1 The general nature of biosphere-atmosphere fluxes

> The atmosphere and its manifold changes have held fascination for men and women ever since human beings have trod this Earth. Its study played an integral role in the evolution of natural philosophy from which all of our present sciences have sprung.
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> F. Sherwood Rowland, Nobel Prize Banquet Speech, 1995

> It is widely believed that the abundance of the principal gases N_2 and O_2 is determined by equilibrium chemistry. One of the larger problems in the atmospheric sciences is that of reconciling that belief with the uncomfortable fact that these same gases are cycled by the Biosphere with a geometric mean residence time in thousands of years.
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> James Lovelock and Lynn Margulis (1974)

Sherwood Rowland's comment at the banquet held to honor receipt, along with Paul Crutzen and Mario Molina, of the 1995 Nobel Prize in Chemistry, places the atmosphere at the center of some of the most influential scientific discoveries to have been made during human history. Within Rowland's comment we can recognize Thales of Miletus who in the sixth century BC struggled to understand the different states of water and the process of evaporation, Lavoisier in the late eighteenth century discerning the exchange of oxygen between organisms and the atmosphere, and Arrhenius in the early part of the twentieth century calculating the relation between the carbon dioxide content of the atmosphere and the earth's surface temperature. The importance of the atmosphere in the history of natural philosophy is clearly underscored by these seminal studies. Within all of these studies, however, is the undeniable influence of the earth's surface and in particular the earth's biosphere, on the chemical composition and dynamics of the atmosphere. The two are linked in a type of "co-dependency" in which processes and change can only be understood through studies that include both biotic and abiotic systems. The requisite nature of the nexus between the biotic and abiotic domains of the earth system is recognizable, albeit in extreme form, in the controversial concept of "Gaian homeostasis" laid out by James Lovelock and Lynn Margulis in 1974. While we (the authors) do not, in its entirety, endorse the tenets of a Gaian earth, we do recognize the value of this concept in defining the biosphere and atmosphere as coupled and interdependent systems. It is this interdependency, and the processes that maintain it, that will be the focus of this book.

In this opening chapter, we present the concept of biosphere-atmosphere interactions through some relatively general aspects of biogeochemical fluxes. We begin by establishing the biosphere and atmosphere as components of an earth system connected through coupled biogeochemical cycles. We then establish the concept of flux, as a unifying principle in the transport of mass and energy, and explore the fundamental driving forces and constraints that govern the directions and magnitudes of fluxes. Finally, we consider some of the general cybernetic features of biosphere-atmosphere exchange, noting in particular the tendencies for non-linear relations and feedbacks, and we present a hierarchical framework within which to understand biosphere-atmosphere interactions. It is important at the outset to make the point that in this book mass and energy will be discussed with regard to *changes in state and exchanges among components of the earth system*. We will not focus on pool sizes or biogeochemical budgeting. This is a challenge because we are much more confident in our ability to observe states of the biosphere and atmosphere, compared to changes in them. It is the interactions among biogeochemical pools and earth system components, however, that drives dynamics in the state variables and thus forces time-dependent changes in those variables. It is the role of biosphere-atmosphere exchange as an agent of change in the earth system that we want to keep as a principal point of focus as we launch into our initial discussions.

1.1 Biosphere-atmosphere exchange as a biogeochemical process

Biogeochemistry is the study of changes in the earth system due to the combined activities of chemical, geological, and biological processes and reactions. Many of the trace gases that are exchanged between the biosphere and atmosphere are produced from the reduction-oxidation (redox) reactions that drive the biogeochemical cycling of elements, principally C, O, N, and S. Biogeochemical cycling is powered by the flow of solar photons through the atmosphere and biosphere, where a part of it is absorbed and used to energize electrons, which in turn drive redox reactions. This coupling between the solar energy flux and redox chemistry is exemplified in the biological processes of photosynthesis and nitrogen fixation. In both processes the energy state of electrons is increased at the expense of solar energy, and those energized electrons are used in the construction of organic compounds. The energy from the electrons is captured within the molecular structure of organic compounds, providing them with a higher energy state than their inorganic precursors. This is biogeochemical cycling in its most basic form, and it is the basis by which energy is used to construct and maintain the biotic component of the earth system.

The fundamental biogeochemical unit within the earth system is the *ecosystem*. Formally, an ecosystem is the sum of the organisms and their environment within a three-dimensional space. However, it is the *synergistic interactions* among biotic and abiotic processes that create interdependencies between organisms and their environment, and which determines the dynamic nature of the ecosystem. Thus, we will treat the ecosystem as *both* the “theater” and the “play” within which organisms transform energy into the redox reactions that drive biogeochemical cycling. Although we will spend most of our time on biogeochemical exchanges within ecosystems, it is important to recognize that ecosystems aren’t truly discrete – they have porous, diffuse boundaries through which exchange occurs with the surroundings. Interactions at those boundaries tie ecosystems into broader regional and global processes.

1.2 Flux – a unifying concept in biosphere-atmosphere interactions

Reciprocity is obvious in biosphere-atmosphere interactions. Reciprocity underlies the interdependencies that mutually bind components of the earth system, and it is reflected in the flows of mass and energy among those components. Within the earth system, changes in the size of biogeochemical pools are forced by unequal reciprocities. Reciprocity in biogeochemical flows is formally described through an analysis of *fluxes*. Proper terminology for flux according to the Système International is *flux density*, which refers to flow (of mass, momentum, or heat) per unit of surface area per unit of time. For brevity and convenience, the terms *flux density* and *flux* will be used interchangeably in this book. In some cases, we will refer to *total flux* within the context of an integral quantity with respect to finite space and time. For example, the total flux for global CO_2 uptake is ~ 123 Pg C yr^{-1}.

Flux forms the basis of the biosphere-atmosphere interactions we will consider in this book; whether it be the exchange of shortwave radiant energy between the sun and earth (a flux of photons), or the movement of water between leaves and the atmosphere (a flux of compound mass). We will be most concerned with the fluxes of mass, momentum, and heat. These entities are described by scalars, in the case of mass and heat, or vectors in the case of momentum. A *scalar* is any quantity that can be described by a quantitative scale, but has no specified direction (e.g., mass or time). A *vector* can be described with a quantitative scale and has an associated direction (e.g., wind velocity). Fluxes, themselves, are vector quantities (they have direction); in accordance with vector mathematics, gross fluxes can be summed to provide net fluxes. Gradients in scalar or vector density are also vector quantities, as they have direction.

Formally, flux is velocity multiplied by density. The nature of a flux as the product between velocity and density can be appreciated through an examination of units. Velocity is expressed in units of m s^{-1} and density (at least for the case of scalars with mass) is expressed in units of mol m^{-3} (or mass m^{-3}). In reconciling the product between velocity and density, the units emerge as mol m^{-2} s^{-1} or mass m^{-2} s^{-1}, which are both examples of flux density.

Following fundamental thermodynamic tendencies, net fluxes of mass and energy will occur in the direction that opposes their associated gradients in density; i.e., *net flux* will occur from higher density toward lower density. The net flux works to diminish the gradient. The magnitude of a flux is dependent on, and proportional to, the magnitude of its associated density gradient. In most biogeochemical systems, density gradients are determined by the location and magnitude of *sources* and *sinks*. The terms “source” and “sink” are used in different ways within the biogeochemistry research community; some usages refer to locations (e.g., “the oceanic sink or terrestrial sink”) whereas others refer to processes (e.g., “photosynthesis as a CO_2 sink or respiration as a CO_2 source”). We will tend to use these terms within the latter context – as processes that determine density gradients and thus drive fluxes. The sources and sinks that drive biogeochemical fluxes of mass are those chemical or biochemical processes that consume or produce compounds. The sources and sinks that determine the direction and magnitude of atmospheric momentum are inertia and viscosity, respectively.

One prominent example of the relations among fluxes, density gradients, and the location of sources and sinks occurs at the hemispheric scale in the record of CO_2 concentration that has been deduced for the past two millennia. In pre-industrial times (prior to the late 1800s), the global carbon budget was roughly in balance; on average, the net CO_2 *source from the biosphere to the atmosphere* almost exactly compensated for the net CO_2 *sink from the atmosphere to the biosphere* (i.e., global respiration was, on average, equal to global gross primary productivity). This balance is deduced from observations of the CO_2 content in ancient ice recovered from deep inside polar ice sheets; air samples taken from the cores reflect a nearly constant atmospheric CO_2 concentration over the millennium prior to the late nineteenth century (Figure 1.1A). Since the Industrial Revolution in the late 1800s, human activities have emitted progressively more CO_2 to the atmosphere, thus creating an additional CO_2 source and unbalancing the natural carbon cycle. The anthropogenic CO_2 added to the atmosphere is partly absorbed by biological processes in ocean and terrestrial ecosystems. However, not all the additional CO_2 can be absorbed, leading to an overall imbalance in global sources and sinks. This imbalance has caused an increase in the earth's atmospheric CO_2 concentration. The pre-industrial balance in the global carbon budget, and subsequent imbalance, provide a convenient lesson in the concept of *continuity*, which we will take up in more detail in a later chapter. Continuity requires that in the presence of equal exchanges of conserved quantities, such as those for mass and energy, within the bounds of a controlled volume, the concentration of the quantity must remain constant. If an imbalance appears in the sources and sinks, and thus in the associated fluxes, it must be reflected as a change in concentration. We can observe the principle of continuity in action in the near-continuous record of atmospheric CO_2 concentration that has been collected since the 1950s from an observatory at Mauna Loa, Hawaii and since the 1970s from the South Pole, and is familiar to most students of the earth system sciences (Figure 1.1B). Oscillations in the atmospheric CO_2 mole fraction reflect seasonal changes in the shifting dominance between photosynthesis and respiration, superimposed on a nearly constant emission of anthropogenic CO_2 pollution. Thus, with the onset of the growing season, the photosynthetic flux of CO_2 from the atmosphere to terrestrial ecosystems (hemispheric sink) is greater than the respiratory flux from ecosystems to the atmosphere (hemispheric source), and the CO_2 mole fraction of the atmosphere decreases as the growing season progresses. This pattern is reversed during the winter. Here, in an example of global proportions, we can fully appreciate the coupling between CO_2 fluxes to density gradients, and the determination of density gradients by the location and magnitude of sources and sinks.

It is important to recognize that a gradient in the density of a scalar or vector is only one determinant of a flux. State variables that characterize the system, such as temperature and pressure, also influence the flux. Temperature, pressure, and density are related through the equation of state, which will be discussed in a future chapter. Furthermore, the flux of one scalar or vector can be coupled to the flux of a different scalar or vector. For example, the flux of solar photons into a leaf is coupled to the flux of CO_2, through the processes of photosynthesis. In general, we will refer to the principal influences on flux magnitude as *driving variables*.

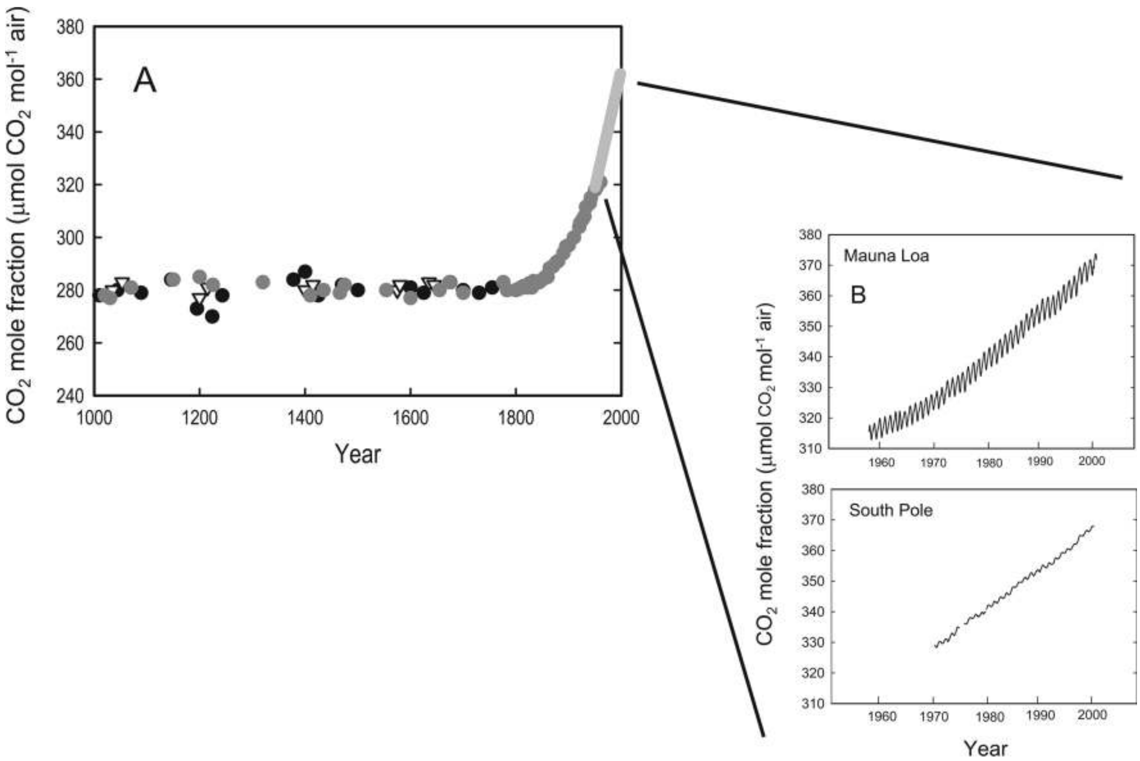

Figure 1.1 **A**. Atmospheric CO_2 mole fraction obtained from measurements using ice cores (prior to the twentieth century) and direct measurements of the atmosphere (since the late twentieth century). The stable CO_2 mole fraction through most of the past millennium is indicative of balanced CO_2 fluxes into and out of the atmosphere, on average, including those associated with the biosphere. The increase in CO_2 mole fraction over the past century is due to higher fluxes of CO_2 from the earth's biosphere to the atmosphere, compared to those from the atmosphere to the biosphere. The different symbols are indicative of different data sets. Redrawn from the Intergovernmental Panel on Climate Change, Policy Makers Report, Working Group 1 (IPCC 2001, p. 6). **B**. Details of the seasonal variations in CO_2 mole fraction measured at Mauna Loa, Hawaii or the South Pole. Data from the US National Oceanic and Atmospheric Administration.

1.3 Non-linear tendencies in biosphere-atmosphere exchange

One of the challenges that we face in describing biosphere-atmosphere interactions is the non-linear form of mathematical relations between fluxes and their associated driving variables (Table 1.1). Non-linear relations originate at the smallest spatial and temporal scales in ecosystems, and are amplified as process relations are transferred to progressively larger and longer scales. As examples of non-linear tendencies, we will briefly consider three processes; two at the sub-cellular scale and one at the leaf-to-landscape scale. In the case of enzymes, the nature of enzyme-substrate interactions changes as the availability of

Table 1.1 Causes and effects of non-linearities in biosphere-atmosphere exchanges

Causes
1. Processes tend to be highly dependent on initial conditions
2. Processes are controlled simultaneously by multiple rate-limiting, forcing variables
3. Processes are influenced by interacting scales of space and time
4. Processes are subject to positive and negative feedbacks
Effects
1. Emergent (synergistic) interactions among processes
2. Power-law scaling between process rates and driving variables
3. Time- and space-dependent patterns of abrupt (amplified or muted) change

$$v = \frac{V_{max}\,[S]}{K_m + [S]}$$

$$R = R_0\, e^{(\ln Q_{10}/10)\Delta T}$$

$$\lambda_w E = \frac{s(R_n - G) + \rho_a\, c_p (c_{aw}^* - c_{aw})/r_H}{s + \gamma \frac{r_V}{r_H}}$$

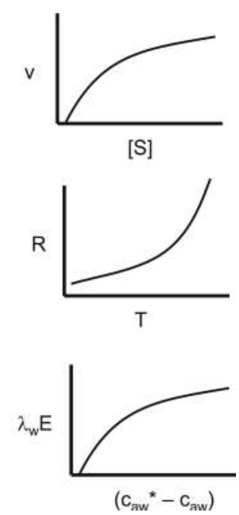

Figure 1.2 General non-linear forms of mathematical relations between some of the important processes and environmental drivers involved in plant-atmosphere exchanges. **Top**. Relation between the enzyme-catalyzed reaction velocity (v) and substrate concentration [S], as determined by biochemical parameters of enzymes (represented in this particular model as V_{max} and K_m). **Middle**. Relation between respiration rate (R) and temperature (T) in plant mitochondria. **Bottom**. Relation between leaf or canopy latent heat exchange and the difference between the saturation concentration of water vapor in air (c_{aw}*) and the actual concentration of water vapor in air (c_{aw}) at a constant temperature.

substrate changes; thus, forcing the relation between velocity and substrate concentration toward non-linearity. We can represent this non-linearity with the Michaelis–Menten model presented in the uppermost equation of Figure 1.2. At low substrate concentration the rate of the reaction is determined by the affinity of the enzyme for the substrate (reflected in the K_m term), the rate by which the enzyme can convert the substrate into product (reflected in the V_{max} term), and the frequency by which enzyme molecules interact with substrate molecules (which is dependent on substrate concentration, [S]). As substrate concentration increases, the rate of the catalyzed reaction is determined less by K_m, and more by V_{max}. Mathematically, the dependence of reaction rate on [S] is resolved as a rectangular hyperbola, reflecting a shift from approximately first-order dependence at low substrate concentration toward approximately zero-order dependence at high substrate concentration.

As a different example, we see that the response of respiration (a flux of CO_2) to temperature is also non-linear, but in a manner that reflects increased capacity for metabolism as temperature increases. In this case, increased temperature forces enzyme and substrate molecules to collide more frequently. Additionally, due to flexibility in protein molecules, changes in temperature can cause changes in the shape of enzymes, which in turn can change the nature of their catalytic interactions with substrates. The net result of these temperature-dependent effects is an amplification, or acceleration, of respiratory reactions as temperature increases. We can describe this acceleration with an increasing power-law function (as shown in the second example equation in Figure 1.2).

In a third example, the transfer of latent heat through evaporation from a leaf to the atmosphere can be described by the Penman–Monteith model (as shown in the third example equation in Figure 1.2). The flux of water from the wet, cellular surfaces inside a leaf is dependent on the atmospheric water vapor concentration. The air in the intercellular spaces of a leaf is typically saturated with water vapor; so it is the air in the ambient atmosphere that determines the overall gradient in water vapor density, and thus the evaporative flux. However, the flux of water from leaves is mitigated by a diffusive resistance, because the evaporation stream is channeled through narrow pores, known as stomata. The diameters of those pores, and thus their diffusive resistances, are sensitive to changes in atmospheric humidity. Furthermore, changes in the loss of latent heat from the leaf causes leaf temperature to decrease, which in turn causes the water vapor concentration inside the leaf to decrease (cooler air holds less moisture at vapor saturation). These multiple effects interact in complex ways as atmospheric humidity changes, forcing the relation between leaf latent heat loss and atmospheric humidity to reflect the non-linear form represented in the Penman–Monteith model.

Non-linear relations provide challenges to the modeling of ecosystem-atmosphere exchanges. Non-linear responses mean that flux densities exhibit large changes (either increase or decrease) in response to small changes in the value of a driving variable. Thus, small errors in defining the values of driving variables can produce large errors in predicted flux. Additionally, non-linear relations do not lend themselves easily to linear averaging; failure to recognize non-linear relations between an averaged dependent variable estimated from an averaged independent variable can also cause significant error. We will consider these errors further when we discuss the details of non-linear flux relations in regard to leaf CO_2 and H_2O exchange.

1.3.1 Feedback – a frequent source of flux non-linearities

The redistribution of mass, momentum, or heat caused by a flux can cause feedback that modifies the flux (see Box 1.1). *Feedback* is defined as mitigation (negative feedback) or amplification (positive feedback) of a flux caused by the flux itself. Feedback is one of the

Box 1.1 The mathematical concept of feedback

We will discuss several examples of feedback as we progress through this book. Feedback will be an important component of metabolic flux control, the coupled responses of stomata to light and CO_2, and the interactions between surface evapotranspiration and atmospheric humidity. Thus, it is important at the outset to get a sense for the nature of feedback. Here, we present a quantitative treatment of feedback as borrowed from the discipline of electrical engineering.

Feedback modifies the degree to which for external forcing variables to affect a flux. Feedback can mute or amplify a flux in the case of negative or positive feedback, respectively. A flux that is subjected to negative feedback will be altered in iterative fashion over time until a new, reduced, but stable flux is achieved (i.e., altered flux causes altered feedback which causes altered flux and so on to a stable point). The new stable flux is often called the set-point (or attractor) and in biology the process involving the negative feedback is often called *homeostasis*. A flux subjected to positive feedback is incapable of reaching a set-point unless the feedback itself is susceptible to negative feedback. In the case of positive feedback, a flux will continue to increase away from its original set-point, eventually reaching an explosive state; an example can be appreciated as the outcome of nuclear fission. The influence of feedback on a flux occurs through a *feedback loop* (Figure B1.1). Thus, we can describe a flux at an arbitrary initial time point (we will call this the input flux, or F_1), which is altered through sensitivity to an external forcing variable, to produce a new flux at a later point in time (we will call this the output flux, or F_2). Returning to our example of negative feedback on forest evapotranspiration, the forcing variable is the amount of solar radiation incident on the ecosystem (in this case influenced by clouds), and F_1 and F_2 would represent the evapotranspiration flux in the presence of solar radiation without clouds or with clouds, respectively. If we start by assuming no feedback, then we can describe the system in the *open-loop mode*. Sensitivity of the flux to the forcing variable is defined by the open-loop gain (G_o), such that: $F_2 = G_oF_1$ and therefore we can define the open-loop gain as: $G_o = F_2/F_1$. If we now engage a closed feedback loop, such that

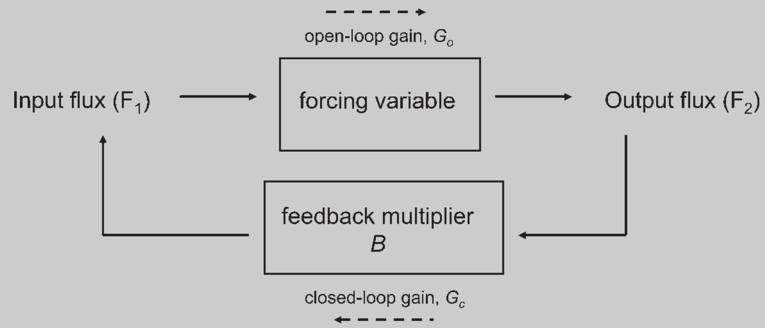

Figure B1.1 Scheme showing information flow in open and closed feedback loops. The open-loop gain (G_o) describes sensitivity of a flux to a forcing variable when the feedback loop is not engaged. The closed-loop gain occurs when the output flux "feeds back" to influence the original flux through a feedback multiplier (B). The closed-loop gain (G_c) describes the sensitivity of the original flux to the feedback multiplier scaled to the output flux.

information (in this case due to increasing clouds) is transferred back to the original flux, modifying it, we can write:

$$F_2 = F_1 G_o + F_2 G_o B, \tag{B1.1.1}$$

where B is the feedback multiplier, being positive in sign for positive feedback and negative in sign for negative feedback. Returning once again to our example of evapotranspiration, B represents the composite of atmospheric processes that convert the evapotranspiration flux into clouds and determine the attenuation of solar radiation by those clouds. We can use algebra to remove F_2 from the right-hand side of Eq. (B1.1.1), resulting in the following equation:

$$F_2 = \frac{F_1 G_o}{1 - G_o B}. \tag{B1.1.2}$$

Equation (B1.1.2) defines the resultant flux (F_2) in *closed-loop mode*. We can define the closed-loop gain (G_c) as F_2/F_1, and using Eq. (B1.1.2) to substitute for F_2, we can write:

$$G_c = \frac{G_o}{1 - G_o B}. \tag{B1.1.3}$$

principal causes of non-linearities in the mathematical relations that describe the earth system. The difficulties in understanding feedback arise because we not only have to understand the quantitative nature of primary interactions between driving variables and fluxes, but also the secondary interactions that have the potential to modify the primary interactions. This creates higher-order interactions and non-linearities in mathematical relations that evolve over time as a flux proceeds. To illustrate the concept of feedback, let's return to the process of latent heat transport, in this case from a forest landscape to the atmosphere. As solar energy is absorbed by the forest, water evaporates from leaves and the soil. Turbulent wind eddies transport the water vertically through the atmosphere to a critical height where some fraction is likely to condense on suspended particles and form clouds. Clouds reflect solar radiation, causing a reduction in the energy flux received by the forest, and reducing the rate of evapotranspiration (Figure 1.3). If there is adequate moisture in the forest and a strong thermal gradient, vertical wind eddies can take on high velocities, creating convective updrafts that form dark, cumulus clouds and trigger precipitation. When taken together, these processes exemplify negative feedback in two ways. First, the flux of energy to the forest has caused the formation of clouds, a condition that reduces the further flux of energy to the forest and thus reduces surface warming. Second, in the condition of adequate moisture, the flux of water vapor from the forest has caused a condition that triggers rain and increased atmospheric humidity, both of which tend to reduce the evaporative flux from the forest.

Feedbacks have come to the forefront of discussions on interactions between the biosphere and the climate system (Field *et al*. 2007). In this case, many of the feedbacks occur at the regional-to-global scale. Fundamental questions that have emerged from this analysis include: (1) whether biospheric carbon fluxes will change sign, from net uptake to net loss, switching from a negative to positive feedback on climate change, respectively; (2) whether changes in the earth's albedo due to melting ice at high latitudes will trigger a

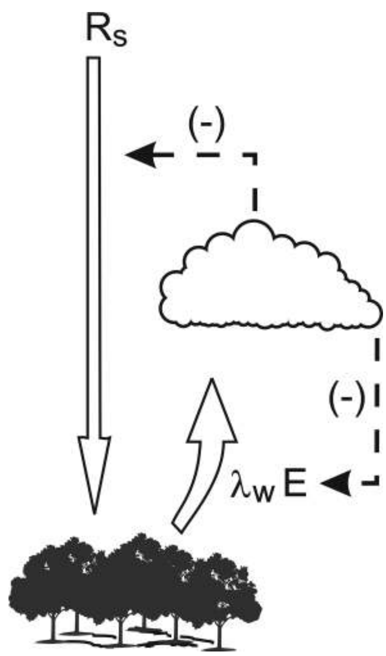

Figure 1.3 Diagrammatic representation of negative feedback with respect to latent heat flux ($\lambda_w E$) from a vegetated surface. The absorption of shortwave radiant (solar) energy (R_S) and consequent evapotranspiration of water vapor results in cloud formation which decreases the further flux of solar energy (a negative feedback), and decreases the rate of further latent heat flux from vegetation (also a negative feedback).

positive feedback by enhancing solar energy absorption; and (3) whether human-caused land-use change will trigger positive or negative feedbacks by altering the distribution of carbon-sequestering ecosystems from the landscape or altering surface albedo. Beyond questions as to the mathematical sign of potential feedbacks, future models of ecosystem-atmosphere interactions will have to be capable of resolving the magnitude of regional and global feedbacks, and the relation among feedbacks with different time constants. Understanding the rate at which feedbacks operate is crucial to predicting the rates by which fluxes can cause acceleration or deceleration of compound turnover in important biogeochemical pools and cause imbalance in the global energy budget in the face of future climate change.

1.4 Modeling – a tool for prognosis and diagnosis in ecosystem-atmosphere interactions

If there is one dominant theme that emerges from this book we hope it is the utility of organizing observations within a framework of quantitative models. Mathematical models provide the means to convert observations into predictions. Models are the tools for