



Thermodynamic Function Of Life

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Abstract

Darwinian Theory portrays life as being overwhelmingly consumed by a fight for survival in a hostile environment. However, from a thermodynamic perspective, life is a dynamic, out of equilibrium process, stabilizing and coevolving in concert with its abiotic environment. The living component of the biosphere on the surface of the Earth of greatest biomass, the plants and cyanobacteria, are involved in the transpiration of vast amounts of water. Transpiration is part of the global water cycle, and it is this cycle that distinguishes Earth from its apparently life barren neighboring planets, Venus and Mars. The dissipation of sunlight into heat in the biosphere and the ensuing water cycle, is by far the greatest entropy producing process occurring on Earth. Life, from this perspective, can therefore be viewed as performing an important thermodynamic function; acting as a dynamic catalyst by aiding abiotic process such as the water cycle, hurricanes, and ocean and wind currents to produce entropy. The role of animals in this view is that of unwitting but dedicated servants of the plants and cyanobacteria, helping them to grow and to spread into initially inhospitable areas.

Introduction

About 4.57 billion years ago, the Earth condensed out of a nebula of gas and dust to be bathed by a volatile early Sun which finally settled down as a main sequence star about 50 million years after its birth. The Earth was born with a primitive atmosphere, oceans, and surface, but these were continually transformed during this initial period by an evolving Sun, heat outflow from the Earth, and by constant bombardment of asteroids, comets, and even large protoplanets (Zahnle et al., 2007). Then, approximately after the end of the period recorded on the moon as the "lunar late heavy bombardment period" (c.a. 3.8 Ga.) probably caused by gravitational effects of the migration of the outer planets, the physical conditions on Earth became more stable, and life emerged.

The emergence of life on Earth has hitherto mostly been considered as an extraordinary accident and its evolution in complexity and global extent considered

as resulting from an inherent survival instinct programmed into the individual operating in a hostile environment. Darwin himself suggested that life was at the mercy of the forces of Nature and would necessarily adapt by means of natural selection to the demands of the external environmental or succumb. However, it has since become apparent that life plays a pivotal role in altering its physical environment (Lovelock, 1988) and what once appeared to be biotic evolution in response to abiotic pressure is now seen as co-evolution of the biotic together with the abiotic to greater levels of complexity, stability, and entropy production (Ulanowicz and Hannon, 1987). Entropy production is the rate of the tendency to explore the multitude of microstates which underlie Nature. Such an understanding, difficult to reconcile within traditional Darwinian theory, fits perfectly well within the framework of non-equilibrium thermodynamics in which dissipative processes spontaneously arise and co-evolve so as to increase the entropy production of the system in its interaction with its environment (Prigogine, 1972, Ulanowicz and Hannon, 1987, Swenson, 1989, Kleidon and Lorenz, 2005, Michaelian, 2005, Michaelian, 2009a).

Life is found everywhere on Earth. On the surface, the components of greatest biomass are the archae, prokaryote, and eukaryote life based on photosynthesis. In the sea, photosynthetic phytoplankton (archaea, diatoms, cyanobacteria, and dinoflagellates) can be found in great density, of up to 10^9 /ml at the surface, and in the rest of the euphotic zone which extends to a depth of 50 meters. Almost all photosynthesis ends at the bottom of the Epipelagic zone at about 200 m. Approaching these depths, special pigments are needed to utilize the only faint blue light that can penetrate. On land, diatoms, cyanobacteria, and plants, which evolved from ocean cyanobacteria some 470 million years ago (Wellman and Gray, 2000; Raven and Edwards, 2001), cover almost every available area, becoming sparse only where conditions are extremely harsh, particularly where liquid water is scarce. Photosynthesizing cyanobacteria have been found thriving in hot springs at over 70 °C (Whitton and Potts, 2000) and on mountain glaciers and Antarctic ice (Parker et al., 1982) where absorption of solar radiation and its dissipation into heat by organic and lithogenic material within the ice provides the vital liquid water (Priscu et al., 2005).

The thermodynamic driving force for the process of photosynthesis that sustains surface life derives from the low entropy of sunlight and the second law of thermodynamics. Only twenty seven years after Darwin's publication of the theory of evolution through natural selection, Boltzmann (1886) wrote: "The general struggle for existence of animate beings is therefore not a struggle for raw materials – nor for energy which exists in plenty in any body in the form of heat -- but a struggle for entropy, which becomes available through the transition of energy from the hot sun to the cold earth". In photosynthesis, high-energy photons in the visible region of the Sun's spectrum are converted by the chloroplasts into low energy photons in the infrared region. Part of the free energy made available in the process is utilized to extract and fix in organic molecules the carbon from the absorbed atmospheric carbon dioxide and thereby maintain and propagate life. In this manner, photosynthetic life obtains its sustenance through the conversion of the low entropy of sunlight into the higher entropy of heat and thereby contributes to the positive entropy production of the Earth in its solar environment.

However, the proportion of the Sun's light spectrum utilized in photosynthesis is small and thus the entropy producing potential of photosynthesis is small. Gates (1980) has estimated that the percentage of available (free) energy in solar radiation that shows up in the net primary production of the biosphere is less than 0.1%. Respiration consumes a similarly small quantity (Gates, 1980). Of all the irreversible processes performed by living organisms, the process generating by far the greatest amount of entropy (consuming the greatest amount of free energy) is the absorption and dissipation of sunlight by organic molecules in the presence of water leading to *evapotranspiration*. Great quantities of water are absorbed by the root systems of plants and brought upwards to the leaves and then evaporated into the atmosphere. More than 90% of the free energy available in the sunlight captured by the leaves of plants is used in transpiration. In the oceans, phytoplankton within the euphotic zone absorb sunlight and transform it into heat that can be efficiently absorbed by the water. The temperature of the ocean surface is thereby raised by phytoplankton (Kahru et al., 1993) leading to increased evaporation, and in this manner promoting the water cycle. Microscopic zooplankton living off the phytoplankton cause continuous agitation of the surface water and thus increase evaporation from the surface by up to three times.

There appears to be no important intrinsic physiological need for the vast amount of transpiration

carried out by land plants. It is known, for example, that only 3% of the water drawn up by plants is used in photosynthesis and metabolism. In fact, most plants can grow normally under laboratory conditions of 100% humidity, at which the vapor pressure in the stoma of the leaves cannot be greater than that of the atmosphere, and therefore transpiration is necessarily zero (Hernández Candia, 2009). Transpiration has often been considered as an unfortunate by-product of the process of photosynthesis in which water is unavoidably given off through the stoma of plants which are open in order to exchange CO₂ and O₂ with the atmosphere (Gates, 1980). Plants consist of up to 90% water by mass and thus appear to expose themselves to great risk of drying by transpiring so much water. Others have argued that transpiration is useful to plants in that it helps to cool the leaves to a temperature optimal for photosynthesis. Such an explanation, however, is only marginally convincing since Nature has produced examples of efficient photosynthesis at temperatures of up to 70 °C (Whitton and Potts, 2000). In any case, there exists other simpler and less free energy demanding strategies to reduce leaf temperature such as smaller or less photo-absorbent leaves. On the contrary, the evolutionary record of life on Earth indicates that plants and phytoplankton have evolved new pigments to absorb ever more completely the Sun's spectrum. Dense pine forests appear black in the midday sun. Most plants appear green, not so much for lack of absorption at these wavelengths, as for the fact that the spectral response of the human eye peaks precisely at these wavelengths (Chang, 2000).

Transpiration is in fact extremely free energy intensive and, which, if we are to believe Darwinian Theory, such a process with little direct utility to the plant, should have been eliminated or suppressed through natural selection. Plants which are able to take in CO₂ while reducing water loss, by either opening their stoma only at night (CAM photosynthesis), or by reducing photorespiration (C₄ photosynthesis, see below), indeed have evolved 32 and 9 million years ago respectively (Osborne and Freckleton, 2009). However, the water conserving photosynthesis has not displaced the older, heavily transpiring C₃ photosynthesis which is still relevant for 95% of the biomass of Earth. Rather, new ecological niches in water scarce areas have opened up for the CAM and C₄ plants, as, for example, the cacti of deserts.

All irreversible processes, from diffusion to hurricanes, including living systems, arise and persist to produce entropy. Entropy production is not coincidental to the process, but rather the reason for the existence of the

process, and this is a fundamental principle of Nature which arises from the microscopic nature of material. Excessive transpiration has not been eliminated from plants, despite the extraordinary free energy costs, precisely because the basic thermodynamic function of a plant is to increase the global entropy production of the Earth in its solar environment, and this is achieved by dissipating high energy photons in the presence of water, thereby augmenting the global water cycle.

Materials and methods

The Water Cycle

Absorption of sunlight in the leaves of plants may increase their temperature by as much as 20°C over that of the ambient air (Gates, 1980). This leads to an increase of the H₂O vapor pressure inside the cavities of the leaf with respect to that of the colder surrounding air. H₂O vapor thus diffuses across this gradient of chemical potential from the wet mesophyll cell walls (containing the chloroplasts), through the intercellular cavities, and finally through the stoma and into the external atmosphere. There is also a parallel, but less efficient, circuit for diffusion of H₂O vapor in leaves through the cuticle, providing up to 10% more transpiration (Gates, 1980). The H₂O chemical potential of the air at the leaf surface itself depends on the ambient relative humidity and temperature, and thus on such factors as the local wind speed and insolation. Diffusion of H₂O vapor into the atmosphere causes a drop in the water potential inside the leaf which provides the force to draw up new water from the root system of the plants.

Evaporation from moist turf (dense cut grass) can reach 80% of that of a natural water surface such as a lake (Gates, 1980), while that of a tropical forest can often surpass by 200% that of such a water surface (Michaelian, 2009b). Single trees in the Amazon rain forest have been measured to evaporate as much as 1180 liters/day (Wullschleger *et al.*, 1998). This is principally due to the much larger surface area for evaporation that a tree offers with all of its leaves. Natural water surfaces, in turn, evaporate approximately 130% of distilled water surfaces due to the increased UV and visible photon absorption at the surface as a result of phytoplankton and other suspended organic materials, including a large component (up to 10⁹/ml at the surface) of viral and dissolved DNA resulting from viral lysing of bacteria (Wommack and Colwell, 2000).

The water vapor transpired by the leaves, or

evaporated by the phytoplankton, rises in the atmosphere, because water vapor at 0.804 g/l is less dense than dry air at 1.27 g/l, to a height corresponding to a temperature of about 259 K (-14 °C) (Newell *et al.*, 1974) at which it condenses around suspended microscopic particles forming clouds. Over oceans, an important constituent of these microscopic particles acting as seeds of condensation are the sulfate aerosols produced by the oxidation of dimethylsulfide released by the phytoplankton themselves (Charlson *et al.*, 1987). Condensation of the water releases an amount of latent heat of condensation (J /kg) into the upper atmosphere, much of which is then radiated into space at infrared wavelengths. In this manner, the Earth maintains its energy balance with space; the total energy incident on the biosphere in the form of sunlight is approximately equal to the total energy radiated by the biosphere into space at infrared wavelengths. Energy is conserved while the entropy of the Universe is augmented in the process, the first and second laws of thermodynamics are respected.

The formation of clouds may at first consideration seem to have a detrimental effect on the water cycle since cloud cover on Earth reflects approximately 20% of light in the visible and ultraviolet regions of the Sun's spectrum (Pidwirny and Budicova, 2008) and absorbs a large part of the direct infrared radiation, thereby reducing the potential for evaporation. However, evapotranspiration is a strong function of the local relative humidity of the air around the leaves of plants or above the surface of the oceans. By producing regions of local cooling during the day, and local heating during the night, on the Earth's surface, clouds are able to maintain the average wind speed at the Earth's surface within dense vegetation (see for example, Speck (2003)) at values above the threshold of 0.25 m/s required to make the boundary-layer resistance to water loss almost negligible in a plant leaf, thus procuring maximal transpiration rates (Gates, 1980).

Sublimation and ablation of ice over the polar regions, promoted in part by photon absorption of cyanobacteria within the ice, is also important to the water cycle, leading to the evaporation of up to 30 cm of ice per year (Priscu *et al.*, 2005).

Production of Entropy

The driving force of all irreversible processes, including the water cycle, is the *production of entropy*. The basic entropy producing process occurring on Earth is the absorption and dissipation of high energy photons to low energy photons, facilitated in large part by the plants and cyanobacteria in the presence of

water. The global entropy production of the Earth can be determined by considering the change in the frequency ν distributions of the radiation incident from

the Sun, $I_{incident}(\nu)$, and that radiated by the

Earth, $I_{radiated}(\nu)$ (Ulanowicz and Hannon, 1987).

The flow of photons can be considered as an ideal gas of Bose-Einstein particles for which the internal temperature T can be related to the frequency ν by the

relation $kT = h\nu$, where K is Boltzmann's constant and h is Planck's constant. Gibb's equation for the flow of entropy ds during time interval dt at a particular frequency ν is (Callen, 1985),

$$\frac{dS(\nu)}{dt} = \frac{1}{T(\nu)} \frac{dE(\nu)}{dt} = \frac{I(\nu)}{T(\nu)} \quad (1)$$

where $I(\nu) = \frac{dE(\nu)}{dt}$

is defined as the energy flow or irradiance at frequency ν , and where we have neglected the volume and chemical potential terms in the Gibb's equation since the volume of the global Earth-space system is constant and the chemical potential for photons is zero (Callen, 1985). The global production of entropy of the Earth in its interaction with its solar environment is then just the difference between the radiated and incident entropy flow integrated over all frequencies

$$P = \int_0^{\infty} \frac{dS_{radiated}(\nu)}{dt} - \frac{dS_{incident}(\nu)}{dt} d\nu.$$

Using equation (1) with $T(\nu) = h\nu/k$ gives

$$P = \frac{k}{h} \int_0^{\infty} (I_{radiated}(\nu) - I_{incident}(\nu)) / \nu d\nu. \quad (2)$$

A very approximate measure of this entropy production for the entire Earth can be obtained by making a black body assumption for the incident and radiated irradiances (Aoki, 1983). The Planck distribution law for the radiation emitted per unit area, per unit solid angle, per unit frequency, for a blackbody at temperature T is (Landau and Lifshitz, 1988)

$$I(\nu)|_r = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}. \quad (3)$$

Taking, $I_{radiated}$ as the average temperature of the

Earth surface, 287 K (14°C), and $I_{incident}$ as the temperature of the surface of the Sun, 6073 K (5800 °C), Eq. (2) with Eq. (3) gives as an approximation for the net entropy production of the Earth of $\text{J cm}^{-2} \text{s}^{-1} \text{K}^{-1}$,

about 50% greater than that of Earth's neighboring apparently lifeless planets of Venus and Mars (Aoki, 1983).

Equation (2) with Eq. (3) demonstrates that there is greater potential for entropy production for absorption and dissipation of high frequency light in the biosphere than for the absorption and dissipation of low frequency light. It is thus probably not coincidental that the present day atmosphere of the Earth has evolved to one of relatively low albedo and high atmospheric transparency such that the most intense highest frequencies of the Sun's spectrum can arrive at the biosphere and be efficiently dissipated by organic molecules in contact with liquid water. For example, there probably existed a thick organic haze, of high albedo in the visible, during part of the Archean from 2.9 – 2.7 Ga., responsible for global glaciations during this period (Zahnle et al., 2007). Organic haze is preferentially produced through ultraviolet photoreactions on an atmosphere with a methane over carbon dioxide ratio greater than or equal to one (CH_4/CO_2) which probably occurred ca. 2.9 Ga. (Lowe and Tice, 2004, Zahnle et al., 2007). Such a large ratio of these gases could have arisen due to enhanced weathering associated with continent formation and the resulting production of calcium carbonates eventually depleting the atmosphere of carbon dioxide (Zahnle et al., 2007). The organic haze existing today on Titan, for example, permits less than 10% of the visible light to reach the surface (Coustenis and Taylor, 1999). With the rapid spread of oxygen producing photosynthetic microbes in the late Archean ca. 2.5 Ga., it is probable that the CH_4/CO_2 ratio was driven below the critical value for haze formation due to oxidation of CH_4 . This scenario, pointing to the role of life in reducing the albedo of Earth's early atmosphere to allow greater entropy production, is consistent with two well established facts from the era; the green house effect necessary to explain the evidence for liquid water given a faint young Sun (the faint young Sun paradox), and evidence for glaciations around 2.9 Ga. (Lowe and Tice, 2004).

Comparison of the approximate calculations of Aoki (1983) for the entropy production of the different planets suggests that the biosphere may play a particularly important role in the entropy production of Earth. About 51% of the available energy arriving from the Sun in short wave radiation is absorbed in the biosphere (at the surface of the Earth), the rest being absorbed by the clouds and upper atmosphere (19%), reflected by the clouds or surface (24%), or scattered by the atmosphere back into space (6%) (Pidwirny and Budicova, 2008). About half of the available energy

arriving at the Earth's surface is used to evaporate the great quantities of water that is eventually returned to the Earth's surface in the form of rain. The other half is roughly equally divided between driving ocean and wind currents. As already mentioned, a negligible proportion of the free energy absorbed by the biosphere (< 0.2%) goes into the respiration and photosynthetic production of biomass. However, most of the visible and near ultraviolet spectra of sunlight (where the Sun is most intense in terms of free energy) is not readily absorbed by pure water, as can be deduced by the transparency of water at these wavelengths. Only infrared light can be efficiently absorbed by water and transferred to the vibrational, and a lesser fraction() to the rotational, degrees of freedom of the water molecules. This absorbed vibrational energy can then cause the breaking of hydrogen bonds binding water molecules and thereby facilitate evaporation at the water surface.

Organic molecules, due to the nature of the strong electronic covalent bonding, are efficient absorbers of sunlight in the visible and ultraviolet regions of the Sun's spectrum. The chlorophyll molecule and associated pigments absorb in the visible region between approximately 400 nm and 700 nm, with chlorophyll A peaking in absorption at 410 nm and 680 nm. The nucleic acids and proteins containing amino acids with aromatic rings (tyrosine, tryptophan, and phenylalanine) are particularly potent absorbers of ultra violet light within the 200-300 nm region due to the $\pi \rightarrow \sigma$, $\pi \rightarrow \sigma^*$, and $\sigma \rightarrow \sigma^*$ electronic transitions, with peak absorption for the nucleic acids at 260 nm and that for proteins at 280 nm (Chang, 2000). Mycosporine-like amino acids (MAA's) found in phytoplankton absorb across the UVB and UVA regions (310-400 nm) (Whitehead and Hedges, 2002). The amount of ultraviolet light reaching the Earth's surface today, particularly in the 2 and thus this region plays a very small part in the entropy production of the biosphere in association with the water cycle, but this may not have been the case at the beginnings of life on Earth (Michaelian, 2009a). During the archaean, the Sun was more active in the ultraviolet and the Earth's atmosphere was more reflective and absorptive in the visible and infrared, while less so in the ultraviolet. This may have been due to a high layer of sulfuric acid clouds as on Venus today, the result of UV photochemical reactions with the most common volcanic gases of SO_2 , CO_2 , and H_2O , or to clouds of water, or to organic haze as on Titan today, the result of UV photochemical reactions on CO_2 and CH_4 (Lowe and Tice, 2004).

The Importance of Life to the Water Cycle

The very existence of liquid water on Earth can be attributed, in part, to the existence of life. Physical mechanisms exist that disassociate water into its hydrogen and oxygen components, for example through photo-dissociation of water by ultraviolet light (Chang, 2000). Photo-dissociation of methane has been suggested as a more important path to losing the hydrogen necessary for water (Catling et al., 2001). Free hydrogen, being very light, can escape Earth's gravity and drift into space, being dragged along by the solar wind. This loss of hydrogen would have led to a gradual depletion of the Earth's water, as appears to have occurred on Venus (Lovelock, 2005). Although Earth's magnetic field has helped reduce the effects of the solar wind on hydrogen loss, life also appears to have played a part. Photosynthetic life releases oxygen from carbon dioxide thereby providing the potentiality for its recombination with the free hydrogen to produce water. For example, hydrogen sulfide is oxidized by aerobic chemoautotrophic bacteria, giving water as a waste product (Lovelock, 1988). Oxygen released by photosynthetic life also forms ozone in the upper atmosphere which protects water vapor and methane in the lower atmosphere from ultraviolet photo-dissociation. In this manner, life on Earth has kept the amount of water on Earth relatively constant since the beginnings of life. Through mechanisms related to the regulation of atmospheric carbon dioxide first espoused in the Gaia hypothesis (Lovelock, 1988), life has also been able to maintain the temperature of the Earth within the narrow region required for liquid water, even though the amount of radiation from the Sun has increased by as much as 30% since the beginnings of life (Newman and Rood, 1977, Gough, 1981).

It has been estimated that about 496,000 km³ of water is evaporated yearly, with 425,000 km³ (86%) of this coming from the ocean surface and the remaining 71,000 km³ (14%) from the land (Hubbart and Pidwirny, 2007). Evaporation rates depend on numerous physical factors such as insolation, photon absorption properties of the atmosphere and water, temperature, relative humidity, and local wind speed. Most of these factors are interconnected and non-linearly coupled. For example, local variations in sea surface temperature due to differential photon absorption rates caused by clouds or local phytoplankton blooms, leads to local wind currents. Global winds are driven by latitude variation of the solar irradiance and absorption, and the rotation of the Earth. Relative humidity is a function of temperature but also a function of the quantity of microscopic particles available for seeds of condensation, a significant amount of which are

supplied by biology (Lovelock, 1988).

The non-linear couplings of the different biotic and abiotic factors affecting the water cycle imply that quantifying the effect of one particular component, such as biology, on the water cycle is very difficult. However, simulations using climate models taking into account most of the important physical factors have been used to estimate the importance of vegetation on land to evapotranspiration and entropy production. Kleidon (2008) has estimated that without plants, average evaporation rates on land would decrease from their actual average values of 2.4 mm/d to 1.4 mm/d, suggesting that plants may be responsible for as much as 42% of the actual evaporation over land.

There appears to be little recognition in the literature of the importance of cyanobacteria and other living and non-living organic matter floating at the ocean surface to evaporation rates. Irrespective of other factors such as wind speed and humidity, there should at least be some relation between evaporation rates and the solar energy deposited in the sea-surface layer. Before attempting a calculation of the effect of biology on evaporation rates over oceans and lakes, it is relevant to review the physical and biological nature of the air-sea surface interface based on knowledge that has emerged over the last two decades.

The ocean skin surface layer of roughly 1 mm thickness has its particular ecosystem of high density in organic material (up to 10^4 the density in water slightly below (Grammatika and Zimmerman, 2001)). This is due to the scavenging action of rising air bubbles from breaking waves and raindrops, surface tension, and natural buoyancy (Grammatika and Zimmerman, 2001). The organic material consists of cyanobacteria, diatoms, viruses, free floating RNA/DNA, and other living and non-living organic material such as chlorophyll and other pigments. Most of the heat exchange between the ocean and atmosphere of today occurs from within this upper 1 mm of ocean water. For example, most of the radiated infrared radiation from the sea comes from the upper 100 m (Schlüssel, 1999). About 52% of the heat transfer from this ocean layer to atmosphere is in the form of latent heat (evaporation), radiated long-wave radiation accounts for 33%, and sensible heat through direct conduction accounts for the remaining 15%.

During the day, infrared (700-10000 nm), visible (400-700 nm), and ultraviolet (290-400nm) light is absorbed at the sea surface. In the NE Atlantic, for example, daytime temperatures at the skin surface have been measured to increase on average by 2.5K (up to 4.0K) compared to the practically constant temperature at an ocean depth of 10m (Schlüssel et

al., 1990). Nighttime temperatures at the surface, on the contrary, are decreased on average by 0.5K (up to 0.8K) with respect to the constant temperature at a depth of 10m. It is thus of interest to determine how much of this day-time heating is due to the organic material in this layer, and the relative contributions due to UV, visible, or infrared radiation. Such a determination will allow an estimate of the effect of life on the evaporation of water over oceans and the associated entropy production, under both clear and cloudy skies. For the sake of calculation, we take the surface skin layer for light absorption and heat exchange to the atmosphere to be 1mm (this should be an upper limit for the relevant thickness for energy exchange since below this depth turbulence and mixing with lower ocean depths becomes relevant (Soloviev and Lukas, 2006) and the amount of organic material drops off significantly (Grammatika and Zimmerman, 2001)).

Three distinct wavelength regions are considered for the calculation; 290-400 nm (UV) (below 290 nm almost all light is absorbed by atmospheric O_3), 400-700 nm (visible), and 700-10000 nm (infrared). The blackbody spectrum of the Earth at 287K (14°C) peaks at 10000 nm so absorption at greater wavelengths than this would not contribute to net heating. There is, in any case, very little energy in sunlight beyond this wavelength. We first calculate the total amount of energy arriving at the sea surface in each wavelength region for a clear sky with no clouds and the sun directly overhead. This can be obtained by integrating the area under a plot of the irradiance at the Earth's surface as a function of wavenumber, such as that given by Gates (1980, Fig. 8.17). The result is given in the first row of table 1.

To calculate the amount of energy deposited per unit time in each wavelength region within the 1mm skin layer of pure ocean water without organic material, we use an average water absorption coefficient corresponding to a wavelength at the middle of the UV and visible wavelength ranges (345 nm and 550 nm respectively), whereas for the infrared region we use the absorption value at 1050 nm since this corresponds to the greatest incident contribution not absorbed by water vapor in the atmosphere (see Fig. 8.17 of Gates, 1980), and because the irradiance drops off sharply at greater wavelengths. Chaplin (2009) give the following absorption coefficients for pure water;

$$A_{\text{V}}^{345} = 1.0 \times 10^{-4} \text{ cm}^{-1}, A_{\text{V}}^{550} = 8.0 \times 10^{-4} \text{ cm}^{-1}, A_{\text{V}}^{1050} = 0.2 \text{ cm}^{-1}$$

The flux of energy deposited in the skin layer is then

$$\Delta I = (I_0 - I(x)) = I_0(1 - \exp(-Ax)) \quad (4)$$

with $x = 0.1 \text{ cm}$ and A is the relevant absorption coefficient. The results are given in the second row of table 1.

To calculate the amount of energy per unit time deposited within the 1mm skin layer of ocean water *with* organic material for each wavelength region, we need the absorption coefficients for the ocean surface microlayer at the different wavelengths. Unfortunately, there do not appear to be any published data in this regard. However, Grammatika and Zimmerman, (2001) suggest that the skin microlayer contains up to 10^4 times the density of organic material as water slightly below. This factor of 10^4 is an order of magnitude greater than that of the ratio between the densities of organic matter in very turbid coastal waters to that of deep sea water (Wommack and Colwell, 2000). We therefore take the absorption coefficients for coastal turbid waters obtained for the Baltic Sea by Bricaud et al. (1981, Fig. 3) as a lower limit surrogate to that of the surface skin layer of the ocean, giving

$$A_{\text{org}}^{345} = 0.1 \text{ cm}^{-1}, A_{\text{org}}^{550} = 8.0 \times 10^{-3} \text{ cm}^{-1}, A_{\text{org}}^{1050} = 0.2 \text{ cm}^{-1}$$

The value for the infrared absorption is the same as that for pure water since organic molecules absorb very little compared to water in this wavelength region. Using equation (4) with these values we obtain the third row of table 1.

By comparing the third row with the second row of table 1 it can be determined that on a clear day, with the sun directly overhead (air mass of 1.0), the organic matter floating in the surface skin layer increases the absorption of energy in this layer by about 13% over what its value would be without this organic matter. Since, for a relatively temperature independent heat capacity of water, the temperature of the skin layer would increase by a similar percentage, and since the water vapor pressure increases exponentially with temperature, the increase in the rate of evaporation would be significantly greater than 13%. This is consistent with the measured increase in the latent outgoing heat flux for nutrient induced phytoplankton blooms in an enclosed area of a lake as determined by Jones et al. (2005). It is interesting to note that the absorption of UV light by organic material in water contributes more than double the amount of that due to absorption of visible light.

The relative contribution to the entropy production in the sea surface microlayer resulting from photon absorption and dissipation in each wavelength region

can now be approximated by calculating the increase in the number of energy microstates resulting from dissipating a high energy photon into many long wavelength photons (10,000 nm, corresponding to the wavelength of the peak in the black-body spectrum of the Earth at 287 K (Gates, 1980)). The relative number of 10,000 nm photons produced by absorption and dissipation in each wavelength region can be obtained by simply dividing the energy of a photon at the central wavelength in each wavelength region by the energy of a 10,000 nm photon and then weighting this number by the proportion of the total flux of energy deposited in the microlayer in this wavelength region (row 3 of Table 1).

The Boltzmann relation gives the entropy produced as just proportional to the natural logarithm of this number of created microstates. Dividing the entropy produced in each wavelength region by the sum total for all regions gives the percentage contribution to the total for each region. The result is given in the fourth row of Table 1. By absorbing and dissipating UV and visible light, the organic matter in the sea surface microlayer contributes about $33.2 + 20.4 = 53.6\%$ to the total entropy production in this layer (fourth row of table 1).

In the case of an overcast day, much less infrared radiation arrives at the ocean surface because of the strong absorption of infrared by water drops in clouds (see Fig. 8.17 of Gates, 1980). We take the water absorption coefficients corresponding to the middle of the regions to be again 345 nm for UV and 550 nm for visible, but 800 nm for infrared (since from Fig. 8.17 of Gates the infrared light distribution transmitted through the atmosphere is shifted notably towards shorter wavelengths due to the preferential absorption of the longer wavelengths by clouds). The results for an overcast day for the sea surface skin layer with and without organic matter are given in table 2.

Comparing the third row with the second row of table 2 it can be determined that on an overcast day, with the sun directly overhead (air mass of 1.0) the organic matter floating in the surface skin layer increases the absorption of energy in this layer by about 400% over what the value would be without the organic matter, with equal contributions coming from UV and visible light. However, the total energy absorbed in this skin layer on an overcast day is only about 5% that of a clear day, due principally to the comparatively small amount of infrared light that makes it through the clouds. By absorbing and dissipating UV and visible light, the organic matter in this layer contributes about $55.2 + 41.3 = 96.5\%$ to the total entropy production on a cloudy day

By absorbing and dissipating UV and visible light on

the surface of oceans and lakes, life therefore augments the entropy production of the Earth in its solar environment. Without life at the surface, a greater portion of light would be reflected, thereby increasing the albedo of Earth (Clarke et al. (1970) gives measurements of the reduction of water albedo due to the presence of organic material), and light would penetrate deeper into the ocean, thereby augmenting the overall bulk blackbody temperature of the ocean (see, for example, Jones et al. (2005) for the effect of phytoplankton on the temperature profile with depth for a lake). Both reduce the entropy production of Earth; the former by reducing the amount of available light to dissipate, and the latter by shifting the frequencies of the daily (day-night) integrated radiated spectrum of the sea surface to higher values (see Eq. (2)) since this excess heat in bulk cannot be as easily coupled to the water cycle as surface heat.

Evidence for Evolutionary Increases in the Water Cycle

Plants, far from eliminating transpiration as a wasteful use of free energy, have in fact evolved ever more efficient water transport and transpiration systems (Sperry, 2003). There are general trends over evolutionary time, and in ecosystem succession over shorter time, to ever increasing transpiration rates. For example, conifer forests are more efficient at transpiration than deciduous forests principally because of the greater surface area offered for evaporation by needles as compared to leaves. Conifers appeared later in the fossil record (late carboniferous) and appear in the late successional stage of ecosystems. Root systems are also much more extended in late evolutionary and successional species, allowing them to access water at ever greater depths (Raven and Edwards, 2001).

New pigments besides chlorophyll have appeared in the evolutionary history of plants and cyanobacteria, covering an ever greater portion of the intense region of the solar spectrum, even though they have little or no effect on photosynthesis, for example, the carotenoids in plants, or the MAA's found in phytoplankton which absorb across the UVB and UVA regions (310-400 nm) (Whitehead and Hedges, 2002). This is particularly notable in red algae, for example, where its total absorption spectrum has little correspondence with its photosynthetic activation spectrum (Berkaloff *et al.*, 1971).

There exist complex mechanisms in plants to dissipate photons directly into heat, by-passing completely photosynthesis. These mechanisms come in a number of distinct classes and involve inducing the

de-excitation of chlorophyll using dedicated enzymes and proteins. Constitutive mechanisms, allow for intersystem crossing of the excited chlorophyll molecule into triplet, long-lived, states which are subsequently quenched by energy transfer to the carotenoids. Inducible mechanisms are mechanisms that can be regulated by the plant itself, for example, changing lumen pH causes the production of special enzymes that permit the non-photochemical de-excitation of chlorophyll. Sustained mechanisms are similar to inducible mechanisms but have been adapted to long term environmental stress. For example, over wintering evergreen leaves produce little photosynthesis due to the extreme cold but continue transpiring by absorbing photons and degrading these to heat through non-photochemical de-excitation of chlorophyll. Hitherto, these mechanisms were considered as "safety valves" for photosynthesis, protecting the photosynthetic apparatus against light-induced damage (Niyogi, 2000). However, their existence and evolution can better be understood in a thermodynamic context as augmenting the entropy production potential of the plant through increasing transpiration rates.

The recent findings of microsporine-like amino acids (MAAs) produced by plants and phytoplankton having strong absorption properties in the UVB and UVA regions lends support to the hypothesis of this paper. Their discovery came first in fungi (Leach, 1965). They are small (< 400 Da), water-soluble compounds composed of aminocyclohexenone or aminocycloheximine rings with nitrogen or imino alcohol substituents (Carreto et al., 1990) which display strong UV absorption maximum between 310 and 360 nm and high molar extinction (Whitehead and Hedges, 2002). These molecules have been assigned a UV photoprotective role in these organisms, but this appears dubious since, in some cases, more than 20 MAAs have been found in the same organism, each with different but overlapping absorption spectrum, determined by the particular molecular side chains (Whitehead and Hedges, 2002). If their principle function were photoprotective, then their existence in a particular plant or phytoplankton would be confined to those microsporine of particular UV wavelengths that cause damage to the photosynthetic apparatus, and not to the whole UV broadband spectrum.

Plants also perform a free energy intensive process known as photorespiration in which O₂ instead of CO₂ is captured by the binding enzyme RuBisCo, the main enzyme of the light-independent part of photosynthesis. This capture of O₂ instead of CO₂ (occurring about 25% of the time) is detrimental to the

plant for a number of reasons, including the production of toxins that must be removed (Govindjee, 2005) and does not lead to ATP production. There is no apparent utility to the plant in performing photorespiration and in fact it reduces the efficiency of photosynthesis. It has often been considered as an “evolutionary relic” (Niyogi, 2000), still existing from the days when O₂ was less prevalent in the atmosphere than today, and CO₂ more so (0.78% CO₂ by volume at the rise of land plants during the Ordovician (ca. 470 Ma) compared with only 0.038% today).

However, such an explanation is not in accord with the known efficacy of natural selection to eliminate useless or wasteful processes. Another theory has photorespiration as a way to dissipate excess photons and electrons and thus protect the plants photosynthesizing system from excess light-induced damage (Niyogi, 2000). Since photorespiration is common to all C₃ plants, independent of their preferred insolation environments, it is more plausible that photorespiration, being completely analogous to photosynthesis with respect to the dissipation of light into heat in the presence of water (by quenching of excited chlorophylls) and subsequent transpiration of water, is retained for its complimentary role in evapotranspiration and thus entropy production.

Plants not only evaporate water during sunlight hours, but also at night (Snyder et al., 2003). Common house plants evaporate up to 1/3 of the daily transpired water at night (Hernández Candía, 2009). Not all the stomata in C₃ and C₄ photosynthetic plants are closed at night and some water vapor also diffuses through the cuticle at night. A physiological benefit to the plant for night transpiration, if indeed one exists, remains unclear. It, of course, can have no relevance to cooling leaves for optimal photosynthetic rates. Explanations range from improving nutrient acquisition, recovery of water conductance from stressful daytime xylem cavitation events, and preventing excess leaf turgor when water potentials become large during the day (Snyder et al., 2003). However, night transpiration is less of an enigma if considered as a complement to the thermodynamic function of life to augment the entropy production of Earth through coupling with the water cycle. In this context, it is also relevant that chlorophyll has an anomalous absorption peak in the infrared between about 4,000 and 10,000 nm (Gates, 1980), just at the wavelengths at which the blackbody radiation of the Earth's surface at 14 °C peaks.

Cyanobacteria have been found to be living within Antarctic ice at depths of up to 2 m. These bacteria and other lithogenic material in the ice absorb solar radiation which causes the formation of liquid water

within the ice even though the outside air temperatures may be well below freezing. This heating from below causes excess ablation and sublimation of the overlying ice at rates as high as 30 cm per year (Priscu *et al.*, 2005).

Finally, by analyzing latent heat fluxes (evaporation) and the CO₂ flux for plants from various published data sets, Wang et al. (2007) have found vanishing derivatives of transpiration rates with respect to leaf temperature and CO₂ flux, suggesting a maximum transpiration rate for plants, i.e. that the particular partition of latent and sensible heat fluxes is such that it leads to a leaf temperature and leaf water potential giving maximal transpiration rates, and thus also maximal production of entropy (Wang et al., 2007).

The Function of Animals

If the primary thermodynamic function of the plants and cyanobacteria is to augment the entropy production of the Earth by absorbing light in the presence of liquid water, it may then be asked: What is the function of higher mobile animal life?

Because of their intricate root system which allows the plants to draw up water for evaporation from great depths, plants are not mobile and depend on insects and other animals for their supply of nutrients, cross fertilization, and seed dissemination and dispersal into new environments. The mobility and the short life span of insects and animals mean that through excrement and eventual death, they provide such a reliable mechanism for dispersal of nutrients and seeds.

Crustaceans and animal marine life in water perform a similar function as insect and animal life on land. These higher forms of life distribute nutrients throughout the ocean surface through excrement and dying. It is noteworthy that dead fish and mammals do not sink rapidly to the bottom of the sea or lake, but remain floating for considerable time on the surface where, as on land, bacteria break down the organism into its molecular components, allowing photon dissipating phytoplankton to reuse the nutrients, particularly nitrogen. It is relevant that many algae blooms produce a neurotoxin with apparently no other end than to kill higher marine life. There is also a continual cycling of nutrients from the depths of the ocean to the surface as deep diving mammals preying on bottom feeders release nutrients at the surface through excrement and death. Because of this nutrient cycling due to the mobility of animals, a much larger portion of the ocean surface is rendered suitable for phytoplankton growth, offering a much larger area for efficient surface absorption of sunlight and evaporation of water than would otherwise be the case.

From this thermodynamic viewpoint, animal life provides a specialized gardening service to the plants and cyanobacteria, which in turn catalyze the absorption and dissipation of sunlight in the presence of water, promoting entropy production through the water cycle. There is strong empirical evidence suggesting that ecosystem complexity, in terms of species diversity, is correlated with potential evapotranspiration (Gaston, 2000). The traditional ecological pyramid should thus be turned on its pinnacle. Instead of plants and phytoplankton being considered as the base that sustains animal life, animals are in fact the unwitting servants of plant and phytoplankton life, obtaining thermodynamic relevance only in how they increase the plant and phytoplankton potential for evaporation of water.

Conclusion

We have argued that the basic thermodynamic function of life (and organic material in general) is to absorb and dissipate high energy photons such that the heat can be absorbed by liquid water and eventually transferred to space through the water cycle. Photosynthesis, although relevant to the spread of cyanobacteria and plant growth, has only minor direct relevance to the thermodynamic function of life, which is the production of entropy. By augmenting the water cycle through increased photon absorption, radiationless dissipation, extended root systems, and larger surface areas for evaporation, life augments the entropy production of the Earth in its interaction with its solar environment. The effect of land surface life on the evaporation of water and entropy production has been quantified by Klieidon (2008). We have made quantitative estimates of the effect of ocean surface life on the water cycle and entropy production. We have presented empirical evidence indicating that the evolutionary history of Earth's biosphere is one of increased photon absorption and dissipation over time, whether over shorter successional, or longer evolutionary, time scales. Finally, we have presented arguments for a revision of the traditional view of life in terms of its thermodynamic entropy producing function, rather than simply as a self perpetuating accident.

Important aspects that remain to be considered under this thermodynamic framework are the oscillation of the Earth between different climate regimes (e.g. glaciations) if this can entropy production can be used as an indicator of Lovelock's preference for glaciations, implications of the proposed function of life to the probability of the existence of life throughout the universe, and the importance of the thermodynamic

function of life in investigations related to the origin of life on Earth.

This thermodynamic perspective on life views it as a catalyst for entropy production through the water cycle, and ocean and wind currents. It ties biotic processes to abiotic processes with the universal goal of increasing Earth's global entropy production and thus provides a framework within which co-evolution of the biotic with the abiotic can be accommodated. Although this view is much in line with the wisdom obtained from the philosophy of Gaia, there is an important distinction. The hypothesis of Gaia suggests that mixed biotic-abiotic control mechanisms have evolved to maintain the conditions on Earth suitable to life, and therefore, in the interest of life. It is here suggested instead that these biotic-abiotic mechanisms have evolved to augment the entropy production of Earth in its solar environment, principally, but not exclusively, through the facilitation of the water cycle. Life, as we know it, is an important, perhaps even inevitable, but probably not indispensable, catalyst for the production of entropy on Earth.

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Illustrations

Illustration 1

Article

The Water Cycle

Absorption of sunlight in the leaves of plants may increase their temperature by as much as 20°C over that of the ambient air (Gates, 1980). This leads to an increase of the H₂O vapor pressure inside the cavities of the leaf with respect to that of the colder surrounding air. H₂O vapor thus diffuses across this gradient of chemical potential from the wet mesophyll cell walls (containing the chloroplasts), through the intercellular cavities, and finally through the stoma and into the external atmosphere. There is also a parallel, but less efficient, circuit for diffusion of H₂O vapor in leaves through the cuticle, providing up to 10% more transpiration (Gates, 1980). The H₂O chemical potential of the air at the leaf surface itself depends on the ambient relative humidity and temperature, and thus on such factors as the local wind speed and insolation. Diffusion of H₂O vapor into the atmosphere causes a drop in the water potential inside the leaf which provides the force to draw up new water from the root system of the plants.

Evaporation from moist turf (dense cut grass) can reach 80% of that of a natural water surface such as a lake (Gates, 1980), while that of a tropical forest can often surpass by 200% that of such a water surface (Michaelian, 2009b). Single trees in the Amazon rain forest have been measured to evaporate as much as 1180 liters/day (Wullschleger *et al.*, 1998). This is principally due to the much larger surface area for evaporation that a tree offers with all of its leaves. Natural water surfaces, in turn, evaporate approximately 130% of distilled water surfaces due to the increased UV and visible photon absorption at the surface as a result of phytoplankton and other suspended organic materials, including a large component (up to 10⁹/ml at the surface) of viral and dissolved DNA resulting from viral lysing of bacteria (Wommack and Colwell, 2000).

The water vapor transpired by the leaves, or evaporated by the phytoplankton, rises in the atmosphere, because water vapor at 0.804 g/l is less dense than dry air at 1.27 g/l, to a height corresponding to a temperature of about 259 K (-14 °C) (Newell *et al.*, 1974) at which it condenses around suspended microscopic particles forming clouds. Over oceans, an important constituent of these microscopic particles acting as seeds of condensation are the sulfate aerosols produced by the oxidation of dimethylsulfide released by the phytoplankton themselves (Charlson *et al.*, 1987). Condensation of the water releases an amount of latent heat of condensation (2.427×10^6 J/kg) into the upper atmosphere, much of which is then radiated into space at infrared wavelengths. In this manner, the Earth maintains its energy balance with space; the total energy incident on the biosphere in the form of sunlight is approximately equal to the total energy radiated by the biosphere into space at infrared wavelengths. Energy is conserved while the entropy of the Universe is augmented in the process, the first and second laws of thermodynamics are respected.

The formation of clouds may at first consideration seem to have a detrimental effect on the water cycle since cloud cover on Earth reflects approximately 20% of light in the visible and ultraviolet regions of the Sun's spectrum (Pidwirny and Budicova, 2008) and absorbs a large part of the direct infrared radiation, thereby reducing the potential for evaporation. However, evapotranspiration is a strong function of the local relative humidity of the air around the leaves of plants or above the surface of the oceans. By producing regions of local cooling during the day, and local heating during the night, on the Earth's surface, clouds are able to maintain the average wind speed at the Earth's surface within dense vegetation (see for example, Speck (2003)) at values above the threshold of 0.25 m/s required to make the boundary-layer resistance to water loss almost negligible in a plant leaf, thus procuring maximal transpiration rates (Gates, 1980).

Sublimation and ablation of ice over the polar regions, promoted in part by photon absorption of cyanobacteria within the ice, is also important to the water cycle, leading to the evaporation of up to 30 cm of ice per year (Priscu *et al.*, 2005).

Production of Entropy

The driving force of all irreversible processes, including the water cycle, is the *production of entropy*. The basic entropy producing process occurring on Earth is the absorption and dissipation of high energy photons to low energy photons, facilitated in large part by the plants and cyanobacteria in the presence of water. The global entropy production of the Earth can be determined by considering the change in the frequency ν distributions of the radiation incident from the Sun, $I_{incident}(\nu)$, and that radiated by the Earth, $I_{radiated}(\nu)$ (Ulanowicz and Hannon, 1987). The flow of photons can be considered as an ideal gas of Bose-Einstein particles for which the internal temperature T can be related to the frequency ν by the relation $kT = h\nu$, where k is Boltzmann's constant and h is Planck's constant. Gibb's equation for the flow of entropy dS during time interval dt at a particular frequency ν is (Callen, 1985),

$$\frac{dS(\nu)}{dt} = \frac{1}{T(\nu)} \frac{dE(\nu)}{dt} = \frac{I(\nu)}{T(\nu)} \quad (1)$$

where $I(\nu) \equiv \frac{dE(\nu)}{dt}$

is defined as the energy flow or irradiance at frequency ν , and where we have neglected the volume and chemical potential terms in the Gibb's equation since the volume of the global Earth-space system is constant and the chemical potential for photons is zero (Callen, 1985). The global production of entropy of the Earth in its interaction with its solar environment is then just the difference between the radiated and incident entropy flow integrated over all frequencies

$$P = \int_0^{\infty} \frac{dS_{\text{radiated}}(\nu)}{dt} - \frac{dS_{\text{incident}}(\nu)}{dt} d\nu.$$

Using equation (1) with $T(\nu) = h\nu/k$ gives

$$P = \frac{k}{h} \int_0^{\infty} (I_{\text{radiated}}(\nu) - I_{\text{incident}}(\nu)) / \nu d\nu. \quad (2)$$

A very approximate measure of this entropy production for the entire Earth can be obtained by making a black body assumption for the incident and radiated irradiances (Aoki, 1983). The Planck distribution law for the radiation emitted per unit area, per unit solid angle, per unit frequency, for a blackbody at temperature T is (Landau and Lifshitz, 1988)

$$I(\nu)|_r = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}. \quad (3)$$

Taking, T_{radiated} as the average temperature of the Earth surface, 287 K (14°C), and T_{incident} as the temperature of the surface of the Sun, 6073 K (5800 °C), Eq. (2) with Eq. (3) gives as an approximation for the net entropy production of the Earth of $1.19 \times 10^{-4} \text{ J cm}^{-2} \text{ s}^{-1} \text{ K}^{-1}$, about 50% greater than that of Earth's neighboring apparently lifeless planets of Venus and Mars (Aoki, 1983).

Equation (2) with Eq. (3) demonstrates that there is greater potential for entropy production for absorption and dissipation of high frequency light in the biosphere than for the absorption and dissipation of low frequency light. It is thus probably not coincidental that the present day atmosphere of the Earth has evolved to one of relatively low albedo and high atmospheric transparency such that the most intense highest frequencies of the Sun's spectrum can arrive at the biosphere and be efficiently dissipated by organic molecules in contact with liquid water. For example, there probably existed a thick organic haze, of high albedo in the visible, during part of the Archean from 2.9 – 2.7 Ga., responsible for global glaciations during this period (Zahnle et al., 2007). Organic haze is preferentially produced through ultraviolet photoreactions on an atmosphere with a methane over carbon dioxide ratio greater than or equal to one ($\text{CH}_4/\text{CO}_2 \geq 1$) which probably occurred ca. 2.9 Ga. (Lowe and Tice, 2004, Zahnle et al., 2007). Such a large ratio of these gases could have arisen due to enhanced weathering associated with continent formation and the resulting production of calcium carbonates eventually depleting the atmosphere of carbon dioxide (Zahnle et al., 2007). The organic haze existing today on Titan, for example, permits less than 10% of the visible light to reach the surface (Coustenis and Taylor, 1999). With the rapid spread of oxygen producing photosynthetic microbes in the late Archean ca. 2.5 Ga., it is probable that the CH_4/CO_2 ratio was driven below the critical value for haze formation due to oxidation of CH_4 . This scenario, pointing to the role of life in reducing the albedo of Earth's early atmosphere to allow greater entropy production, is consistent with two well established facts from the era; the green house effect necessary to explain the evidence for liquid water given a faint young Sun (the faint young Sun paradox), and evidence for glaciations around 2.9 Ga. (Lowe and Tice, 2004).

Comparison of the approximate calculations of Aoki (1983) for the entropy production of the different planets suggests that the biosphere may play a particularly important role in the entropy production of Earth. About 51% of the available energy arriving from the Sun in short wave radiation is absorbed in the biosphere (at the surface of the Earth), the rest being absorbed by the clouds and upper atmosphere (19%), reflected by the clouds or surface (24%), or scattered by the atmosphere back into space (6%) (Pidwirny and Budicova, 2008). About half of the available energy arriving at the Earth's surface is used to evaporate the great quantities of water that is eventually returned to the Earth's surface in the form of rain. The other half is roughly equally divided between driving ocean and wind currents. As already mentioned, a negligible proportion of the free energy absorbed by the biosphere ($< 0.2\%$) goes into the respiration and photosynthetic production of biomass. However, most of the visible and near ultraviolet spectra of sunlight (where the Sun is most intense in terms of free energy) is not readily absorbed by pure water, as can be deduced by the transparency of water at these wavelengths. Only infrared light can be efficiently absorbed by water and transferred to the vibrational, and a lesser fraction ($< 10^{-4}$) to the rotational, degrees of freedom of the water molecules. This absorbed vibrational energy can then cause the breaking of hydrogen bonds binding water molecules and thereby facilitate evaporation at the water surface.

Organic molecules, due to the nature of the strong electronic covalent bonding, are efficient absorbers of sunlight in the visible and ultraviolet regions of the Sun's spectrum. The chlorophyll molecule and associated pigments absorb in the visible region between approximately 400 nm and 700 nm, with chlorophyll A peaking in absorption at 410 nm and 680 nm. The nucleic acids and proteins containing amino acids with aromatic rings (tyrosine, tryptophan, and phenylalanine) are particularly potent absorbers of ultra violet light within the 200-300 nm region due to the $\pi \rightarrow \sigma$, $\pi \rightarrow \sigma^*$, and $\sigma \rightarrow \sigma^*$ electronic transitions, with peak absorption for the nucleic acids at 260 nm and that for proteins at 280 nm (Chang, 2000). Mycosporine-like amino acids (MAA's) found in phytoplankton absorb across the UVB and UVA regions (310-400 nm) (Whitehead and Hedges, 2002). The amount of ultraviolet light reaching the Earth's surface today, particularly in the <290 nm UVC wavelength region, is very small compared to that of UVB+UVA and visible light due to absorption by ozone and O₂ and thus this region plays a very small part in the entropy production of the biosphere in association with the water cycle, but this may not have been the case at the beginnings of life on Earth (Michaelian, 2009a). During the archaean, the Sun was more active in the ultraviolet and the Earth's atmosphere was more reflective and absorptive in the visible and infrared, while less so in the ultraviolet. This may have been due to a high layer of sulfuric acid clouds as on Venus today, the result of UV photochemical reactions with the most common volcanic gases of SO₂, CO₂, and H₂O, or to clouds of water, or to organic haze as on Titan today, the result of UV photochemical reactions on CO₂ and CH₄ (Lowe and Tice, 2004).

The Importance of Life to the Water Cycle

The very existence of liquid water on Earth can be attributed, in part, to the existence of life.

Physical mechanisms exist that disassociate water into its hydrogen and oxygen components, for example through photo-dissociation of water by ultraviolet light (Chang, 2000).

Photo-dissociation of methane has been suggested as a more important path to losing the hydrogen necessary for water (Catling et al., 2001). Free hydrogen, being very light, can escape Earth's gravity and drift into space, being dragged along by the solar wind. This loss of hydrogen would have led to a gradual depletion of the Earth's water, as appears to have occurred on Venus (Lovelock, 2005). Although Earth's magnetic field has helped reduce the effects of the solar wind on hydrogen loss, life also appears to have played a part. Photosynthetic life releases oxygen from carbon dioxide thereby providing the potentiality for its recombination with the free hydrogen to produce water. For example, hydrogen sulfide is oxidized by aerobic chemoautotrophic bacteria, giving water as a waste product (Lovelock, 1988). Oxygen released by photosynthetic life also forms ozone in the upper atmosphere which protects water vapor and methane in the lower atmosphere from ultraviolet photo-dissociation. In this manner, life on Earth has kept the amount of water on Earth relatively constant since the beginnings of life. Through mechanisms related to the regulation of atmospheric carbon dioxide first espoused in the Gaia hypothesis (Lovelock, 1988), life has also been able to maintain the temperature of the Earth within the narrow region required for liquid water, even though the amount of radiation from the Sun has increased by as much as 30% since the beginnings of life (Newman and Rood, 1977, Gough, 1981).

It has been estimated that about 496,000 km³ of water is evaporated yearly, with 425,000 km³ (86%) of this coming from the ocean surface and the remaining 71,000 km³ (14%) from the land (Hubbart and Pidwirny, 2007). Evaporation rates depend on numerous physical factors such as insolation, photon absorption properties of the atmosphere and water, temperature, relative humidity, and local wind speed. Most of these factors are interconnected and non-linearly coupled. For example, local variations in sea surface temperature due to differential photon absorption rates caused by clouds or local phytoplankton blooms, leads to local wind currents. Global winds are driven by latitude variation of the solar irradiance and absorption, and the rotation of the Earth. Relative humidity is a function of temperature but also a function of the quantity of microscopic particles available for seeds of condensation, a significant amount of which are supplied by biology (Lovelock, 1988).

The non-linear couplings of the different biotic and abiotic factors affecting the water cycle imply that quantifying the effect of one particular component, such as biology, on the water cycle is very difficult. However, simulations using climate models taking into account most of the important physical factors have been used to estimate the importance of vegetation on land to evapotranspiration and entropy production. Kleidon (2008) has estimated that without plants, average evaporation rates on land would decrease from their actual average values of 2.4 mm/d to 1.4 mm/d, suggesting that plants may be responsible for as much as 42% of the actual evaporation over land.

There appears to be little recognition in the literature of the importance of cyanobacteria and other living and non-living organic matter floating at the ocean surface to evaporation rates. Irrespective of other factors such as wind speed and humidity, there should at least be some relation between evaporation rates and the solar energy deposited in the sea-surface layer. Before attempting a calculation of the effect of biology on evaporation rates over oceans and lakes, it is relevant to review the physical and biological nature of the air-sea surface interface based on knowledge that has emerged over the last two decades.

The ocean skin surface layer of roughly 1 mm thickness has its particular ecosystem of high density in organic material (up to 10^4 the density in water slightly below (Grammatika and Zimmerman, 2001)). This is due to the scavenging action of rising air bubbles from breaking waves and raindrops, surface tension, and natural buoyancy (Grammatika and Zimmerman, 2001). The organic material consists of cyanobacteria, diatoms, viruses, free floating RNA/DNA, and other living and non-living organic material such as chlorophyll and other pigments. Most of the heat exchange between the ocean and atmosphere of today occurs from within this upper 1 mm of ocean water. For example, most of the radiated infrared radiation from the sea comes from the upper 100 μ m (Schlussel, 1999). About 52% of the heat transfer from this ocean layer to atmosphere is in the form of latent heat (evaporation), radiated long-wave radiation accounts for 33%, and sensible heat through direct conduction accounts for the remaining 15%.

During the day, infrared (700-10000 nm), visible (400-700 nm), and ultraviolet (290-400nm) light is absorbed at the sea surface. In the NE Atlantic, for example, daytime temperatures at the skin surface have been measured to increase on average by 2.5K (up to 4.0K) compared to the practically constant temperature at an ocean depth of 10m (Schlüssel et al., 1990). Nighttime temperatures at the surface, on the contrary, are decreased on average by 0.5K (up to 0.8K) with respect to the constant temperature at a depth of 10m. It is thus of interest to determine how much of this day-time heating is due to the organic material in this layer, and the relative contributions due to UV, visible, or infrared radiation. Such a determination will allow an estimate of the effect of life on the evaporation of water over oceans and the associated entropy production, under both clear and cloudy skies. For the sake of calculation, we take the surface skin layer for light absorption and heat exchange to the atmosphere to be 1mm (this should be an upper limit for the relevant thickness for energy exchange since below this depth turbulence and mixing with lower ocean depths becomes relevant (Soloviev and Lukas, 2006) and the amount of organic material drops off significantly (Grammatika and Zimmerman, 2001)).

Three distinct wavelength regions are considered for the calculation; 290-400 nm (UV) (below 290 nm almost all light is absorbed by atmospheric O₃), 400-700 nm (visible), and 700-10000 nm (infrared). The blackbody spectrum of the Earth at 287K (14°C) peaks at 10000 nm so absorption at greater wavelengths than this would not contribute to net heating. There is, in any case, very little energy in sunlight beyond this wavelength. We first calculate the total amount of energy arriving at the sea surface in each wavelength region for a clear sky with no clouds and the sun directly overhead. This can be obtained by integrating the area under a plot of the irradiance at the Earth's surface as a function of wavenumber, such as that given by Gates (1980, Fig. 8.17). The result is given in the first row of table 1.

To calculate the amount of energy deposited per unit time in each wavelength region within the 1mm skin layer of pure ocean water without organic material, we use an average water absorption coefficient corresponding to a wavelength at the middle of the UV and visible wavelength ranges (345 nm and 550 nm respectively), whereas for the infrared region we use the absorption value at 1050 nm since this corresponds to the greatest incident contribution not absorbed by water vapor in the atmosphere (see Fig. 8.17 of Gates, 1980), and because the irradiance drops off sharply at greater wavelengths. Chaplin (2009) give the following absorption coefficients for pure water;

$$A_0^{345} = 1.0 \times 10^{-4} \text{ cm}^{-1} \quad A_0^{550} = 8.0 \times 10^{-4} \text{ cm}^{-1} \quad A_0^{1050} = 0.2 \text{ cm}^{-1}.$$

The flux of energy deposited in the skin layer is then

$$\Delta I = (I_0 - I(x)) = I_0 (1 - \exp(-Ax)) \quad (4)$$

with $x = 0.1$ cm and A is the relevant absorption coefficient. The results are given in the second row of table 1.

To calculate the amount of energy per unit time deposited within the 1mm skin layer of ocean water *with* organic material for each wavelength region, we need the absorption coefficients for the ocean surface microlayer at the different wavelengths. Unfortunately, there do not appear to be any published data in this regard. However, Grammatika and Zimmerman, (2001) suggest that the skin microlayer contains up to 10^4 times the density of organic material as water slightly below. This factor of 10^4 is an order of magnitude greater than that of the ratio between the densities of organic matter in very turbid costal waters to that of deep sea water (Wommack and Colwell, 2000). We therefore take the absorption coefficients for costal turbid waters obtained for the Baltic Sea by Bricaud et al. (1981, Fig. 3) as a lower limit surrogate to that of the surface skin layer of the ocean, giving

$$A_{\text{org}}^{345} = 0.1 \text{ cm}^{-1}, A_{\text{org}}^{550} = 8.0 \times 10^{-3} \text{ cm}^{-1}, A_{\text{org}}^{1050} = 0.2 \text{ cm}^{-1}$$

The value for the infrared absorption is the same as that for pure water since organic molecules absorb very little compared to water in this wavelength region. Using equation (4) with these values we obtain the third row of table 1.

By comparing the third row with the second row of table 1 it can be determined that on a clear day, with the sun directly overhead (air mass of 1.0), the organic matter floating in the surface skin layer increases the absorption of energy in this layer by about 13% over what its value would be without this organic matter. Since, for a relatively temperature independent heat capacity of water, the temperature of the skin layer would increase by a similar percentage, and since the water vapor pressure increases exponentially with temperature, the increase in the rate of evaporation would be significantly greater than 13%. This is consistent with the measured increase in the latent outgoing heat flux for nutrient induced phytoplankton blooms in an enclosed area of a lake as determined by Jones et al. (2005). It is interesting to note that the absorption of UV light by organic material in water contributes more than double the amount of that due to absorption of visible light.

The relative contribution to the entropy production in the sea surface microlayer resulting from photon absorption and dissipation in each wavelength region can now be approximated by calculating the increase in the number of energy microstates resulting from dissipating a high energy photon into many long wavelength photons (10,000 nm, corresponding to the wavelength of the peak in the black-body spectrum of the Earth at 287 K (Gates, 1980)). The relative number of 10,000 nm photons produced by absorption and dissipation in each wavelength region can be obtained by simply dividing the energy of a photon at the central wavelength in each wavelength region by the energy of a 10,000 nm photon and then weighting this number by the proportion of the total flux of energy deposited in the microlayer in this wavelength region (row 3 of Table 1). The Boltzmann relation gives the entropy produced as just proportional to the natural logarithm of this number of created microstates. Dividing the entropy produced in each wavelength region by the sum total for all regions gives the percentage contribution to the total for each region. The result is given in the fourth row of Table 1. By absorbing and dissipating UV and visible light, the organic matter in the sea surface microlayer contributes about $33.2 + 20.4 = 53.6\%$ to the total entropy production in this layer (fourth row of table 1).

In the case of an overcast day, much less infrared radiation arrives at the ocean surface because of the strong absorption of infrared by water drops in clouds (see Fig. 8.17 of Gates, 1980). We take the water absorption coefficients corresponding to the middle of the regions to be again 345 nm for UV and 550 nm for visible, but 800 nm for infrared (since from Fig. 8.17 of Gates the infrared light distribution transmitted through the atmosphere is shifted notably towards shorter wavelengths due to the preferential absorption of the longer wavelengths by clouds). The results for an overcast day for the sea surface skin layer with and without organic matter are given in table 2.

Comparing the third row with the second row of table 2 it can be determined that on an overcast day, with the sun directly overhead (air mass of 1.0) the organic matter floating in the surface skin layer increases the absorption of energy in this layer by about 400% over what the value would be without the organic matter, with equal contributions coming from UV and visible light. However, the total energy absorbed in this skin layer on an overcast day is only about 5% that of a clear day, due principally to the comparatively small amount of infrared light that makes it through the clouds. By absorbing and dissipating UV and visible light, the organic matter in this layer contributes about $55.2 + 41.3 = 96.5\%$ to the total entropy production on a cloudy day

By absorbing and dissipating UV and visible light on the surface of oceans and lakes, life therefore augments the entropy production of the Earth in its solar environment. Without life at the surface, a greater portion of light would be reflected, thereby increasing the albedo of Earth (Clarke et al. (1970) gives measurements of the reduction of water albedo due to the presence of organic material), and light would penetrate deeper into the ocean, thereby augmenting the overall bulk blackbody temperature of the ocean (see, for example, Jones et al. (2005) for the effect of phytoplankton on the temperature profile with depth for a lake). Both reduce the entropy production of Earth; the former by reducing the amount of available light to dissipate, and the latter by shifting the frequencies of the daily (day-night) integrated radiated spectrum of the sea surface to higher values (see Eq. (2)) since this excess heat in bulk cannot be as easily coupled to the water cycle as surface heat.

Evidence for Evolutionary Increases in the Water Cycle

Plants, far from eliminating transpiration as a wasteful use of free energy, have in fact evolved ever more efficient water transport and transpiration systems (Sperry, 2003). There are general trends over evolutionary time, and in ecosystem succession over shorter time, to ever increasing transpiration rates. For example, conifer forests are more efficient at transpiration than deciduous forests principally because of the greater surface area offered for evaporation by needles as compared to leaves. Conifers appeared later in the fossil record (late carboniferous) and appear in the late successional stage of ecosystems. Root systems are also much more extended in late evolutionary and successional species, allowing them to access water at ever greater depths (Raven and Edwards, 2001).

New pigments besides chlorophyll have appeared in the evolutionary history of plants and cyanobacteria, covering an ever greater portion of the intense region of the solar spectrum, even though they have little or no effect on photosynthesis, for example, the carotenoids in plants, or the MAA's found in phytoplankton which absorb across the UVB and UVA regions (310-400 nm) (Whitehead and Hedges, 2002). This is particularly notable in red algae, for example, where its total absorption spectrum has little correspondence with its photosynthetic activation spectrum (Berkaloff *et al.*, 1971).

There exist complex mechanisms in plants to dissipate photons directly into heat, by-passing completely photosynthesis. These mechanisms come in a number of distinct classes and involve inducing the de-excitation of chlorophyll using dedicated enzymes and proteins. Constitutive mechanisms, allow for intersystem crossing of the excited chlorophyll molecule into triplet, long-lived, states which are subsequently quenched by energy transfer to the carotenoids. Inducible mechanisms are mechanisms that can be regulated by the plant itself, for example, changing lumen pH causes the production of special enzymes that permit the non-photochemical de-excitation of chlorophyll. Sustained mechanisms are similar to inducible mechanisms but have been adapted to long term environmental stress. For example, over wintering evergreen leaves produce little photosynthesis due to the extreme cold but continue transpiring by absorbing photons and degrading these to heat through non-photochemical de-excitation of chlorophyll. Hitherto, these mechanisms were considered as “safety valves” for photosynthesis, protecting the photosynthetic apparatus against light-induced damage (Niyogi, 2000). However, their existence and evolution can better be understood in a thermodynamic context as augmenting the entropy production potential of the plant through increasing transpiration rates.

The recent findings of microsporine-like amino acids (MAAs) produced by plants and phytoplankton having strong absorption properties in the UVB and UVA regions lends support to the hypothesis of this paper. Their discovery came first in fungi (Leach, 1965). They are small (< 400 Da), water-soluble compounds composed of aminocyclohexenone or aminocycloheximine rings with nitrogen or imino alcohol substituents (Carreto et al., 1990) which display strong UV absorption maximum between 310 and 360 nm and high molar extinction (Whitehead and Hedges, 2002). These molecules have been assigned a UV photoprotective role in these organisms, but this appears dubious since, in some cases, more than 20 MAAs have been found in the same organism, each with different but overlapping absorption spectrum, determined by the particular molecular side chains (Whitehead and Hedges, 2002). If their principle function were photoprotective, then their existence in a particular plant or phytoplankton would be confined to those microsporine of particular UV wavelengths that cause damage to the photosynthetic apparatus, and not to the whole UV broadband spectrum.

Plants also perform a free energy intensive process known as photorespiration in which O₂ instead of CO₂ is captured by the binding enzyme RuBisCo, the main enzyme of the light-independent part of photosynthesis. This capture of O₂ instead of CO₂ (occurring about 25% of the time) is detrimental to the plant for a number of reasons, including the production of toxins that must be removed (Govindjee, 2005) and does not lead to ATP production. There is no apparent utility to the plant in performing photorespiration and in fact it reduces the efficiency of photosynthesis. It has often been considered as an “evolutionary relic” (Niyogi, 2000), still existing from the days when O₂ was less prevalent in the atmosphere than today, and CO₂ more so (0.78% CO₂ by volume at the rise of land plants during the Ordovician (ca. 470 Ma) compared with only 0.038% today).

However, such an explanation is not in accord with the known efficacy of natural selection to eliminate useless or wasteful processes. Another theory has photorespiration as a way to dissipate excess photons and electrons and thus protect the plants photosynthesizing system from excess light-induced damage (Niyogi, 2000). Since photorespiration is common to all C₃ plants, independent of their preferred insolation environments, it is more plausible that photorespiration, being completely analogous to photosynthesis with respect to the dissipation of light into heat in the presence of water (by quenching of excited chlorophylls) and subsequent transpiration of water, is retained for its complimentary role in evapotranspiration and thus entropy production.

Plants not only evaporate water during sunlight hours, but also at night (Snyder et al., 2003). Common house plants evaporate up to 1/3 of the daily transpired water at night (Hernández Candía, 2009). Not all the stoma in C₃ and C₄ photosynthetic plants are closed at night and some water vapor also diffuses through the cuticle at night. A physiological benefit to the plant for night transpiration, if indeed one exists, remains unclear. It, of course, can have no relevance to cooling leaves for optimal photosynthetic rates. Explanations range from improving nutrient acquisition, recovery of water conductance from stressful daytime xylem cavitation events, and preventing excess leaf turgor when water potentials become large during the day (Snyder et al., 2003). However, night transpiration is less of an enigma if considered as a complement to the thermodynamic function of life to augment the entropy production of Earth through coupling with the water cycle. In this context, it is also relevant that chlorophyll has an anomalous absorption peak in the infrared between about 4,000 and 10,000 nm (Gates, 1980), just at the wavelengths at which the blackbody radiation of the Earth's surface at 14 °C peaks.

Cyanobacteria have been found to be living within Antarctic ice at depths of up to 2 m. These bacteria and other lithogenic material in the ice absorb solar radiation which causes the formation of liquid water within the ice even though the outside air temperatures may be well below freezing. This heating from below causes excess ablation and sublimation of the overlying ice at rates as high as 30 cm per year (Priscu *et al.*, 2005).

Finally, by analyzing latent heat fluxes (evaporation) and the CO₂ flux for plants from various published data sets, Wang *et al.* (2007) have found vanishing derivatives of transpiration rates with respect to leaf temperature and CO₂ flux, suggesting a maximum transpiration rate for plants, i.e. that the particular partition of latent and sensible heat fluxes is such that it leads to a leaf temperature and leaf water potential giving maximal transpiration rates, and thus also maximal production of entropy (Wang *et al.*, 2007).

The Function of Animals

If the primary thermodynamic function of the plants and cyanobacteria is to augment the entropy production of the Earth by absorbing light in the presence of liquid water, it may then be asked: What is the function of higher mobile animal life?

Because of their intricate root system which allows the plants to draw up water for evaporation from great depths, plants are not mobile and depend on insects and other animals for their supply of nutrients, cross fertilization, and seed dissemination and dispersal into new environments. The mobility and the short life span of insects and animals mean that through excrement and eventual death, they provide such a reliable mechanism for dispersal of nutrients and seeds.

Crustaceans and animal marine life in water perform a similar function as insect and animal life on land. These higher forms of life distribute nutrients throughout the ocean surface through excrement and dying. It is noteworthy that dead fish and mammals do not sink rapidly to the bottom of the sea or lake, but remain floating for considerable time on the surface where, as on land, bacteria break down the organism into its molecular components, allowing photon dissipating phytoplankton to reuse the nutrients, particularly nitrogen. It is relevant that many algae blooms produce a neurotoxin with apparently no other end than to kill higher marine life. There is also a continual cycling of nutrients from the depths of the ocean to the surface as deep diving mammals preying on bottom feeders release nutrients at the surface through excrement and death. Because of this nutrient cycling due to the mobility of animals, a much larger portion of the ocean surface is rendered suitable for phytoplankton growth, offering a much larger area for efficient surface absorption of sunlight and evaporation of water than would otherwise be the case.

From this thermodynamic viewpoint, animal life provides a specialized gardening service to the plants and cyanobacteria, which in turn catalyze the absorption and dissipation of sunlight in the presence of water, promoting entropy production through the water cycle. There is strong empirical evidence suggesting that ecosystem complexity, in terms of species diversity, is correlated with potential evapotranspiration (Gaston, 2000). The traditional ecological pyramid should thus be turned on its pinnacle. Instead of plants and phytoplankton being considered as the base that sustains animal life, animals are in fact the unwitting servants of plant and phytoplankton life, obtaining thermodynamic relevance only in how they increase the plant and phytoplankton potential for evaporation of water.

Illustration 2

Table 1

CLEAR SKIES	UV (290-400 nm)	Visible (400-700 nm)	Infrared (700-10000 nm)
Energy flux reaching Earth's surface (total 1029.3 W/m ²)	50.5 W/m ² direct 33.7 W/m ² skylight ----- 84.2 W/m ² Global (8.2%)	428.2 W/m ² direct 53.9 W/m ² skylight ----- 482.1 W/m ² Global (46.8%)	456.3 W/m ² direct 6.7 W/m ² skylight ----- 463.0 W/m ² Global (45%)
Energy flux absorbed in 1 mm skin layer (pure water).	0.84x10 ⁻³ W/m ² ($A_0^{345} = 1.0 \times 10^{-4} \text{ cm}^{-1}$)	38.6x10 ⁻³ W/m ² ($A_0^{550} = 8.0 \times 10^{-4} \text{ cm}^{-1}$)	9.16 W/m ² ($A_0^{1050} = 0.2 \text{ cm}^{-1}$)
Energy flux absorbed in 1 mm skin layer (ocean water with organic material).	0.84 W/m ² ($A_{org}^{345} = 0.1 \text{ cm}^{-1}$)	0.39 W/m ² ($A_{org}^{550} = 8.0 \times 10^{-3} \text{ cm}^{-1}$)	9.16 W/m ² ($A_{org}^{1050} = 0.2 \text{ cm}^{-1}$)
% of total entropy production in ocean skin.	33.2	20.4	46.4

Table 1. Values of energy deposition per unit time in the sea surface microlayer and the contribution to entropy production for the different wavelength regions assuming clear skies.

Illustration 3

Table 2

OVERCAST SKIES	UV (290-400 nm)	Visible (400-700 nm)	Infrared (700-10000 nm)
Energy flux reaching Earth's surface (Cloud Light, Fig. 8.17 Gates) (total 341.6 W/m ²)	22.04 W/m ² (6.5)%	274.7 W/m ² (80.4%)	44.86 W/m ² (13.13%)
Energy flux absorbed in 1 mm skin layer (pure water).	0.22x10 ⁻³ W/ m ² ($A_0^{345} = 1.0 \times 10^{-4} \text{ cm}^{-1}$)	0.022 W/m ² ($A_0^{550} = 8.0 \times 10^{-4} \text{ cm}^{-1}$)	0.09 W/m ² ($A_0^{800} = 0.02 \text{ cm}^{-1}$)
Energy flux absorbed in 1 mm skin layer (ocean water with organic material).	0.22 W/m ² ($A_{org}^{345} = 0.1 \text{ cm}^{-1}$)	0.22 W/m ² ($A_{org}^{550} = 8.0 \times 10^{-3} \text{ cm}^{-1}$)	0.09 W/m ² ($A_{org}^{800} = 0.02 \text{ cm}^{-1}$)
% of total entropy production in ocean skin.	55.2	41.3	3.5

Table 2. Values of energy deposition per unit time and contribution to the entropy production for the different wavelength regions assuming overcast skies.

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