Chapter 2
Photon Dissipation Rates as an Indicator of Ecosystem Health

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Abstract Ecosystems arise and evolve predominantly through the thermodynamic imperative of dissipating the solar photon flux into heat. Organic pigments coupled to water inside cyanobacteria, algae, and plants provide the dissipative structures for this entropy production. Viruses, bacteria, insects, and animals play the role of diversifiers and nutrient and seed dispersers in favor of the proliferation and dispersal of pigments over Earth's entire surface. The past few decades has seen an enormous negative human impact on the majority of Earth's ecosystems, antagonistic to human nominal supportive role in photon dissipation. Discerning whether or not efforts to reverse the damage are having the desired effect requires an accurate measure of ecosystem health. This chapter describes an indicator of global ecosystem health based on the entropy production of the ecosystem as a whole, which recognizes solar photon dissipation as its ultimate thermodynamic function. Thermodynamic justification for using the "red-edge" as an even simpler remotely sensed indicator of ecosystem health is also given.

Keywords Ecosystems • Ecosystem health • Albedo • Entropy production • Red edge

2.1 Introduction

We are only recently, and very reluctantly, coming to understand that, although we are, and have been since our existence, an integral part of natural ecosystems, our newly acquired ability to perturb them through technological innovation, and our ability to over exploit them through consumer economies, although providing for our own enormous proliferation and a naïve sense of "well-being", is the greatest threat to ecosystem health and stability and thus to our own very existence. Our recent assault on ecosystems has been relentless, from deforestation over the globe, the extinction or near extinction of many of Earth's large animals, ocean surface contamination with oil, plastics and other chemicals, coral reef destruction throughout the oceans, to the continually rising levels of contaminant aerosols and

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CO_2 in the atmosphere, which has recently passed the psychologically important 400 ppm mark (Shukman 2013).

Destruction of Earth's ecosystems proceeds at an alarming rate while sterile debate rages over whether the perturbations are man-made or whether ecosystems can absorb the blows. The fiercest confrontations pit free market entrepreneurs and governments intent on short term profit and development against an enlightened and pro-active public with a genuine concern for the environment but without sufficient expertise to disentangle the complexities. Scientists, unfortunately, have been employed by both camps in order to simulate legitimacy in favor of corresponding interests. In reality, however, the situations are extremely complex and not easily understood, even by the specialists, leaving room for uncertainty and skepticism, and thus providing a cover for the continued assault on the environment by industry, governments, and individuals.

There are, however, reasons for optimism in this rather bleak scenario. Dire predictions for the fate of the human species made by renowned scientists such as James Lovelock (2007) have fomented a keen interest in the subject. We have seen the creation of a new field of multidisciplinary research coined "Ecohealth," along with many new multidisciplinary journals, such as EcoHealth (2004), Earth System Dynamics (2010), and Ecosystem Services (2012), among many others. These journals are devoted to understanding the complex dynamics of ecosystems, identifying specific dangers, and bringing together scientists and policy makers in order to achieve a long term healthy coexistence of humans with their environment.

We may finally have begun to recognize our fundamental role as protectors and proliferators of ecosystems. Scientists have embarked on international projects to characterize the destruction of ecosystems and are attempting to quantify the relation to global climate change (Hall et al. 2008). What is urgently needed at this time, as a precursor to embarking upon serious corrective intervention, be it preventative or restorative, is a simple indicator of ecosystem health. The indicator should be accurate and reproducible, easy to implement through remote sensing, and, of course, accepted as being scientifically sound by the majority of experts.

In this chapter, building on the work of Prigogine (1967) and Prigogine et al. (1972), Ulanowicz and Hannon (1987), Schneider and Kay (1994), and some of my own work (Michaelian 2005, 2011, 2012), I present a general thermodynamic framework for addressing ecosystem health. The generality of this framework derives from the fact that all irreversible processes in nature, from the water cycle, hurricanes, ocean and atmospheric currents, human societies, to ecosystems, arise, persist, and evolve to dissipate a general thermodynamic potential; to disperse the conserved thermodynamic quantities (energy, momentum, angular momentum, charge, etc.), over ever more microscopic degrees of freedom, or, in thermodynamic terms, to produce entropy. Although a rigorous theoretical derivation is still lacking, there is ample empirical evidence indicating that the evolutionary trend of nature is towards a structuring and coupling of material into irreversible processes that augment the global entropy production, as long as there exists a driving force over the system, the generalized thermodynamic potential (for example, the solar photon flux in the case of ecosystems). Therefore, "healthy" irreversible processes, those robust processes with small probability of collapsing, have sustained and copious entropy production, while those vulnerable, unstable, processes will generally have smaller and fluctuating, or even a decreasing, entropy production.

This thermodynamic framework to be presented for gauging ecosystem health, based on the entropy production of irreversible processes, has its foundations in the formalism of the *thermodynamics of irreversible processes*, which was developed during the first half of the last century by deDonder, Onsager, Prigogine, and Nicolis among others. Although non-equilibrium thermodynamics is still a specialty subject and normally not part of the curricula of most scientists, the thermodynamics of irreversible processes has been steadily advancing our understanding of the origin, persistence, proliferation, and evolution of complex dissipative processes and structures. Irreversible thermodynamics is an indispensable tool for understanding the complexities and addressing the uncertainties in earth system dynamics, and it is therefore incumbent on practitioners in the field to ensure that knowledge of this subject becomes widely disseminated. I have, therefore, included a brief introduction to the thermodynamics of irreversible processes in Sect. 2.4.

2.2 Traditional Indicators of Ecosystem Health and Their Limitations

Ecosystem health, although still lacking a concise and practical definition, has traditionally been associated with ideas such as, ecological integrity, capability of self-restoration, biodiversity, and resilience. Evaluations of poor ecosystem health have included one or more of the following indicators.

1. Extinction of a “keystone” species, such as, for example, a top predator, allowing smaller predators to proliferate, thereby stressing the herbivore species.
2. Dieback of particular plant species indigenous to an area.
3. General reduction in biodiversity of a region.
4. Migration of foreign species into a region, or of native species out of a region.
5. Greater vulnerability to disease and temporary stress, such as that produced by insects, drought, flooding, or fire.
6. Reduction in nutrient content of the soils or the accumulation of wastes or contaminants.

Such local indicators of ecosystem health require difficult and expensive monitoring at the ground level and can therefore provide only coarse grained measurements. Local surveillance is also prone to delayed assessment, individual subjectivity, and may miss important global changes. Furthermore, although the above indicators are certainly indicative of change, they do not necessarily register poor health. For example, in both the natural processes of species migration and ecosystem succession there are rather abrupt changes in the composition of species in a given region. Also, many species, particularly insects, have a natural many year cycle of accelerated proliferation and succumbing to disease or starvation, which, in turn, has an important impact on the local populations of specific plants and animals. An example demonstrating how traditional local indicators are of relatively little value in real ecosystem surveillance, due to coarse graininess and delayed assessment capability, is the recent surprising finding of “massive aspen dieback” in our northern boreal forests attributed to severe drought, which may be related to climate change (Michaelian et al. 2011). So sketchy are our present surveillance techniques, in fact, that there is still unresolved controversy over whether recent climate change has led to a “greening” or “browning” of North American boreal forests (Alcaraz-Segura et al. 2009).

More general and global indicators of ecosystem health have been proposed, such as gauging primary productivity using, for example, remote detection of chlorophyll density (Wong and He 2013) or the novel detection of large tree trunks using 70 cm radar reflection with the satellite “Biomass” to be launched by ESA in 2020 (Quegan et al. 2013). In remote detection of chlorophyll, one observes, from above the ocean surface or the tree canopy using planes or satellites, the amount of solar light reflected in the green at 550 nm or the fluorescent photochemical quenching signal of chlorophyll at 685 nm (Babin et al. 1996). An example of this is the now routine satellite technique to measure the extent and density of cyanobacteria and algal blooms on the ocean surface (Shen et al. 2012). Although locally high chlorophyll levels on the ocean surface are often thought to negatively affect the underlying ecosystem health, since these blooms remove oxygen and can add lethal toxins (Shen et al. 2012), seeding of the ocean surface with iron nutrients to stimulate growth of cyanobacterial blooms has been suggested as a means of sequestering excess carbon dioxide from the atmosphere and thereby stabilizing global ecosystems (Lovelock 2007). Remote sensing of chlorophyll density focuses on plants, phytoplankton, and cyanobacteria, and thus correctly recognizes the overwhelming importance of these organisms as primary components of the biosphere, at the base of the food chain of all organisms. These phototrophs also constitute, by far, the greatest biomass of the biosphere and are at the base of photon dissipation and thus should be duly considered in any reliable indicator of ecosystem health.

Although the remote sensing of chlorophyll density to ascertain ecosystem health is relevant and relatively easy to implement, from the more general thermodynamic perspective it is deficient since it fails to recognize that photosynthesis is only one very small portion of the total thermodynamic work that plants and cyanobacteria perform, perhaps only as little as 0.2 % (Gates 1980). Chlorophyll is only one of many organic pigments involved in photon dissipation. All phototrophic organisms contain a vast assortment of pigments (see Table 2.1, Sect. 2.7), which absorb and dissipate over the entire range of the solar spectrum, from the ultraviolet to the infrared (although generally limited to wavelengths shorter than the “red-edge” at approximately 700 nm; see Sect. 2.7). The thermodynamic importance of the dissipative function of these pigments has been universally ignored and their existence has instead been rather cursorily assigned to “antenna” molecules or to “protectors” of the photosynthetic system (Owens 1996). This, however, is inconsistent with a number of facts: (1) photosynthesis saturates in plants and surface cyanobacteria at about 100 Wm^{-2}, only approximately 10 % of midday solar photon intensities; (2) the carotenoids, the so-called "protective pigments," have, in reality, little effect on chlorophyll bleaching by UV light (Zvezdanovic and Markovic 2008); and (3) photosynthesis is not optimized in plants under variation of external conditions, but rather transpiration is optimized (Wang et al. 2007). The great assortment of pigments finds a much more plausible reason for being in the thermodynamic imperative of nature to form dissipative structures that augment the global entropy production of the Earth in its solar environment (Michaelian 2011, 2012); the greater the absorption and dissipation of photons of highest entropy-producing potential (the short wavelength region), the greater the entropy production of the ecosystem and thus the greater the thermodynamic imperative for its existence. Global entropy production, rather than chlorophyll density, is the variable that correctly characterizes ecosystem health.

2.3 Entropy Production and Ecosystem Health

Boltzmann (1886) first suggested that all life was surviving off entropy production. Schrödinger (1944) emphasized this succinctly in his motivating book "What is Life," and Prigogine (1967) and Prigogine et al. (1972) suggested how living processes could be treated within a precise mathematical formalism, which would become known as *classical irreversible thermodynamics*. However, it was not until the publication of a seminal paper by Ulanowicz and Hannon (1987) that it was realized that entropy production was an important ecosystem variable that could be used to study the dynamics of ecosystem succession and evolution. Ulanowicz proposed using remote sensing to determine the entropy production as the difference in the integrated entropy spectrum of the photons leaving and entering an ecosystem. The entropy flux was calculated by Ulanowicz at a given wavelength λ to be approximately the energy in the photon flux at that wavelength, $e(\lambda)$, divided by a temperature, $T(\lambda)$, i.e., $S(\lambda) = e(\lambda)/T(\lambda)$. The temperature was determined by assuming the photon flux to be a Bose-Einstein gas in thermal equilibrium giving $T(\lambda) = hc/k\lambda$, where h and k are the Planck and Boltzmann constants, respectively, and c is the speed of light. Ulanowicz suggested that "mature" ecosystems would have a more red-shifted emitted spectrum and thus greater entropy production. According to Ulanowicz and Hannon, not only would the emitted spectrum of ecosystems be red shifted with respect to that of areas barren of life, but the albedo (ratio of the reflected to incident light integrated over the visible region of the spectrum) measured over living areas would be lower than over areas barren of life.

Schneider and Kay (1994) took up the proposal of Ulanowicz and Hannon and applied the thermodynamic formalism to remotely sensed temperature data obtained by Luvall and Holbo (1991). Given a constant incident photon spectrum and assuming a black-body spectrum for the emitted radiation, ecosystems measured at a lower temperature would have a more red-shifted emitted black-body spectrum and hence greater entropy production. In this way, Schneider and Kay demonstrated that old growth forest ecosystems had a greater entropy production than new growth forests and, in turn, the latter had a greater entropy production than clear cut areas. A reverse trend was found, as Ulanowicz had predicted, for the albedo, for example, the albedo over old growth forest was measured to be as low as 5 % while that over clear cut areas increased to 25 % (see also Betts and Ball 1997). This work showed that it was indeed possible to distinguish between stages of ecosystem succession using thermodynamic principles and employing simple remote sensing temperature measurements. In summary, for a given incident photon flux, older, more established, ecosystems have greater entropy production and thus a lower black-body temperature, and this relation between entropy production and the maturity of the ecosystem is now well corroborated.

Wang et al. (2007) have shown that under variation of external conditions, and even under stressful situations, plants optimize transpiration rather than photosynthesis. Transpiration removes the heat of the dissipated photons at the leaf surface by converting it into latent heat of the evaporation of water and thus is directly associated with photon dissipation. Together, photon dissipation and transpiration account, by far, for the greatest free energy dissipation performed by plants (Hernández Candia 2009; Michaelian 2012). If, by extension, it is also true that ecosystems optimize the rate of solar photon dissipation under variation of external conditions, as Ulanowicz proposed and the empirical analysis of Schneider and Kay suggests, and therefore that healthy ecosystems have greater entropy production than unhealthy or stressed ecosystems, then a measure of ecosystem entropy production should be a reliable indicator of its health.

The author is not aware of any published data with regard to remote temperature sensing comparing healthy with unhealthy ecosystems. Although using recorded temperature values as a measure of ecosystem health should not be discounted *a priori*, there are, however, a number of complications and problems related to such an approach: (1) ecosystem temperatures are a function of the intensity of the incoming solar radiation; (2) comparisons of the temperature must be made over extended periods and therefore are prone to atmospheric and seasonal variations; and (3) ecosystems do not emit light in a black-body spectrum (Gates 1980) and therefore an equilibrium temperature is not even a well-defined concept for ecosystems. Here, instead, I consider a more accurate determination of the true entropy production of an ecosystem and define this number as the best possible indicator of its present state of health.

The true entropy production due to photon dissipation can be directly obtained from the differences between the incident and emitted entropy flux of the light spectra as Ulanowicz suggested. However, it is not necessary to assume that ecosystems are black-bodies, an approximation in error of between 30 and 40 % (Michaelian 2012), and which, in fact, can be questioned on the grounds that ecosystems are out of equilibrium structures. After providing a brief introduction to non-equilibrium thermodynamics in Sect. 2.4, in Sect. 2.5 of this chapter I determine an accurate value for the entropy production of an ecosystem using equations for the entropy of a photon flux derived by Planck (1913), including a contribution for photon scattering without absorption. The analysis takes as input the incident and emitted photon spectra and produces a single number, our "indicator" of ecosystem health, for the entropy production of the global area under observation.

In Sect. 2.7, I describe an alternative indicator of ecosystem health, still based on total entropy production, but now obtained through a more simple remotely sensed determination of the *red-edge*; the wavelength at which the absorption of light by plants, algae, and cyanobacteria decreases rapidly from very high values (which occurs at wavelengths of around 700 nm). The proposed thermodynamic justification for the association of the red-edge with ecosystem health is that, under nutrient or other physical stresses, photosynthetic organisms would prioritize the production and maintenance of primarily those organic pigments that dissipate the highest energy photons available, since this maximizes entropy production under the given restrictive conditions. The entropy production of an ecosystem may thus be directly related to the remotely sensed position of its absorption red-edge (Michaelian 2013, 2014). The red-edge is therefore a simple and reliable indicator of ecosystem health, not requiring full spectrum integration over wavelength and independent of atmospheric conditions, although, as with a full calculation of entropy production by integrating over wavelength, it has a detectable seasonal variation (Gates 1980) related to nutrient flow variations.

2.4 Thermodynamics of Dissipative Systems

Before discussing the photon dissipation process in plants, algae, and cyanobacteria, it is first relevant to describe the formalism of irreversible thermodynamics that is needed to treat out of equilibrium dissipative processes in general.

There are two types of structures in nature: equilibrium structures and dissipative structures. Equilibrium structures arise as the result of nature minimizing a potential (such as, for example, the Gibb's free energy) for an isolated, or near-isolated, system. Examples are, crystalline structures, protein folded structures, and the spherical shape of the Earth. Dissipative structures, on the other hand, arise as the result of the application of a generalized thermodynamic potential over a system, such as a gradient of heat, material concentration, or an electric or photonic potential. Under such a potential, material tends to organize into dissipative structures, or as more correctly stated, into dissipative *processes*, which foment the dissipation of these potentials. Examples of dissipative processes are hurricanes, ocean and atmospheric currents, convection cells, the water cycle, ecosystems, and human societies. One such dissipative process, only recently considered in detail (Michaelian 2011, 2012) and of fundamental importance to us here, is the formation, proliferation, and propagation over Earth's surface of organic pigments and water, which together dissipate the solar photon flux.

Equilibrium thermodynamic formalism is strictly applicable only to isolated, or near isolated, systems, and deals with the relations between the macroscopic variables of a system, for example, temperature, pressure, volume, and energy, which become uniquely specified, homogeneous and constant in the time relaxed state of the system known as the “equilibrium state.” For systems that are isolated, but not initially in equilibrium, another variable of interest is the entropy, which measures the progress of evolution towards the equilibrium state of the system. Entropy is a measure of how well the conserved quantities of an isolated system, e.g., energy, momentum, angular momentum, charge, etc., are distributed over the microscopic internal degrees of freedom of the system. The width of this distribution tends to increase through time-dependent processes in nature. The second law of thermodynamics states that an isolated system will evolve towards a state in which the dispersion of the conserved quantities over the microscopic degrees of freedom is maximal. For example, for the case of the conserved variable “energy” in material systems, these microscopic internal degrees of freedom are the translational, vibrational, rotational, and electronic degrees of freedom of the atoms or molecules composing the system. In the equilibrium state, the entropy of any macroscopic system is at a global maximum.

The relations between the microscopic degrees of freedom and the macroscopic variables measured in the laboratory that uniquely define the macro-state of the system in equilibrium (e.g., temperature, pressure, volume, energy, entropy) were obtained by Boltzmann, under some particular, but surprisingly universal, assumptions, through a probabilistic analysis, which is now known as *statistical mechanics*.

For discussing non-isolated open systems, such as ecosystems, which can exchange matter, energy, momentum, angular momentum, charge, etc. with their environment, the formalism at our disposal is somewhat more limited, having been founded since only the middle of the last century. For most practical situations, under the physical conditions prevalent on Earth’s surface, we can use an extension of equilibrium thermodynamics known as *classical irreversible thermodynamics*, which was formulated by Lars Onsager, Ilya Prigogine, and others. Basically, this approach is applicable to systems in which *local* equilibrium can be assumed, i.e., although the system as a whole is out of equilibrium, very small, but still macroscopic regions (on the order of 10^{23} particles) within the system can be considered, to a good approximation, to be in equilibrium. Thus, the normal thermodynamic variables of equilibrium thermodynamics, and the equations relating these variables (e.g., the Gibb’s equation), retain their validity on a local space and time scale, and thus become functions of position and time. The utility of this approach has been adequately demonstrated in more than half a century of successful application to a great variety of dissipative systems (Lebon et al. 2008).

Specifically, application of classical irreversible thermodynamic formalism is valid if the system meets the following conditions.

1. That the external constraints, the generalized thermodynamic potentials, over the system are relatively constant in time, with respect to natural decay times of the induced dissipative processes.
2. That even though the system as a whole is out of equilibrium, every small, but still macroscopic part of the system, is at a “local equilibrium.” This ensures, as mentioned above, that all the normal equilibrium thermodynamic variables

retain their usual significance, but now are functions of position and time within the system. It also implies the validity of the Gibbs equation relating these local variables, $ds = \frac{de}{T} - \frac{P}{T}dv + \sum_i \mu_i dn_i$, where all variables have their usual thermodynamic meaning, but are now functions of position and time. For this condition of local equilibrium to be satisfied for chemical reactions, it is required that the reactions are sufficiently slow that the reactants retain a Maxwell-Boltzmann distribution of their velocities. For diffusion and transport processes, it is required that the material is sufficiently dense that there are enough collisions to ensure local equilibrium, which can be shown to be valid for all but the most rarefied gases.

The change in entropy in time of open systems can be written as a sum of two parts, that of the internal production of entropy within the system due to irreversible process occurring therein, and a part describing the exchange of entropy of the system with its external environment,

$$\frac{ds}{dt} = \frac{d_i s}{dt} + \frac{d_e s}{dt}. \tag{2.1}$$

The second law of thermodynamics extended to open systems states that the entropy production due to irreversible processes occurring inside the system must be positive definite, $\frac{d_i s}{dt} \geq 0$, while the flow, into or out of the system, $\frac{d_e s}{dt}$, has no definite sign.

The entropy production of any system can be written as a sum over the generalized forces X_k times their corresponding flows J_k,

$$\frac{d_i s}{dt} = \sum_k X_k J_k, \tag{2.2}$$

where the sum is over all irreversible processes occurring within the system. For example, for the irreversible process of heat flow in a discrete two component system with temperatures T_1 and T_2, the generalized flow is that of heat, $\frac{dQ}{dt}$, and the generalized force is $\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$, so that the entropy production is

$$\frac{d_i s}{dt} = \frac{dQ}{dt}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{2.3}$$

For a continuous (non discrete) system, this equation for the entropy production σ due to heat flow becomes (Prigogine 1967)

$$\sigma = -\sum_i \frac{Q_i}{T^2}\frac{\partial T}{\partial x^i}, \tag{2.4}$$

where Q_i is the heat flow in coordinate direction x^i.

For systems in which the external constraints are constant (fixed forces over the system), it can be shown that the system will eventually come to a *stationary state* in which all the local thermodynamic variables (e, s, T, p, etc.) remain constant in time, although they may be functions of position. In the case that the flows are linearly related to the forces, it was shown by Prigogine (1967) that there is a unique stable stationary state and that this state occurs at a minimum of entropy production with respect to variation of the free forces (those non-fixed forces that arise in a system due to the applied external force, for example, a concentration gradient arising due to an imposed heat flow). However, if there are non-linear relations between the flows and forces, then there may be many locally stable stationary states with different entropy production that are available to the system. The tendency of such systems is to evolve from one stationary state to another through bifurcations, generally in the direction of increasing entropy production (Prigogine 1967). This evolution through bifurcations implies that the system or process acquires a history. For example, in ecosystems this evolution is observable and is known as *succession*. This thermodynamic evolution is also, most probably, an accurate explanation of general biotic, and coupled biotic-abiotic, evolution. There is an empirical trend over time observed in many Earth systems, both biotic and abiotic, towards greater entropy production (Kleidon and Lorenz 2005).

In Sect. 2.5 of this chapter, it will be shown that, since by far the most important external generalized thermodynamic potential over ecosystems is the photon potential, the entropy production due to all processes occurring in an ecosystem, $\frac{d_i s}{dt}$, can be determined from an analysis of the spectrum of solar light incident on the ecosystem and the spectrum of light emitted back into the atmosphere by the ecosystem. The conversion of UV and visible light into infrared light is the dissipation that ecosystems perform, and the rate of dissipation, or the entropy production, is related to the magnitude of the shift integrated over wavelength of the emitted spectrum towards the infrared with respect to the incident solar spectrum. The technique proposed here for determining ecosystem health is therefore simply integrating over the difference between the incident and emitted spectra and carrying out a straight forward analysis, taking into account specific details, such as the albedo and emissivity of the organic material in ecosystems and the coupling of ecosystems to other dissipative processes, such as the water cycle (Michaelian 2012).

2.5 Entropy Production as an Indicator of Ecosystem Health

Photon dissipation by ecosystems is a coupled process involving various stages. In the first stage, a high energy photon from the sun is absorbed on an organic pigment molecule of plants, algae, or cyanobacteria. The electronic excitation energy is dissipated through various de-excitation processes, the principal of which is known as internal conversion, to the translational and vibrational modes of the surrounding water molecules, thereby increasing the local temperature of the water. A certain amount of liquid water is thus converted into gas, removing the latent heat of vaporization from the organism. The H_2O gas rises in the atmosphere to a height at which the temperature is low enough for condensation around microscopic particles, leaving part of its heat of condensation to escape into space in the form of many infrared photons. A single high energy photon (visible or ultraviolet) is thus converted into many (20 or more) infrared photons, conserving the total energy but producing entropy in the process, since the initial photon energy has been distributed over the many more degrees of freedom of the numerous infrared photons. Most of the entropy production, about 63 % (Kleidon and Lorenz 2005), occurs at the surface of Earth during the first stage of the process where the incident photon is absorbed and dissipated by organic pigments. A further approximately 2.6 % can be attributed to the latent heat flux of the ensuing water cycle (Kleidon and Lorenz 2005). Details of how biology catalyses the hydrological cycle can be found in Michaelian (2012) and will not be discussed further here except to say that this coupling is important to keep in mind when determining our indicator of ecosystem health based on remote sensing satellite data that detects light emission from both the ecosystem and the atmosphere.

The entropy production of a specific area of the Earth's surface can be determined by considering the change in the frequency ν or wavelength λ distributions of the radiation incident from the Sun, $I_{in}(\nu)$ [Jm^{-2}] or $I_{in}(\lambda)$ [$Jm^{-3}\ s^{-1}$], and that radiated by the area, $I_{rad}(\nu)$ or $I_{rad}(\lambda)$, including the change in the directional isotropy of the radiation. Planck (1913) determined that the entropy flux $L(\nu)$ [$Jm^{-2}\ K^{-1}$] due to a given photon energy flux $I(\nu)$ takes the following form (Wu and Liu 2010)

$$L(\nu) = \frac{n_0 k \nu^2}{c^2}\left[\left(1+\frac{c^2 I(\nu)}{n_0 h \nu^3}\right)\ln\left(1+\frac{c^2 I(\nu)}{n_0 h \nu^3}\right) - \left(\frac{c^2 I(\nu)}{n_0 h \nu^3}\right)\ln\left(\frac{c^2 I(\nu)}{n_0 h \nu^3}\right)\right] \tag{2.5}$$

where n_0 denotes the polarization state, $n_0 = 1$ or 2 for polarized or unpolarized photons, respectively, k is the Boltzmann constant, c is the speed of light, and h is Planck's constant. In terms of wavelength ($\lambda = c/\nu$), the corresponding expression is (Wu et al. 2011)

$$L(\lambda) = \frac{n_0 k c}{\lambda^4}\left[\left(1+\frac{\lambda^5 I(\lambda)}{n_0 h c^2}\right)\ln\left(1+\frac{\lambda^5 I(\lambda)}{n_0 h c^2}\right) - \left(\frac{\lambda^5 I(\lambda)}{n_0 h c^2}\right)\ln\left(\frac{\lambda^5 I(\lambda)}{n_0 h c^2}\right)\right] \tag{2.6}$$

which has the units [$Jm^{-3}\ K^{-1}\ s^{-1}$]. The entropy flux (per unit area) passing through a given surface is thus

$$J = \int_0^\infty d\lambda \int_\Omega L(\lambda)\cos(\theta)\, d\Omega \tag{2.7}$$

where θ is the angle of the normal of the surface to the incident photon beam, and Ω is the solid angle subtended by the source at the surface. The total entropy flux crossing the surface is then just Eq. (2.7) integrated over the entire surface area.

The total entropy production per unit area of the ecosystem is then

$$J = J_{rad} - J_{in}. \tag{2.8}$$

The radiated part J_{rad} is composed of two parts, that due to emission after absorption J^{e}_{rad} and that due to reflection without absorption J^{r}_{rad}. For the ecosystem, we may assume isotropic emission into a 2π solid angle and predominantly Lambertian reflection also into a 2π solid angle, since scattering from leaves is predominantly diffuse (Gates 1980) and multiple scattering from many leaf surfaces occurs in ecosystems. Therefore, with Eq. (2.7), Eq. (2.8) becomes

$$J = \int_0^{\infty} d\lambda \left[2\pi L_{rad}(\lambda) - \int_{\Omega} L_{in}(\lambda) \cos\left(\theta_{in}\right) d\Omega_{in} \right] \tag{2.9}$$

where θ_{in} is the angle of the incident solar radiation with respect to the normal of the detection surface and Ω_{in} is the solid angle subtended by the sun as seen from the surface of Earth. For example, if we take the sun directly overhead ($\theta_{in} = 0$) and the detection surface perpendicular to the zenith, then Eq. (2.9) can be simplified to give

$$Health = J = \int_0^{\infty} 2\pi L_{rad}(\lambda) - 0.04 L_{in}(\lambda) d\lambda \tag{2.10}$$

where $L_{rad}(\lambda)$ is obtained from Eq. (2.6) with $\mathrm{I}_{\mathrm{rad}}(\lambda)$ measured by the detecting spectrometer and $L_{in}(\lambda)$ obtained from Eq. (2.6) with $\mathrm{I}_{\mathrm{in}}(\lambda)$ the solar spectrum at Earth's surface with the sun directly overhead. The factor of 0.04 accounts for the solid angle subtended by the Sun at the Earth's surface. The [SI] units of this indicator of ecosystem health (entropy production) are [J K^{-1} m^{-2} s^{-1}].

The distance above the ecosystem at which the spectrometer is flying, and the solid angle of the detector, will determine the extent of the ecosystem considered. Satellite measurements are most global, but will include other coupled abiotic dissipative processes as mentioned above, such as the water cycle and ocean and wind currents, which are spawned by the heat generated through photon dissipation in the ecosystem. One would also have to consider photon dispersion by clouds and the atmosphere.

A few remarks are in order with respect to this measure of ecosystem health based on Eq. (2.10), or more generally (2.9). First, it is an instantaneous measure, which will vary throughout the day and is not completely accurate since part of the energy absorbed by the ecosystem during the day is released at night, and this radiation is not included in the instantaneous measure. A more accurate measure would integrate Eq. (19) over the 24 h diurnal cycle, but would be significantly more complex to perform. The same applies to the annual cycle. Second, Eq. (2.9) is more accurate than simple temperature measurements, since there is no assumption of thermodynamic equilibrium (a black-body spectrum) and the entropy production is not based on heat flow equations, which can result in up to 40 % error in the calculated entropy production (Michaelian 2012). Third, by considering the full spectrum of the radiated entropy flow as the emitted plus reflected, $L_{rad}(\lambda) = L^{e}_{rad}(\lambda) + L^{r}_{rad}(\lambda)$, the above calculation also takes into account the entropy production due to the Lambertian scattering of the component that is reflected and referred to as the albedo, which accounts for roughly 8.3 % (assuming a wavelength independent albedo) of the total entropy production integrated over the whole of Earth's surface (Michaelian 2012).

2.6 Albedo as an Indicator of Ecosystem Health

Bond albedo, α, is a measure of the ratio of the reflected solar radiation to the incoming solar radiation. It is specified once the limits on the wavelengths, λ_1 and λ_2, for the integration are specified:

$$\alpha = \frac{\int_{\lambda_1}^{\lambda_2} I_r(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} I_i(\lambda) d\lambda},$$

where $I_i(\lambda)$ and $I_r(\lambda)$ are the incident (solar) and reflected (over the same wavelength region) energy fluxes, respectively. The limits of integration, λ_1 and λ_2, are usually confined to the visible region of the Sun's spectrum and must be specified in quantitative statements.

Earth's albedo has been determined mainly by satellite observations but also by measuring the lunar Earth shine (Goode et al. 2001). Its accepted value integrated over Earth's surface in the visible range 400–700 nm is 0.296 ± 0.002, implying that 29.6 % of incident light in the visible range is reflected back to space. Although there is no dissipation to longer wavelengths (more photons), there is still entropy produced due to the isotropic expansion of the directed solar photon beam into a 2π solid angle. As an example, in the case of Venus, more than one half of its total entropy production is due to simple Lambertian reflection off the clouds (Michaelian 2012).

As originally proposed by Ulanowicz and Hannon (1987), albedo itself may be an approximate indicator of ecosystem health. This is related to the fact that absorption with dissipation (to longer wavelengths) into a 2π solid angle always produces more entropy than simple dispersion into a 2π solid angle. Thus, the higher the albedo, the lower the potential entropy production of an area. This fact can be used to gauge ecosystem health. For example, Ollinger et al. (2008) have found an interesting anti-correlation between nitrogen in the forest canopy and forest albedo, which deserves to be studied in more detail.

2.7 The Red-Edge as an Indicator of Ecosystem Health

It is a curious fact that the great majority of phototropic organisms have strong absorption throughout the UV and visible regions of the sun's spectrum but a sudden pronounced drop in absorption at approximately 700 nm. This sudden drop in absorption is known as the "red-edge." Beyond the red-edge, almost all light is either reflected or transmitted by the organism until around 1,400 nm, where the strong absorption bands of water in the organisms become important. See Fig. 2.1.

The red-edge has been attributed to a gap in the molecular energy levels between the lowest energy vibrational state of the 1st electronic excited state and the highest energy vibrational state of the electronic ground state (Gates 1980). A second explanation, which is also given by Gates (1980), is that it may be an evolved characteristic since plant leaves would heat up to beyond optimal temperatures for photosynthesis if the leaves also absorbed the solar energy beyond the red-edge. However, these explanations do not appear convincing, particularly given the fact that photosynthesis is most efficient at wavelengths around the red-edge. The first explanation can now be rejected, since there have now been found many deep ocean living bacteria that have strong electronic absorption within the gap beyond the red-edge and that, in fact, use the faint very red light from deep sea hydrothermal

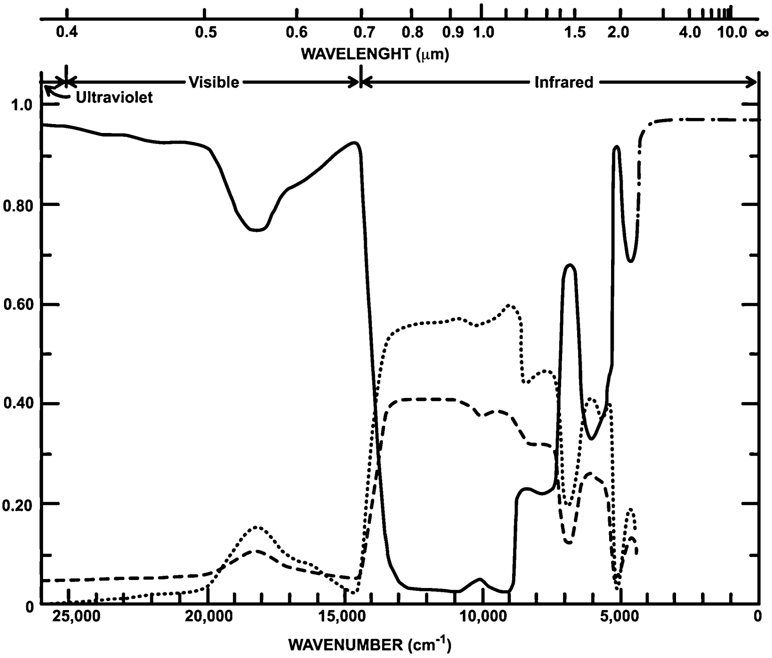

Fig. 2.1 Absorption spectrum (*solid line*) of a cottonwood leaf showing the red-edge, the pronounced drop in absorption at approximately 700 nm. The reflection of the upper surface (*dashed line*) and transmission through the leaf (*dotted line*) are also given (From Gates 1980)

vents for efficient photosynthesis (Kiang et al. 2007; Beatty et al. 2005). Anoxygenic photosynthesis has been discovered using wavelengths as long as 1,015–1,020 nm (Trissl 1993; Scheer 2003). The second explanation of Gates appears also to be lacking, since plants could have equally well evolved to reflect the UV and blue light with only a strong absorption peak centered around 700 nm where, in fact, photosynthesis is most efficient (Kiang et al. 2007).

Here I present a simple and approximate calculation to show instead that the red-edge can be explained given the finite size and dead-time (excited state decay time) of present day organic pigments under the premise of the optimization of entropy production in organisms dissipating the solar photon flux. The solar photon flux integrated over the whole spectrum at the Earth's surface at the equator and at midday is of the order of 2×10^{26} photons per square meter per second. This copious flux saturates present day organic pigments given their finite size and dead-time. It would thus be most profitable, from the viewpoint of entropy production, to dedicate resources to absorption and dissipation only at those shorter wavelengths where dissipation has the greatest potential for entropy production. Below, I show how the position of the red-edge in wavelength can indeed be determined accurately from the incident photon flux, the finite size of the common pigments, and their measured dead-times.

If plants, cyanobacteria, and algae have evolved for producing entropy through the dissipation of the solar photon flux, then if these organisms were in some way stressed, through nutrient limitation, climate, or disease, the first pigments to be foregone would be those dissipating towards the red since these have relatively less entropy production potential per unit photon. It therefore follows that healthy organisms or ecosystems will have a red-edge more towards the red, while unhealthy organisms or ecosystems would have their red-edge shifted from nominal values towards the blue.

Plants, cyanobacteria and algae absorb strongly from the far ultraviolet (240 nm) to the red-edge (700 nm). Some of the major pigment groups involved in the absorption are listed in Table 2.1 along with their respective absorption maxima wavelength, size, and approximate non-fluorescent de-excitation time. (Note that there are usually many

Table 2.1 Average size and excited state decay times for the major pigment groups

Pigment	Abs. Max. λ [nm]	Size [nm^2]	De-excitation time [ns]	Organisms
Nucleotides	260	1.5	0.005	All
Aromatic amino acids	280	1.0	0.5	All
Mycosporines	300–450	1.5	0.4	Algae, cyanobacteria
Carotenoids	450	2.5	<0.1	Plants, algae
Porphyrinas	400–430, 600–700	5.25	1.0	Plants, algae, cyanobacteria
Flavanoides	265, 530	1.5	<10	Plants
Ficobilines	550–600	3.5	–	Algae, cyanobacteria

different pigments within a group and different decay channels, which are strongly environment dependent for these molecules. Table 2.1 lists average values of the group and non-radiative decay times, where these are available.)

Table 2.1 indicates that pigments that dissipate in the region of the solar spectrum reaching Earth's surface today (300–2,000 nm) have an average size of less than about 5 nm^2 and an average lifetime in the excited state of about 0.5 ns, during which they have an almost zero probability for absorbing another photon. Pigments, however, need a support structure, for example, chlorophyll is bound to proteins and lipids of thylakoide membranes (Hoshina et al. 1984). They also need a water environment to attain rapid de-excitation through internal conversion (the times listed in Table 2.1) and to provide a solvent for delivering nutrients and removing damaged pigments. For example, for the pigment chlorophyll, each molecule occupies an area of 5.25 nm^2 and they make up only 5 % of the chloroplasts by weight. This means that each chlorophyll pigment needs a minimum effective surface area of approximately $5.25\ nm^2/(0.05)^{2/3} = 38.7\ nm^2$, which implies a maximal effective areal density of chlorophyll pigments of $2.6 \times 10^{16}\ m^{-2}$.

If we now consider the fact that the average finite dead-time of organic pigments that absorb in the visible range is approximately 0.5 ns (Table 2.1), then the maximum photon flux that present day organisms could handle (absorb and dissipate) is $2.6 \times 10^{16}\ m^{-2}/0.5 \times 10^{-9}\ s = 5.2 \times 10^{25}\ m^{-2}\ s^{-1}$, which is only about 26 % of the actual photon flux at Earth's surface at midday at the equator.

Given this thermodynamic explanation for evolutive change, it may be reasonable to presume that plants, algae, and cyanobacteria would dedicate this dissipation potential to the higher energy region of the surface solar spectrum where the resulting entropy production per photon from dissipation would be greatest. By considering the intensity distribution (number of photons per unit wavelength interval) of the surface spectrum, it is, therefore, possible to determine what should be the approximate location of the red-edge in wavelength given the maximum photon flux manageable of $5.2 \times 10^{25}\ m^{-2}\ s^{-1}$. To calculate this position, we use the approximation of a black-body incident solar spectrum at the top of the atmosphere with a temperature of the sun's surface (5,800 K) and include the effect of absorption and scattering due to the gasses in Earth's atmosphere (see Fig. 2.2).

The red-edge in the absorption spectrum, as determined using the simulated solar spectrum at Earth's surface obtained from a black-body solar spectrum and including absorption mainly due to water in Earth's atmosphere (Fig. 2.3b), is very close to the actual measured red-edge in the absorption spectrum measured for a real leaf (Fig. 2.3a). This provides a plausible thermodynamic explanation of the red-edge, which should be corroborated in further, more detailed, studies. It also suggests that the red-edge could be used as an indicator to measure ecosystem health under the premise that ecosystems have evolved to optimize entropy production through photon dissipation and that the first pigments to be forgone when an ecosystem is perturbed or under stress are those that absorb and dissipate towards the red, since these have the smallest entropy production potential.

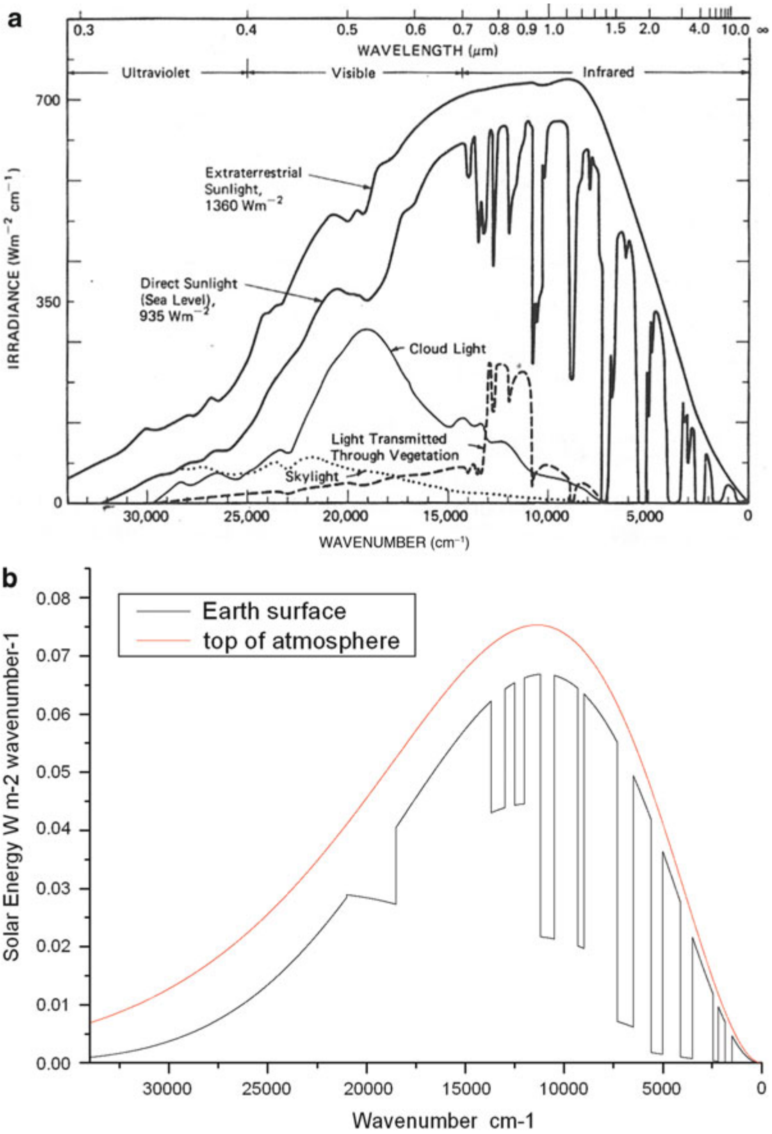

Fig. 2.2 (**a**) Measured solar photon spectrum at the top of Earth's atmosphere and at Earth's surface. Taken from Gates (1980). (**b**) Corresponding simulated solar spectrums making a black body assumption and including absorption by water in Earth's atmosphere. The integrated energy flow for the simulation is calculated to be 1,353 Wm^{-2} at the top of the atmosphere and 891 Wm^{-2} at Earth's surface

Even without the hindsight of this thermodynamic explanation, the red-edge had already been recognized as a useful indicator of plant and ecosystem health (Carter and Miller 1994; Carter et al. 1996; Eitel et al. 2011). Carter et al. (1996) showed that for loblolly pine and slash pine, the narrow band 694/760 nm reflectance ratio

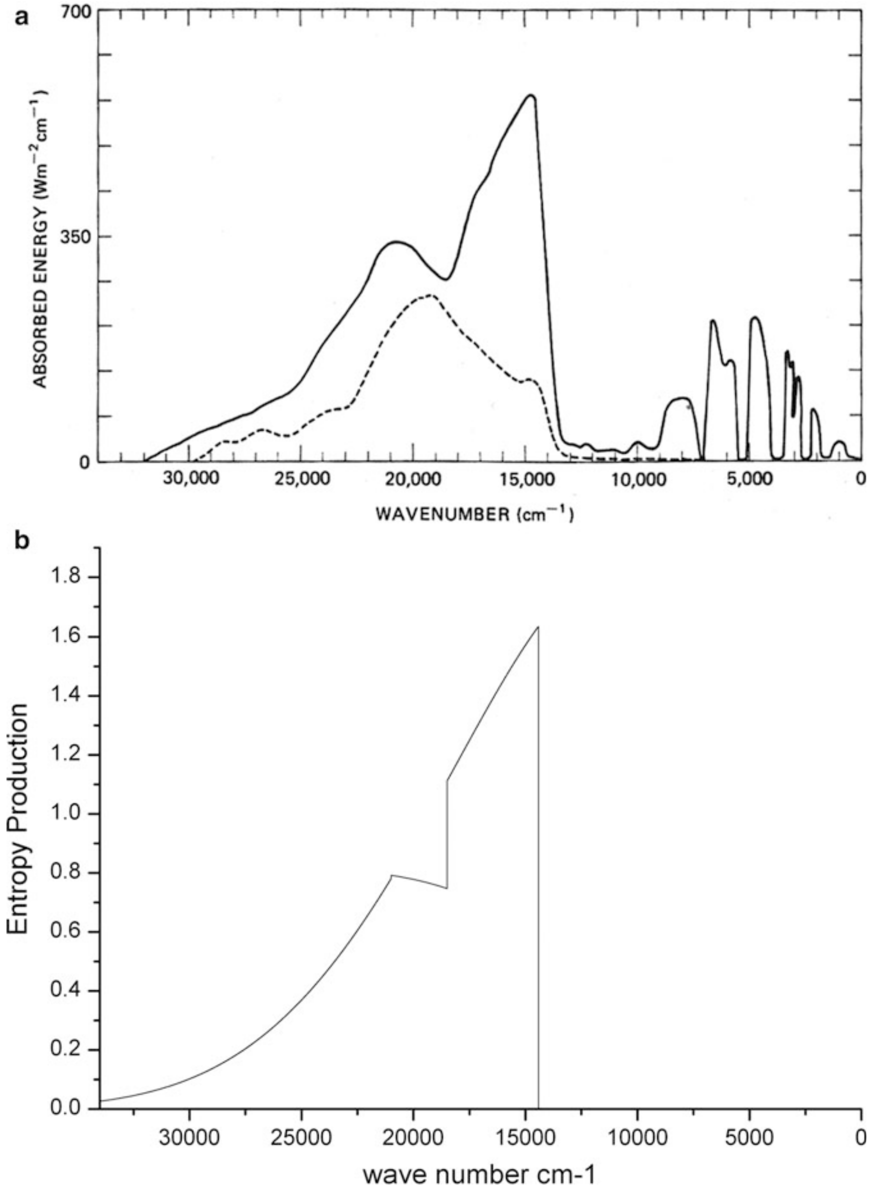

Fig. 2.3 (**a**) The measured absorption of a leaf convoluted with the incident solar spectrum showing the pronounced red-edge. Taken from Gates (1980). (**b**) The calculated position of the red-edge assuming that pigments can handle 5.2×10^{25} photons m^{-2} s^{-1} (26 % of the total, see text)

(red-edge/near infrared) allowed plant stress to be detected 16 days prior to signs of stress becoming visually apparent. By measuring the difference in the remotely (satellite) sensed wavelength intervals (690–730 nm), known as band 4, and (760–850 nm), known as band 5, Eitel et al. (2011) were able to detect stress in a

New Mexico conifer woodland 16 days earlier than by using any other remotely sensed measurements based on measuring reflection. They conclude "broadband satellite data containing the red-edge band is useful and important as a sensitive indicator for monitoring forest health at the landscape scale" (Eitel et al. 2011). It is hoped that the above thermodynamic explanation of the red-edge will help to refine these remotely sensed measurements into an even more sensitive indicator of ecosystem health.

2.8 Discussion

In a previous article (Michaelian 2012), we applied Eqs. (2.6, 2.7, and 2.8) above to determine the global entropy production on Earth and its nearest neighbors, Venus and Mars. Our results showed that Earth's entropy production per unit surface area is approximately twice that of either Venus or Mars, and thus, using our entropy production indicator of ecosystem health, we could humorously claim that the ecosystems on Earth are healthier than those on either Venus or Mars. However, ecosystems are just one form of dissipative system and since the measures of the incident and emitted spectrum were global in the above article, we can really only claim that global dissipative processes on Earth are stronger than the dissipative processes on either Venus or Mars.

This also leads us to the important point that if the conditions are not identical or very similar, e.g., constituent nutrients and water, incident photon intensity, etc., then a comparison of absolute entropy production does not say much about the respective health. For example, it is well known that tropical forests dissipate more photons per unit area than boreal forests, but it would be meaningless to claim that tropical forests are therefore "healthier" than boreal forests. However, it is well known that tropical forests are much more resistant to insect and disease (generally more stable) than boreal forests, and this type of resilience or stability must certainly be related to greater entropy production if the tendency of nature is towards greater global entropy production. For example, the coupling of the water cycle to ecosystems is much more pronounced in tropical regions. Entropy production is simply the product of a generalized thermodynamic flow times a generalized thermodynamic force (Prigogine 1967). It is much harder to perturb strong flows and cause a system to collapse than it is to perturb weak flows and cause a collapse (or, more precisely, to cause a change into a new non-equilibrium thermodynamic stationary state).

Finally, since the red-edge is a very distinctive characteristic of living organisms that can be remotely detected from space, it has been proposed as an indicator for scanning extra-solar system planets for life (Seager et al. 2005). However, the analysis above indicates that we should not expect to find the red-edge at the same or similar wavelengths as we do on Earth. The position of the red-edge on an extra-solar planet would depend on the details of the spectrum (intensity-wavelength distribution) of the star at the surface of the planet and the elapsed time of evolution of pigment size and excited state lifetime since the beginning of life on the planet. It may be, however, that a pronounced drop in absorption could be clearly distinguishable in the reflection data of a planet, even if we would have to call this a "blue-edge," for example.

Conclusions

Rapid deterioration of Earth's ecosystems due to human excesses has left us in a dangerous situation in which, unless we respond and change our ways, our own survival is at risk. Any response will first require a careful assessment of ecosystem health and a measure of the effect of our intervention. Such an approach requires a reliable and remotely sensed indicator of ecosystem health.

This chapter has been dedicated to describing an indicator of ecosystem health based on the most important thermodynamic function of all life, that of the dissipation of the solar photon flux. The indicator measures the global entropy production of the ecosystem, which is determined by integrating over the difference in the entropy flow in the incoming and outgoing photon fluxes. It is suggested that the red-edge can be used as a simplified indicator of ecosystem health since it is probably a good measure of the total entropy production. The validity of various assumptions used in deriving this relationship remains to be investigated in more detail in subsequent works.

The dissipation of the solar photon flux is an entropy producing process in which energy is dispersed over ever more microscopic degrees of freedom. As such, the dissipation process has a natural thermodynamic imperative and non-equilibrium thermodynamic principles indicate that nature will arrange material into structures and processes that tend to augment this entropy production. The whole of biological evolution, and even coupled biotic-abiotic evolution, can be described in these terms. There is no better indicator of biological evolution than the evolution in the increase in spectral absorbance range and dissipative efficiency of the organic pigments along with their dispersal (together with water) over an ever greater surface area of Earth.

It is only through the principles of non-equilibrium thermodynamics that we find a reason for the existence and evolution of ecosystems and for the existence and evolution of our own species, and it is these principles that we must learn to understand and respect if we are to attain stability through thermodynamic harmony with our environment.

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