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# Biological catalysis of the hydrological cycle: life's thermodynamic function

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## Abstract

Darwinian theory depicts 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 a vast amount 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 by organic molecules in the biosphere and its coupling to the water cycle (as well as other abiotic processes), is by far the greatest entropy producing process occurring on Earth. Life, from this perspective, can be viewed as performing an important thermodynamic function; acting as a dynamic catalyst by aiding irreversible 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.

## 1 Introduction

About 4.57 billion years ago, the Earth condensed out of a nebula of gas and dust to be illuminated by a volatile Sun which finally settled down as a main sequence star about 50 million years after its birth (Zahnle et al., 2007). 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 a cataclysmic era, recorded on the moon as the “lunar late heavy bombardment” (ca. 3.8 Ga), possibly caused by gravitational effects of the migration of the outer planets (Zahnle et al., 2007), the physical conditions on Earth stabilized and life emerged.

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The emergence of life on Earth has mostly been considered as an extraordinary event and its evolution in complexity and global extent considered as the result of 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. However, it has since become apparent that life plays a pivotal role in shaping its physical environment (Lovelock, 1988). 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, perhaps stability, and, of most interest here, greater entropy production (Ulanowicz and Hannon, 1987).

Entropy production is the rate of the tendency of Nature to explore the multitude of microstates which underlies the macroscopic world that we perceive. Such a co-evolution of the biotic with the abiotic, difficult to reconcile within traditional Darwinian theory, fits perfectly well within the framework of non-equilibrium thermodynamics in which dissipative systems spontaneously arise, couple, and co-evolve in such a manner so as to increase the global entropy production of the Earth in its interaction with its solar environment (Onsager, 1931; Prigogine, 1972; Ulanowicz and Hannon, 1987; Swenson, 1989; Kleidon and Lorenz, 2005; Michaelian, 2005, 2009, 2010).

Life is found almost everywhere on Earth, becoming sparse only where water is scarce. On the Earth's surface, the greatest biomass consists of archaea, prokaryote, and eukaryote life based on photosynthesis. In the sea, photosynthetic phytoplankton (archaea, diatoms, cyanobacteria, and dinoflagellates) can be found in great density at the surface (up to  $10^9$ /ml), and in the rest of the euphotic zone which extends to a depth of 50 m. 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 the overlying water. 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 touched by water. Photosynthesizing cyanobacteria have been found thriving in hot-springs at

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over 70 °C (Whitton and Potts, 2000) and on mountain glaciers and within Antarctic ice (Parker et al., 1982) where absorption of solar radiation and its dissipation into heat by organic and lithogenic material within the ice generates the vital liquid water (Priscu et al., 2005).

The thermodynamic force for driving the process of photosynthesis which sustains surface life derives from the low entropy of sunlight and the second law of thermodynamics. Only twenty seven years after 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, a high-energy photon in the visible region of the Sun’s spectrum is converted by the chloroplasts into 20 or more low energy photons in the infrared region. A small part of the free energy made available in the process is utilized to extract and fix organic carbon from atmospheric carbon dioxide. In this manner, photosynthetic life is maintained and propagated through the conversion of low entropy of sunlight into the higher entropy of heat, and thereby contributes to the global entropy production of Earth.

However, the part of the solar 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 into heat 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. Over 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

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it into heat that can be efficiently absorbed by the surface water. The temperature of the ocean surface is thereby raised (Kahru et al., 1993) leading to increased evaporation and promotion of the water cycle. Moreover, an extensive surface ecosystem, consisting of microscopic zoo-plankton living off the phytoplankton, causes continuous agitation of the surface water, increasing by nearly three-fold the evaporation rate from the surface.

There appears to be no important 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, 2009; Hernández and Michaelian, 2010). Transpiration is often considered as an unfortunate by-product of photosynthesis in which water is unavoidably given off through the stoma of plants which are open in order to exchange CO<sub>2</sub> and O<sub>2</sub> with the atmosphere (Gates, 1980). Plants consist of up to 90% water by mass and thus appear to expose themselves to great risk by transpiring so much water. Another argument is that transpiration is useful to plants since it helps to cool the leaves to a temperature optimal for photosynthesis. This, however, is inconsistent with the fact that 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 the history of life on Earth indicates that plants and phytoplankton have evolved new pigments over time to absorb ever more completely the Sun's spectrum. Dense pine forests appear black in the midday sun. 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, according to Darwinian theory, such a process, with little direct utility to the plant, should have been eliminated

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or suppressed through natural selection. Plants which are able to take in  $\text{CO}_2$  while reducing water loss, by either opening their stoma only at night (CAM photosynthesis), or by reducing photorespiration ( $\text{C}_4$  photosynthesis, see below), indeed have evolved 32 and 9 million years ago respectively (Osborne and Freckleton, 2009). However, these water conserving photosynthesis have not displaced the older, heavily transpiring  $\text{C}_3$  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  $\text{C}_4$  plants, for example, the cacti of deserts.

It is here proposed that excessive photon absorption and transpiration have 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 interaction with its solar environment, and this is achieved by dissipating high energy photons into heat in the presence of water, thereby augmenting the global water cycle and ocean and wind currents. Cyanobacteria floating at the surface of oceans and lakes heat the surface water and thereby play an analogous thermodynamic role as plants over land.

## 2 Life catalysing the hydrological cycle

Absorption of sunlight at the leaves of plants increases their temperature by as much as  $20^\circ\text{C}$  over that of the ambient air (Gates, 1980). This leads to an increase of the  $\text{H}_2\text{O}$  vapor pressure inside the cavities of the leaf with respect to that of the colder surrounding air. Water vapor thus diffuses across this gradient of chemical potential from the wet mesophyll cell walls (containing the chloroplasts), through the inter-cellular cavities, and finally through the stoma and into the external atmosphere. There is also a parallel, but less important, circuit for diffusion of  $\text{H}_2\text{O}$  vapor in leaves through the cuticle, providing up to 10% more transpiration (Gates, 1980). The  $\text{H}_2\text{O}$  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.

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Diffusion of H<sub>2</sub>O 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. Single trees in the Amazon rain forest have been measured to evaporate as much as 1180 l/d (Wullschlegel 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 30% more than 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 10<sup>9</sup>/ml) of viral and dissolved DNA resulting from viral lysing of bacteria (Wommack and Colwell, 2000).

The water vapor transpired by leaves, or evaporated by 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 to form clouds. Over oceans, an important constituent of these microscopic 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<sup>6</sup> J/kg) into the upper atmosphere, much of which is then radiated into space in an approximate black-body spectrum at −14°C. In this manner, the Earth maintains its energy balance with space; the total energy incident on the biosphere in the form of sunlight is 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, as required by the first and second laws of thermodynamics respectively.

The formation of clouds may seem to have a detrimental effect on the water cycle since cloud cover on Earth reflects approximately 20% of light in the visible and

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ultraviolet regions of the Sun's spectrum (Pidwirny and Budicova, 2008). Clouds absorb the major part of the direct infrared radiation, thereby reducing the potential for evaporation at the Earth's surface. 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 local cool regions during the day, and local warm regions during the night, clouds are able to maintain the average wind speed at the Earth's surface within dense vegetation 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 (see for example, Speck; 2003), thereby procuring maximal transpiration rates (Gates, 1980).

Sublimation and ablation of ice over the polar regions (up to 30 cm per year; Priscu et al., 2005), promoted in part by photon absorption on cyanobacteria within the ice, provides another important contribution to the hydrological cycle.

### 3 Entropy production through photon dissipation

All irreversible processes, living systems included, arise and persist to produce entropy. Entropy production is not coincidental to the process, but rather the reason for its very existence. A fundamental characteristic of Nature is the search for routes to greater global entropy production (Onsager, 1931). This results from the microscopic nature of material and the multitude of ways to distribute the extensive thermodynamic quantities (energy, momentum, angular momentum, etc.) over the myriad of microscopic degrees of freedom. Macroscopic states consistent with a larger number of microstates are simply more probable and thus Nature tends to move towards these macrostates of greater microstate multiplicity. This tendency towards increasing probability is what is identified as entropy production.

Onsager (1931) has shown how diverse irreversible processes can couple in order to remove impediments to greater global entropy production (Morel and Fleck, 1989). In general, the more complex the dissipative structuring in space and time (i.e. involving



many coupled irreversible processes with embedded hierarchal levels and interactions of long spatial and temporal extent) the greater the overall entropy production in the systems interaction with its external environment (Onsager, 1931; Prigogine et al., 1972; Lloyd and Pagels, 1988).

The Earth is an approximately closed thermodynamic system subjected to a constant flow of photons from the Sun in a spectrum roughly corresponding to that of a black-body at a temperature of the surface of the Sun (5800°C). About 30% of the light is reflected directly back into space. The rest is absorbed by various components of the Earth system and converted into photons of longer wavelength. The absorption and dissipation of high energy photons into low energy photons is facilitated in large part by the plants and cyanobacteria in the presence of water. An estimate of the relevance of life to entropy production can be obtained by comparing the global entropy production of Earth with that of its apparently lifeless neighboring planets Venus and Mars. The global entropy production of the planets can be determined by considering the change in the frequency  $\nu$  distributions of the radiation incident from the Sun,  $I_{\text{in}}(\nu)$ , and that radiated by the planet,  $I_{\text{rad}}(\nu)$  (Ulanowicz and Hannon, 1987). The flow of photons can be considered as an ideal gas of non-interacting Bose-Einstein particles for which the internal temperature  $T$  is related to the frequency  $\nu$  by the relation  $kT = h\nu$ , where  $k$  and  $h$  are Boltzmann's and Planck's constants respectively. The Gibbs equation for the flow of entropy  $dS$  during time interval  $dt$  at a particular frequency  $\nu$  is (Callen, 1985),

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

where  $I(\nu) \equiv dE(\nu)/dt$  is defined as the energy flow or irradiance at frequency  $\nu$ , and where the volume and chemical potential terms in the Gibbs equation have been neglected since the volume of the global Earth-space system is constant and the chemical potential for photons is zero (Callen, 1985). The global entropy production  $P$  of the planet in its interaction with its solar environment is then just the difference between its

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radiated and incident entropy flow integrated over all frequencies,

$$P = \int_0^{\infty} \frac{dS_{\text{rad}}(\nu)}{dt} - \frac{dS_{\text{in}}(\nu)}{dt} d\nu. \quad (2)$$

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

$$P = \frac{k}{h} \int_0^{\infty} (I_{\text{rad}}(\nu) - I_{\text{in}}(\nu)) / \nu d\nu. \quad (3)$$

A very approximate measure of this entropy production for a planet 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)

$$I(\nu)|_T = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}. \quad (4)$$

Taking,  $T_{\text{rad}}$  as the average temperature of the Earth's surface, 287 K (14°C), and  $T_{\text{in}}$  as the temperature of the surface of the Sun, 6073 K (5800°C), Eq. (3) with Eq. (4) 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 apparently lifeless neighboring planets of Venus and Mars (Aoki, 1983).

Equation (3) with (4) indicates that there is greater potential for entropy production for absorption and dissipation of high frequency photons in the biosphere than for low frequency ones. It is thus probably not coincidental that the Earth's atmosphere 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 there be more efficiently dissipated into heat by organic molecules in contact with liquid water.

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 free 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 quantity 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. A negligible proportion of the free energy absorbed by the biosphere (<0.2%) goes into the metabolism 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 is efficiently absorbed by water and transferred to the vibrational, and to a lesser extent to the rotational, degrees of freedom of the water molecules.

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 the proteins containing amino acids with aromatic rings (tryptophan, tyrosine, phenylalanine), are particularly potent absorbers of ultraviolet light within the 200–300 nm region due to the collective electronic excitations of the rings (Chang, 2000). Mycosporine-like amino acids (MAAs) found in phytoplankton absorb across the UVB and UVA regions (310–400 nm) (Whitehead and Hedges, 2002). This absorbed energy can then cause the breaking of hydrogen bonds binding water molecules, facilitating evaporation at the water surface. Organic molecules can thus be considered as catalysts that allow a greater portion of the Sun's free energy to be dissipated through the water cycle.

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The amount of ultraviolet light reaching the Earth's surface today of wavelength less than 290 nm (UVC) is very small compared to that of the UVB+UVA+visible light due to a middle aged Sun and absorption by ozone and oxygen and thus UVC plays a very small part in the entropy production of the biosphere and associated water cycle.

5 This, however, may not have been the case at the very beginnings of life on Earth (Michaelian, 2009, 2010). During the archaean, the Sun was much 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; (1) a high layer of sulfuric acid clouds as on Venus today, the result of UV photochemical reactions  
10 on the common volcanic gases of SO<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O, (2) to clouds of water which preferentially filter infrared over UV (compare Tables 1 and 2), or (3) to organic haze as on Titan today, the result of UV photochemical reactions on CO<sub>2</sub> and CH<sub>4</sub> (Lowe and Tice, 2004). Life may thus have originated as a catalyst for dissipating photons in the UVC region and coupling the resultant heat to the water cycle (Michaelian, 2009,  
15 2010).

#### 4 Quantifying the importance of life to the hydrological cycle

The very existence of liquid water on Earth can be attributed, in large part, to the existence of life (Lovelock, 1988). Physical mechanisms exist that disassociate water into its hydrogen and oxygen components, for example, the photo-dissociation of water by ultraviolet light (Chang, 2000). Free hydrogen, being very light, can escape Earth's  
20 gravity and drift into space, being dragged along by the solar wind. Photo-dissociation of methane has been suggested to be another important path to loosing the hydrogen necessary for water (Catlin et al., 2001). This loss of hydrogen would have lead to a gradual depletion of the Earth's water, as appears to have occurred on Venus (Love-  
25 lock, 2005). The Earth's magnetic field may have helped reduce the effects of the solar wind on hydrogen loss. Photosynthetic life releases oxygen from carbon dioxide thereby providing the potentiality for its recombination with the free hydrogen to

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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 examined in the Gaia hypothesis (Lovelock, 1988), life has also been able to maintain the temperature of Earth within the narrow region required for liquid water (Ventura et al., 2007), even though the total radiation from the Sun has increased by as much as 30% since the beginnings of life (Newman and Rood, 1977; Gough, 1981).

About 496 000 km<sup>3</sup> of water is evaporated yearly, with 425 000 km<sup>3</sup> (86%) of this coming from the ocean surface and the remaining 71 000 km<sup>3</sup> (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 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 living organisms (Lovelock, 1988).

The non-linear couplings of the different biotic and abiotic factors affecting the water cycle imply that quantifying the effect of one component, such as biology, on the water cycle is 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 over land would decrease from their actual average values of 2.4 mm/d to 1.4 mm/d, suggesting that plants may

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be responsible for as much as 42% of the actual evaporation over land.

Makarieva and Gorshkov (2007) have described a biotic pump which operates as a result of a non-equilibrium vertical distribution of water vapor occurring over heavily transpiring woodland areas. Condensation of water vapor above the forest canopy reduces its partial pressure, leading to a region of low pressure above the forest which sucks in moisture laden air from neighboring water bodies. Such a pump drives atmospheric moisture from the oceans to much greater distances inland than would otherwise be obtained without forest cover. A prominent example of this is the Amazon river basin where atmospheric moisture originating at the Atlantic ocean is transported several thousand kilometers inland rather than the hundreds of kilometers expected without a biotic pump. It may be that establish views on global atmospheric circulation will be revolucionized by the new theory, since instead of differential solar heating being behind the global atmospheric circulation, Makarieva and Gorshkov suggest that it is condensation-induced by heavily transpiring forests. The biotic pump allows vegetation to exist over a much greater area of the Earth's surface, providing in this manner, an important contribution to the global water cycle and entropy production.

In contrast to the numerous published works on land transpiration, 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. Jones et al. (2005) have determined that phytoplankton can, through increased photon absorption, increase surface temperatures and therefore the outgoing latent heat flux of a lake. Irrespective of other factors such as wind speed and humidity, evaporation rates should at least correlate with the amount of solar energy absorbed in the sea-surface layer. An indication of the passive effect of biology on evaporation rates over oceans and lakes can be made based on a comparison of the different factors responsible for energy absorption. Before attempting such a comparison, however, it is first relevant to review the physical and biological nature of the air-sea surface interface from which evaporation occurs.

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The ocean surface skin layer of roughly 1 mm thickness has particular importance to ocean ecosystems since it is the region of mass, energy and momentum transfer with the atmosphere (Hardy, 1982; Soloviev and Lukas, 2006). The upper 50  $\mu\text{m}$  of this layer (the microlayer) hosts an ecosystem of particularly high organic density, up to  $10^4$  the density of water only slightly below (Hardy, 1982; 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. At depths of between 1  $\mu\text{m}$  and 10  $\mu\text{m}$  many species of zooplankton in concentrations up to 10 times that of water slightly below exist (Hardy, 1982). Most of the heat exchange between the ocean and atmosphere of today occurs from within the upper 1 mm of ocean water. For example, most of the radiated infrared radiation from the sea comes from the upper 100  $\mu\text{m}$  (Schlüssel, 1990). 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 (700–10 000 nm), visible (400–700 nm), and ultraviolet (290–400 nm) 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 2.5 K (up to 4.0 K under low wind conditions) compared to the practically constant temperature at an ocean depth of 10 m (Schlüssel et al., 1990). Nighttime temperatures at the surface, on the contrary, decrease on average by 0.5 K (up to 0.8 K) with respect to the constant temperature at a depth of 10 m. It is thus of interest to determine how much of this day-time heating is due to the organic material in this layer, and to separate the relative contributions due to UV, visible, and infrared radiation. Such a determination, for both clear and cloudy skies, will allow an estimate of the effect of life on the evaporation over oceans and an estimate of the associated entropy production. For the sake of calculation, we take the surface skin layer for light absorption and heat exchange to the



atmosphere to be 1 mm (this should be a maximum limit for the relevant thickness for energy exchange since below this depth turbulence and mixing with lower ocean water 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<sub>3</sub> and O<sub>2</sub>), 400–700 nm (visible), and 700–10 000 nm (infrared). There is very little energy in sunlight beyond 10 000 nm. The total amount of energy arriving at the sea surface in each wavelength region is first calculated 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 (e.g., 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 1 mm 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 regions (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 (Fig. 8.17 of Gates, 1980), and because the irradiance drops off sharply at wavelengths greater than this. Chaplin (2009) give the following absorption coefficients at these wavelengths for pure water;  $A_0^{345} = 1.0 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_0^{550} = 8.0 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_0^{1050} = 0.2 \text{ cm}^{-1}$ .

The flux of energy deposited in the skin layer is then

$$\delta I = (I_0 - I(x)) = I_0(1 - \exp(-Ax)) \quad (5)$$

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 1 mm skin layer of ocean water with organic material for each wavelength region, the absorption coefficients for the ocean surface microlayer at the different wavelengths are needed.

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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 Eq. (5) 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 stated 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. In a first approximation, the surface temperature increase would be proportional to the increase in energy deposition. The Clausius-Clapeyron equation gives that the saturation water vapor pressure in equilibrium with water increases exponentially with water temperature and thus the increase in the rate of evaporation may 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) and with an approximate 30% increase in evaporation measured for natural waters with respect to distilled water. It is interesting to note that the absorption of UV light by organic material in water contributes more than double the amount of energy deposited in this layer due to absorption of visible light, suggesting that UV light and organic material may have had a long association with the hydrological cycle.

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 the arriving photon energy into many 10 000 nm long wavelength photons, 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 spectral region by the energy of a 10 000 nm photon and then weighting this number by the corresponding 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 proportional to the natural logarithm of this number of created microstates. Dividing the entropy produced in each wavelength region by the sum over all regions gives the percentage contribution to the total for each region (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.

In the case of an overcast sky, or high humidity, much less infrared radiation arrives at the ocean surface because of the strong absorption of infrared light by water in the atmosphere (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 (1980) 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

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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.

Comparing rows two and three of both tables, it is apparent that the organic material at the ocean surface increases the energy deposition from the UV spectral region by 1000 fold, and from the visible region by 10 fold. 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 for the reduction of water albedo at different frequencies 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 effects reduce the entropy production of Earth; greater albedo reduces the amount of available light to dissipate, and penetration of light to greater depth shifts the radiated spectrum (day+night integrated) to higher frequencies (see Eq. 4) since this excess bulk heat cannot be as easily coupled to the water cycle as can surface heat.

## 5 Evidence for evolutionary increases in the hydrological 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 to ever increasing transpiration rates over both evolutionary time scales and over shorter ecosystem succession time scales. For example, conifer forests are more efficient at transpiration than deciduous forests principally because of the greater surface area offered by needles for evaporation 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 extensive in

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late evolutionary and successional species, allowing them to access water at greater depths (Raven and Edwards, 2001).

5 Pigments distinct from chlorophyll have appeared over the evolutionary history of plants and cyanobacteria, covering an ever greater portion of the intense region of the solar spectrum. Such pigments are known to have little or no effect on photosynthesis, for example, the carotenoids in plants, or the micosporine-like amino acids (MAAs) found in phytoplankton which absorb across the UVB and UVA regions (310–400 nm) (Whitehead and Hedges, 2002). MAAs are small (<400 Da), water-soluble compounds composed of aminocyclohexenone or aminocycloheximine rings with nitrogen or imino  
10 alcohol constituents (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  
15 their principle function were photoprotective, then their existence in a particular plant or phytoplankton would be confined to those particular UV wavelengths that cause damage to the photosynthetic apparatus, and not to the whole UV broadband spectrum. It is particularly notable that the total absorption spectrum of red algae, for example, has little correspondence to its photosynthetic activation spectrum (Berkaloff et al., 1971).

20 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 operate by inducing the de-excitation of chlorophyll using dedicated enzymes and proteins. Constitutive mechanisms, allow for inter-system crossing of the excited chlorophyll molecule into triplet, long-lived, states which are subsequently  
25 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

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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 now be better understood from a thermodynamic view as augmenting the entropy production potential of the plant by increasing transpiration rates.

Plants also perform a free energy intensive process known as photo-respiration in which  $O_2$  instead of  $CO_2$  is captured by the binding enzyme RuBisCo, the main enzyme of the light-independent part of photosynthesis. This capture of  $O_2$  instead of  $CO_2$  (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 et al., 2005) and does not lead to ATP production. There is no apparent utility to the plant in performing photo-respiration and, in fact, it reduces the efficiency of photosynthesis. It has been considered as an evolutionary relic (Niyogi, 2000), still existing from the days when  $O_2$  was less prevalent in the atmosphere than today, and  $CO_2$  much more so (0.78%  $CO_2$  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 photo-respiration as a way to dissipate excess photons and electrons and thus protect the plants photosynthesizing system from excess light-induced damage (Niyogi, 2000). Since photo-respiration is common to all C3 plants, independent of their preferred insolation environments, it is more plausible that photo-respiration, being completely analogous to photosynthesis with respect to the dissipation of light into heat in the presence of water (by quenching of excited chlorophyll molecules) and subsequent transpiration of water, is retained for its complimentary role in transpiration and thus entropy production.

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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, 2009; Hernández and Michaelian, 2010). Not all the stoma in C3 and C4 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). Night transpiration is less of an enigma if considered within the thermodynamic framework in which the plant is a catalyst for the hydrological cycle. In this context, it is also relevant that chlorophyll has an anomalous absorption peak in the infrared between about 4000 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 increased ablation and sublimation of the overlying ice at rates as high as 30 cm per year (Prisco et al., 2005).

Finally, by analyzing latent heat fluxes (evaporation) and the CO<sub>2</sub> 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 CO<sub>2</sub> 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 contribution to the hydrological cycle and production of entropy (Wang et al., 2007).

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6 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, then it may be inquired as to 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 dispersal into new environments. The mobility and the short life span of insects and animals mean that, through excrement and eventual death, they provide a reliable mechanism for the dispersal of nutrients and seeds.

Zooplankton, crustaceans, and animal marine life in water perform a similar function as insect and animal life on land. These more mobile forms of life distribute nutrients throughout the ocean surface through excrement and death. It is noteworthy that dead fish and sea 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 animal powered nutrient cycling, a much larger area 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,

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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 from their ability to increase the plant and phytoplankton potential for evaporation of water.

## 7 Conclusions

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 in a much degraded form through the water cycle. Photosynthesis, although relevant to the spread of cyanobacteria and plant growth, is only a minor contribution to the thermodynamic function of life of entropy production. By catalysing the water cycle through; increased photon absorption, radiation-less photon dissipation, extended root systems, larger surface areas for transpiration, and an extensive sea-surface ecosystem, life augments the entropy production of the Earth in its interaction with its solar environment. Here we have presented quantitative estimates of the effect of ocean surface life on the hydrological cycle and entropy production. Empirical evidence was presented 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 given arguments for considering a revision of the traditional view of the origin and evolution of life in terms of its thermodynamic entropy producing function, rather than in terms of a somewhat tautological fight for survival.

Important aspects that remain to be considered under this thermodynamic framework are; (1) the oscillation of the Earth between different climate regimes (e.g. glaciations) as related to entropy production, (2) implications of the proposed function of life to the existence of life throughout the universe, and (3) the importance of considering the

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thermodynamic function of life in investigations of the origin of life on Earth (Michaelian, 2009, 2010).

The thermodynamic perspective presented here ties biotic processes to abiotic processes, co-evolving towards the universal goal of increasing Earth's global entropy production. Although this view is completely consistent with, and has been inspired by, the wisdom of Gaia (Lovelock, 1988, 2005), there is a distinction; the hypothesis of Gaia suggests that mixed biotic-abiotic control mechanisms have evolved to maintain the conditions on Earth suitable to life, that is, 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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**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.

CLEAR SKIES	UV (290–400 nm) W/m <sup>2</sup>	Visible (400–700 nm) W/m <sup>2</sup>	Infrared (700–10 000 nm) W/m <sup>2</sup>
Energy flux reaching Earth's surface (total 1029.3 W/m <sup>2</sup> )	50.5 direct 33.7 skylight  84.2 global (8.2%)	428.2 direct 53.9 skylight  482.1 global (46.8%)	456.3 direct 6.7 skylight  463.0 global (45%)
Energy flux absorbed in 1 mm skin layer (pure water)	$0.84 \times 10^{-3}$ ( $A_0^{345} = 1.0 \times 10^{-4} \text{ cm}^{-1}$ )	$38.6 \times 10^{-3}$ ( $A_0^{550} = 8.0 \times 10^{-4} \text{ cm}^{-1}$ )	9.16 ( $A_0^{1050} = 0.2 \text{ cm}^{-1}$ )
Energy flux absorbed in 1 mm skin layer (ocean water)	0.84 ( $A_{\text{org}}^{345} = 0.1 \text{ cm}^{-1}$ )	0.39 ( $A_{\text{org}}^{550} = 8.0 \times 10^{-3} \text{ cm}^{-1}$ )	9.16 ( $A_{\text{org}}^{1050} = 0.2 \text{ cm}^{-1}$ )
% of total entropy production in ocean skin	33.2	20.4	46.4

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

OVERCAST SKIES	UV (290–400 nm) W/m <sup>2</sup>	Visible (400–700 nm) W/m <sup>2</sup>	Infrared (700–10 000 nm) W/m <sup>2</sup>
Energy flux reaching Earth's surface (total 341.6 W/m <sup>2</sup> )	22.04 (6.5%)	274.7 (80.4%)	44.86 (13.1%)
Energy flux absorbed in 1 mm skin layer (pure water)	$0.22 \times 10^{-3}$ ( $A_0^{345} = 1.0 \times 10^{-4} \text{ cm}^{-1}$ )	0.022 ( $A_0^{550} = 8.0 \times 10^{-4} \text{ cm}^{-1}$ )	0.09 ( $A_0^{800} = 0.02 \text{ cm}^{-1}$ )
Energy flux absorbed in 1 mm skin layer (ocean water)	0.22 ( $A_{\text{org}}^{345} = 0.1 \text{ cm}^{-1}$ )	0.22 ( $A_{\text{org}}^{550} = 8.0 \times 10^{-3} \text{ cm}^{-1}$ )	0.09 ( $A_{\text{org}}^{800} = 0.02 \text{ cm}^{-1}$ )
% of total entropy production in ocean skin	55.2	41.3	3.5

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