Annual GEE declined during a severe drought in late summer 1995, but only by a modest 10 percent. However, the concurrent decline in total forest respiration was much greater (1,000 kilograms of carbon per hectare), and the amount of sunshine was above average. Consequently, net carbon sequestration for 1995 was relatively large (Table 10.2) despite increased water stress on the trees. This result may appear counterintuitive as “sequestration” normally connotes carbon storage as wood in growing trees. However, the soil carbon compartment plays a large role in net carbon storage. This result suggests that whereas trees were able to tap into deep soil water via roots, the microbiially dominated respiration flux was sensitive to dry surface conditions and declined proportionally more than photosynthesis. This contrast in susceptibility to drought between production and respiration is likely a characteristic of mesic forest ecosystems, in contrast to grasslands, savannas, or similar ecosystems.

Closer examination of the late summer drought of 1995 reveals additional features of the relationships among forest respiration, soil temperature, and rainfall. The strong dependence of soil respiration, and by extension forest respiration, on soil temperature is often expressed as what is termed a “Q_{10}” value. Q_{10} specifies the change in soil respiration

EXCHANGES BETWEEN FOREST AND ATMOSPHERE 217
of CO₂ from soil pores by the winter, spring, and fall respiration of warm soil temperature. Soil temperature corresponds to grams carbon per hectare. In 1997–98, a winter snow insulated the soils and 1997–98 illustrates the processes. Although respiration per hectare per day during an unusually low average winter of snow cover and frozen soil.

Interannual variations in carbon sequestration at the Harvard Forest, warmer springs, warmer autumns increased cloud cover. Each of the northern continents in recent decades increased.

Comparison of the Harvard Forest Old-Growth Boreal Forests

Further insight into the carbon cycle gained by comparisons with other comparable data exist. Since 1994, NASA’s Earth and Planetary Sciences (EPS) program has supported a NASA-supported Boreal Ecosystem-Atmosphere Study (BES) site. The Thompson site differs strikingly from all other sites in forest conditions, environment, and scale. This area of Canada is dominated by soils 1 to 2 meters deep, over 200 meters thick deposited in glacial Lake Agassiz. It is largely covered by sphagnum and feathermosses.

Overall, carbon fluxes (both gains and losses) at the Harvard Forest with the colder temperatures, very deep soils, and waterlogged soils at the ARM tower function at the two sites are similar, despite the cold and long winters. This area has a forest in the spring occurs, and the evergreen spruce forests have thawed above freezing. Furthermore, the soils are deep due to the insulating effect of the peat layer.
of CO₂ from soil pores by the wind. In other years, smaller increases in winter, spring, and fall respiration have been correlated with anomalously warm soil temperatures such as fall 1993, when a 2°C increase in soil temperature corresponded to an increase in respiration of 200 kilograms carbon per hectare. In winter 1994, higher-than-normal respiration was observed despite colder-than-normal air temperatures as deep snow insulated the soils and kept them much warmer than the air. The winter of 1997–98 illustrates the complexity of weather effects on soil processes. Although respiration rates exceeded 30 kilograms carbon per hectare per day during an unusually warm late fall, respiration rates were lower than average during mid-winter months because of the lack of snow cover and frozen soils (see Figure 10.8).

Interannual variations in NEE and climate indicate that carbon sequestration at the Harvard Forest increases significantly in response to warmer springs, warmer autumn nights, diminished snow pack, and decreased cloud cover. Each of these trends has been observed over northern continents in recent decades, except for cloud cover, which has increased.

**Comparison of the Harvard Forest with an Old-Growth Boreal Forest**

Further insight into the processes that control carbon storage is gained by comparisons with other quite different forests for which comparable data exist. Since 1994, Harvard Forest researchers from the Department of Earth and Planetary Sciences at Harvard have operated a second eddy-flux tower site near Thompson, Manitoba, as part of the NASA-supported Boreal Ecosystem Atmosphere Study (BOREAS). The Thompson site differs strikingly from the site in central Massachusetts in forest conditions, environment, and carbon dynamics (Figure 10.7). This area of Canada is dominated by old black spruce forest on organic soils 1 to 2 meters deep, overlying poorly drained lake clays that were deposited in glacial Lake Agassiz. The ground cover is a deep carpet of sphagnum and feathermosses.

Overall, carbon fluxes (both uptake and effluxes) in the spruce forest are less than at the Harvard Forest (Figure 10.8). This result is consistent with the colder temperatures, shorter growing season, and nutrient-poor, waterlogged soils at the northern site. Seasonal patterns of ecosystem function at the two sites are also quite different. Surprisingly, despite the cold and long winters, the shift from CO₂ efflux to uptake by the forest in the spring occurs in Manitoba before Harvard Forest because the evergreen spruce forest is able to begin photosynthesis as soon as the surface soils have thawed and air temperatures are consistently above freezing. Furthermore, the wet peat soils are slow to warm at depth because of their insulating moss layer and evergreen forest.
Figure 10.7. Installation of instruments on the tower of the NASA-supported Boreal Ecosystem Atmosphere Study (BOREAS) old black spruce site, which was established in 1992 at a site 50 kilometers west of Thompson, Manitoba. The vegetation is dominated by black spruce with a ground cover of feathermoss and sphennum. The site is underlain by peat deposits at least 1 meter deep, with a clay layer below. Air samples are drawn from the top of the 30-meter tower. Photograph by J. W. Munger.

canopy. Consequently, soil respiration rates remain low in the boreal forest until well into the summer.

In contrast, the surface soil at the mostly deciduous Harvard Forest begins to warm under direct sunlight in the spring as soon as the snow cover is gone. On warm spring days before the leaves emerge, the litter and surface soils are actually warmer than they are in the middle of the summer, and respiration rates increase sharply in response. Some herbs and scattered hemlocks and pines do begin to photosynthesize at the Harvard Forest during this early spring period, but the CO2 uptake by this small amount of vegetation doesn’t compensate for the large increase in respiration. Consequently, net CO2 uptake does not usually begin in deciduous-dominated forests of central Massachusetts until leaves in the canopy emerge in late May or early June.

By early to mid-summer the deciduous vegetation at the Harvard Forest has reached maximum net uptake rates that are three to four times those in Manitoba (Figure 10.8). Smaller net CO2 uptake by the black spruce forest results from the conifer foliage and very high soil temperature in the deep peat layer has warmed slightly by a period of cool closer to net CO2 efflux in Massachusetts. The rate of uptake between relatively large and uptake and efflux in Massachusetts. The rate of uptake between relatively large and uptake and efflux in Massachusetts. The rate of uptake between relatively large

![Figure 10.8. Mean daily net ecosystem exchange (kg C ha\(^{-1}\) day\(^{-1}\)).](image)

The cumulative carbon uptake has been higher at the Harvard Forest due to steady sawtooth pattern of large and small sumertime uptake (Figure 10.8). Net CO2 uptake and uptake within and between years. Overall, the forest took up nearly 100 tons of carbon from 1992 and 2000, which is consistent with the large net CO2 uptake observed in a middle-aged forest stand. Measurements at Harvard Forest show that the forest takes up carbon during the growing season, which is consistent with the boreal forests.
Figure 10.8. Mean daily net ecosystem exchange (NEE) of carbon for the Harvard Forest and the BOREAS old black spruce site in Manitoba. Note different vertical scales. Although the northern site is colder, it begins net carbon uptake earlier in the spring because the conifers are able to photosynthesize as soon as the surface soils thaw. Declining NEE during mid-summer at the BOREAS site is a consequence of the slow onset of increased soil respiration as the deeper peat layers warm. At the Harvard Forest the deciduous vegetation is able to take advantage of the warm summer temperatures for photosynthesis, and there is no reservoir of readily decomposable organic matter to be respired.

spruce forest results from the lower photosynthetic efficiency of the conifer foliage and very high soil respiration rates that develop when the deep peat layer has warmed up in mid-summer. Large oscillations between uptake and efflux in Manitoba result from the approximate balance between relatively large rates for GEE and R. When GEE is reduced slightly by a period of cool cloudy or hot dry weather, the balance shifts to net CO₂ efflux. In fact, in some years the boreal forest ceases to take up carbon at about the same time the deciduous forest at the Harvard Forest is achieving its maximum uptake rates.

The cumulative carbon uptake at the Harvard Forest exhibits a steady sawtooth pattern of large wintertime efflux and generally larger summertime uptake (Figure 10.9). Perturbations in the rates of efflux and uptake within and between years are largely due to climatic factors. Overall, the forest took up nearly 18 metric tons of carbon between 1992 and 2000, which is consistent with our expectations for a healthy middle-aged forest stand. Measurements of tree growth and accumulated
Figure 10.9. Annual trajectory and sum of carbon dynamics at the Harvard Forest and boreal forest site. The annual sums for net ecosystem exchange are shown as bars along the top of the graph, whereas lines show the trajectory of carbon storage or release. The second-growth temperate forests at the Harvard Forest are rapidly accumulating carbon, whereas the old boreal forest is nearly at equilibrium.

Woody detritus corroborate this assessment of the average net carbon balance at the Harvard Forest. In contrast, carbon fluxes at the boreal site have been nearly in balance over the period of observation. Small shifts in the carbon exchange rates and annual net balance depend on the interplay between temperature and moisture at this site. Historical and ecological differences between the two stands are also key determinants of their carbon dynamics. The Harvard Forest stand, like much of New England, is relatively young and still recovering and growing after agricultural clearing, logging, and the 1938 hurricane. The old black spruce forest stand has not experienced disturbance by wildfire in approximately 150 years; consequently, a thick organic soil-and-moss layer retains many nutrients and insulates the soil, reducing productivity. Slow tree growth and accumulation of carbon in surface peat are balanced by decomposition of carbon in deep peat layers.

Chapter 19 will discuss the implications of these observations in a broader regional and historical context. We will see that many environmental and historical factors regulate the carbon cycle at the Harvard Forest. These factors can be divided into categories, from those that act on the short term (days, hours; for example, temperature and sunlight) to those that control the forest on timescales of decades or longer (for example, succession and soil organic matter). To understand the Harvard Forest in a global context, we have to understand quantitatively how these factors interact, a difficult scientific, intellectual, and practical challenge.

Exchanges of Nitrogen
Reactive Hydrocarbons
FORMATION OF NOX, NOY
Fossil fuel combustion emits NOX, NOY, and SOX in the atmosphere to nitrogen compounds. This group of nitrogen compounds augments NOX and NOY, which are formed by air oxidation of nitrogen oxides such as nitric oxide (NO), nitrogen dioxide (NO2), and reactive nitrogen compounds. NOX and NOY are important components of the atmosphere because they react with other organic nitrates. Since NOX and NOY are also formed by industrial processes, their presence in the atmosphere may be a result of natural and anthropogenic sources.

During the oxidation of NOX, NOY, NOX, and NOY, NOX radicals catalyze the formation of NOY radicals. NOY radicals react with ozone (O3) to form NOX radicals and other products. Reactive nitrogen compounds usually abundant in the rural environment, NOX is often the primary contributor to NOX concentrations in the atmosphere. Consequently, NOX is often the major source of NOX concentrations in the atmosphere. Therefore, a direct result of the production of NOX and NOY is the formation of secondary pollutants, such as O3, which can have a significant impact on human health and the environment.

DAILY CYCLES OF CONCENTRATIONS
Typical daily patterns observed in the atmosphere at the Harvard Forest are shown in Figure 10.10. During the day, NOX concentrations are lower than at night, because of the larger consumption of NOX by ozone (O3) and the production of NOY radicals. The pattern is different from that observed in other parts of the United States, where NOX concentrations are higher in the winter months. The seasonal variation in NOX concentrations is higher in the northern latitudes, where the production of NOX is higher in the spring and summer months.

In summary, the Harvard Forest is a unique ecosystem that is responsive to changes in the atmosphere. The fluxes of carbon and nitrogen are strongly influenced by climate and land use, and the forest is a key component of the carbon cycle at the global scale. Understanding the interactions between the forest and the atmosphere is essential for predicting the future of the ecosystem and its role in the global carbon cycle.
Exchanges of Nitrogen Oxides, Ozone, and Reactive Hydrocarbons

FORMATION OF NO<sub>x</sub>, NO<sub>y</sub>, AND OZONE IN THE ATMOSPHERE

Fossil fuel combustion emits nitric oxide (NO), which rapidly converts in the atmosphere to nitrogen dioxide (NO<sub>2</sub>) and nitrate radical (NO<sub>3</sub>). This group of nitrogen compounds, which collectively are denoted NO<sub>x</sub>, reacts in the atmosphere on a timescale of hours to days to form nitric acid (HNO<sub>3</sub>) and nitrate (NO<sub>3</sub>−) aerosol, which fall on terrestrial ecosystems as precipitation or dry deposition. Inputs of human-produced nitrogen compounds augment the natural deposition of nitrogen. Some NO<sub>x</sub> reacts with hydrocarbons to form peroxyacetyl nitrate (PAN) and other organic nitrates. Since nitrogen is a limiting nutrient and these anthropogenic inputs from the atmosphere can be large relative to natural levels, the deposition of these nitrogen compounds is an important ecological process. At the EMS we measure directly the input of all of these nitrogen compounds using a sensor that reduces them collectively to NO on a gold catalyst and then quantifies this total, which is denoted as NO<sub>y</sub>.

During the oxidation of reactive hydrocarbons in the atmosphere, NO<sub>x</sub> radicals catalyze the formation of ozone (O<sub>3</sub>), the irritant in smog. Ozone reacts with many materials, especially cell membranes. It damages the photosynthetic apparatus of plants and is harmful to human breathing ability. Reactive hydrocarbons are naturally emitted from vegetation during the growing season (see the following discussion) and are usually abundant in the rural atmosphere throughout the summer. Consequently, NO<sub>x</sub> is often the limiting factor for O<sub>3</sub> production. The modern increase in surface O<sub>3</sub> levels and heavily polluted and smoggy air is therefore a direct result of the expansion of fossil fuel combustion by industry and especially automobiles. Together, NO<sub>x</sub>, NO<sub>y</sub>, and their by-product O<sub>3</sub> represent the most abundant air pollutants that affect vegetation.

DAILY CYCLES OF CONCENTRATION AND DEPOSITION

Typical daily patterns observed for NO<sub>x</sub>, NO<sub>y</sub>, and O<sub>3</sub> concentrations in the atmosphere at the Harvard Forest are shown in Figure 10.10. Throughout the year, concentrations of NO<sub>x</sub> and NO<sub>y</sub> are at least twice as high when winds are from the southwest as opposed to the northwest and north, because of the large urban source areas of pollution along the East Coast. The pattern is different for O<sub>3</sub>, which is a secondary pollutant produced in the atmosphere from other reactants. In winter months, O<sub>3</sub> concentrations are lower in polluted southwestern air because pollutants initially consume O<sub>3</sub>, and, under cold temperatures and reduced light, O<sub>3</sub> production proceeds slowly. There is not enough time for abundant O<sub>3</sub> to be generated before the air masses reach central Massachusetts. In summer, however, reactions speed up, and polluted air from

EXCHANGES BETWEEN FOREST AND ATMOSPHERE

223
the southwest is markedly enriched in $O_3$ compared with the air associated with northwesterly winds, which has been depleted by deposition and through dilution with cleaner air.

Concentrations of NO$_x$ and NO$_y$ increase at night as pollutants from regional sources are trapped in the stable air near the ground. After sunrise, solar heating drives the convective mixing of air throughout the lower atmosphere above the forest, and NO$_x$ and NO$_y$ concentrations decrease as the surface layer of air is diluted with cleaner air from above. Ozone concentrations at the surface vary in the opposite sense; they are highest in daytime, since sunlight drives production, and low at night when $O_3$ is destroyed by reaction with the vegetation and soil. Stronger daily cycles of reactive trace gas concentrations are observed in the summer than in winter. Contributing factors are the presence of a leaf canopy to react with the pollutants and the deeper planetary boundary layer for the mixing of air in the atmosphere during summer.

Fluxes of pollutants to the forest depend on atmospheric concentrations, the rate of vertical mixing of air above and into the forest canopy, the reactivity of the gas, and characteristics of the canopy and plant surface affected. The typical daily cycles for reactive nitrogen and $O_3$ deposition to the forest canopy show generally higher fluxes in the daytime (Figure 10.10, second panel). Enhanced deposition rates and higher ambient concentrations of NO$_y$ are associated with winds from the southwest rather than the northwest in both summer and winter. Fluxes of NO$_y$ during the winter are independent of time of day. If NO$_y$ deposition were limited by vertical exchange, the maximum flux would correspond to the midday peak in friction velocity. Similarly, if photochemical production of HNO$_3$ limited NO$_y$ deposition, the fluxes would track solar radiation. Instead, the eddy fluxes of NO$_y$ increase sharply after sunrise to a maximum before noon and then decline during the afternoon to low nighttime values. Peak NO$_y$ fluxes precede both the maximum in friction velocity and photochemical activity. This pattern represents evidence for the conversion of NO$_x$ to HNO$_3$ at night on the surfaces of small particles in the atmosphere. This process produces about 20 percent of atmospheric HNO$_3$ in summer and is by far the dominant oxidation process occurring in the lower atmosphere during the winter months.

Eddy fluxes of $O_3$ during winter at the Harvard Forest have a distinct midday maximum, which is independent of wind direction and coincident with maximum vertical transport into the canopy. In summer, $O_3$ fluxes are identical for both clean and polluted wind sectors, despite the 50 percent difference in $O_3$ concentration (Figure 10.10). Peak fluxes generally occur near or just before noon, coinciding with peak solar irradiation (PPFD), and there is a strong relationship between $O_3$ flux and both radiation and canopy conductance (uptake of gases by vegetation). These results are consistent with findings from other ecosystems that $O_3$
Figure 10.10. Hourly variations of concentrations for nitrogen oxide radicals (NO\textsubscript{x} = NO, NO\textsubscript{2}, and NO\textsubscript{3}) (top panel), total oxidized nitrogen (NO\textsubscript{y} = NO\textsubscript{y}, peroxyacetyl nitrate, nitric acid, and other nonradicals) (second panel), and ozone (O\textsubscript{3}, third panel) are shown for winter (left) and summer (right) as a function of prevailing wind direction. Thick lines indicate southwest (SW) winds coming over urbanized and industrial areas, whereas clean northwestern (NW) winds are shown as thin lines. Note that the y-axis scales are larger in winter for NO\textsubscript{x} and NO\textsubscript{y} concentrations. Hourly variations of fluxes of total oxidized nitrogen (FNO\textsubscript{y}, fourth panel), ozone (FO\textsubscript{3}, fifth panel), and momentum (sixth panel; u* equals the square root of negative of horizontal and wind covariance) are also shown. Modified from Munger et al. 1996, 12649, 12651, with permission of the American Geophysical Union (copyright 1996, American Geophysical Union).
is actively taken up by vegetation, along with the CO₂ necessary for photosynthesis, through stomates, pores in leaf surfaces controlled by plants.

**Annual Cycles and Fluxes**

The seasonal cycle of NO₃⁻ concentration paralleled that of NOₓ; highest in winter and lowest in summer (Figure 10.10). In contrast, concentrations of the secondary pollutant O₃ peaked in the summer (Figure 10.10), when the twenty-four-hour mean concentrations were twice those in winter. More important for vegetation health, the extrema (for example, 90th percentile O₃ concentrations between 10 A.M. and 6 P.M.) increased even more sharply, exceeding 70 parts per billion (the threshold for damage to plants) ten to twenty times during the growing season in most years (see also models of O₃ effects in Chapter 17). Ozone levels are higher still in the adjoining Connecticut River Valley 30 kilometers to the west, where pollution plumes from the south are entrained and trapped.

Ozone damage to plants is related to uptake into leaves rather than to ambient concentration. Uptake is a major component of total deposition rates. For example, average daily deposition rates (Figure 10.11) are fairly constant from November through March at doses less than 200 micromoles per square meter per day and increase as the understory foliage emerges and coniferous vegetation begins to photosynthesize in April. Rates continue to rise through the spring in parallel with increasing foliar activity and hours of daylight to a maximum during June of 500 micromoles per square meter per day.

However, despite measuring high concentrations of O₃, we cannot de-
Figure 10.12. Monthly mean values of reactive nitrogen at the Harvard Forest from dry deposition (light shading) and precipitation (dark shading). Sampling uncertainty for each monthly estimate is indicated by thin vertical segments. The combined uncertainties of the total deposition are shown by solid lines. The average NOx emissions within 250 kilometers of the Harvard Forest (from emissions inventories of the Environmental Protection Agency) are shown by the horizontal dashed line. Reproduced from Munger et al. 1998, 8359, with permission of the American Geophysical Union (copyright 1998, American Geophysical Union).

tect a negative effect of O₃ concentrations on photosynthesis, indicating that any such influence must be modest. Since O₃ concentrations and fluxes are correlated with wind direction and sunlight, it is difficult to discern various contributions to the observed variance of CO₂ fixation that occurs with different weather patterns. Consequently, we cannot document for certain that O₃ pollution is affecting photosynthesis or canopy development (see, again, Chapter 17). Furthermore, ozone damage to plants tends to be cumulative, and reduction in CO₂ uptake might lag behind the O₃ concentrations or depend on the cumulative sum of O₃.

The observations at the Harvard Forest illustrate the patterns and processes that control nitrogen deposition across New England. Total inputs of reactive nitrogen amount to 6.7 kilograms of nitrogen per hectare per year (Figure 10.12), which is small relative to the total pool of fixed nitrogen in the forest or to the net mineralization rate (80 to 100 kilograms nitrogen per hectare per year). The summertime input of reactive nitrogen by wet and dry deposition is about twice the wintertime rate and is comparable to the regional mean NOₓ emission rate. Oxidation of NOₓ to HNO₃ or other depositing (organic nitrogen) compounds is the principal factor determining the rate for removal of reactive nitrogen from the atmosphere. Wet or dry weather affect the relative contribution between wet and dry deposition, but not the total deposition.

Oxidation of NOₓ to HNO₃ by O₃ occurs through a complex set of reactions in which the final step can be catalyzed by particles in the atmosphere. This happens mainly in winter and on summer nights because

EXCHANGES BETWEEN FOREST AND ATMOSPHERE 227
the intermediates are rapidly photolyzed and destroyed during daylight hours. Both the hydroxyl radical (OH) and O₃ were important oxidants of NOₓ throughout the year. The enhanced rate of NOₓ deposition in the morning hours observed at the Harvard Forest during the summer provided strong evidence for the importance of this oxidation pathway. Also, we found that significant reactions of NOₓ with the products of oxidation of biogenic hydrocarbons (isoprene and terpenes), forming depositing species, were needed to account for observed nitrogen deposition.

From the observations at the Harvard Forest we can derive the mean lifetimes for oxidation of NOₓ and deposition of the products over the year. We estimate that 45 percent of anthropogenic NOₓ in the boundary layer of the northeastern United States is removed in 1 day during summer but that the rate drops to 27 percent in winter. Removal of 95 percent took 3.5 and 5 days in summer and winter, respectively. Hence, in order to be transported to remote regions, NOₓ must either be pumped from the boundary layer or be converted to more stable species (for example, PAN) and then be pumped to the upper troposphere, where stability is increased by the cold ambient temperatures. These results indicate that regions more than 1 day downwind from a major emissions region could receive more nitrogen deposition in winter than summer, possibly affecting acidic runoff from snowmelt.

**Forest Emissions of Reactive Hydrocarbons**

Forests not only receive reactive compounds from the atmosphere, but also act as important sources for hydrocarbons like isoprene and terpene. This is an important process and consideration for the Harvard Forest and much of southern New England because the present vegetation assemblage is dominated by oak (*Quercus* spp.), which is a strong emitter of isoprene. Measurement of isoprene fluxes for an entire summer revealed that temperature, light, and growth stage of the canopy control emissions. Young leaves did not emit isoprene for the first two weeks after emergence and did not reach their maximum emission rate until the fourth week. After normalizing for the influence of temperature and light, we see that the basal isoprene emission rate remained nearly constant for the height of the growing season in July and August and then decreased steadily through September and October when emissions ceased (Figure 10.13). The seasonal changes in isoprene emission rates significantly affect rates of regional O₃ production because isoprene is a natural catalyst for O₃. Isoprene emissions also influence the fate of NOₓ because of the reactions with intermediates in the isoprene oxidation path. Although isoprene is the dominant light hydrocarbon species emitted by this forest, we also have documented small but significant production of ethylene, propene, and 1-butene. Al-
though we have no data for terpene concentrations or emissions, we expect them to be emitted by conifers as well. The large variations in compounds emitted and the emission strengths among tree species suggest an important mechanism by which vegetation change may affect the atmosphere.

**Effects of Exchanges on Forests and the Atmosphere**

Long-term observations show that net fluxes of oxides of nitrogen and $O_3$ to stands at the Harvard Forest are generally moderate. Inputs of nitrogen compounds represent about 8 to 10 percent of the overall mineralization rate of nitrogen for this ecosystem. Ozone fluxes and concentrations at the Harvard Forest occasionally reach levels that are known to be associated with acute vegetation damage, but to date, any effect on forest photosynthesis is undetectable.

In contrast, the influence of the forest on the atmosphere may be more significant. The forest removes considerably more $O_3$ than would be taken up by an ecosystem dominated by low-stature vegetation or by the artificial surfaces that predominate in urban areas. This uptake depletes $O_3$ concentrations in the planetary boundary layer, thereby reducing pollutant exposures downwind. Deposition is probably less important as a factor in regulating ambient concentrations of $NO_x$ and $NO_y$, but emissions of reactive hydrocarbons by the forest appear to be quite
important as a source for reactivity and as a sink for NO$_x$ through formation of organic nitrates.

The observational perspective and unique data sets provided by the Harvard Forest EMS materially aid the analysis of regional air pollution and improve understanding of the transport of pollutants to the global environment. The long-term nature of the record has been particularly important in this regard. We have learned that NO$_x$ is rather short-lived in the lower atmosphere in both summer and winter. To determine the quantities of reactive species exported to the global environment, we evidently must focus attention on the critical importance of the formation of long-lived, nondepositing species. We have advanced our ability to quantify the effects of forest vegetation on the atmosphere and the influence of pollutants on the forest.