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Interactive Comment

Interactive comment on "Biological catalysis of the hydrological cycle: life's thermodynamic function" *by* K. Michaelian

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Response to anonymous referee:

I thank the anonymous referee for his/her comments. I apologize for any repetitiveness in my answers here where the questions raised by the anonymous referee are similar to those of Prof. Schymanski.

General Comments

The thermodynamic perspective taken in my manuscript of coupling life and evolution with the hydrological cycle not only provides an explication of some "evolutionary disadvantageous aspects of life" (as seen from the Darwinian perspective), but, more importantly, provides new insight into the evolutionary dynamics of coupled biotic-abiotic systems. This view suggests that Nature displays a tendency to couple irreversible biological processes with other irreversible processes (biotic or abiotic) when this coupling increases the net entropy production of Earth in its solar environment. These couplings have been previously emphasized in the hypothesis of Gaia (Lovelock, 1988), but their thermodynamic origin was not identified. The thermodynamic view also offers a new perspective on the problem of the origin of life itself (Michaelian, 2011a).

In a preliminary response to the anonymous referee and to Prof. Schymanski (Michaelian, 2011b), I clarified that my paper neither invokes, nor requires, the "maximum entropy production principle". The paper simply associates Onsager's principle of increasing entropy production resulting from the coupling of irreversible processes, with the evidence (e.g. Zotin, 1984) for an increase in the amount of coupling of irreversible biotic processes over the history of Earth. The hypothesis of my paper is that biological irreversible processes also couple with abiotic irreversible processes, in particular, that biology catalyzes the hydrological cycle. This coupling augments the global entropy production of Earth in its solar environment in accordance with Onsager's principle, but not necessarily in accordance with the maximum entropy production principle.

I suggested in my preliminary response (Michaelian, 2011b) that the particular history of Earth with regard to entropy production, would depend very much on particular initial conditions (even microscopic) and subsequent external perturbations (even microscopic) since the Earth system under the solar photon flux is out of equilibrium and non-linear. Therefore, the comparison of the entropy production rate of Earth with its neighboring planets, as the referee indicates, can only be taken as suggestive of life's involvement. It does not necessarily confirm that life augments the entropy production of Earth. However, since Earth is the only planet that does not follow the trend of decreasing entropy production per unit area with distance from the Sun, and since Earth is the highest entropy producer per unit area among the planets with an atmosphere (see revised text), it is certainly very suggestive. If Earth was found to have a lower entropy production than its neighbors, then the data would not support my thesis. The presented data on planetary entropy production is thus not without information content, although it is not conclusive. I have changed the relevant section to reflect this stance.

In the introduction to the revised version, I have mentioned the mechanism by which the thermodynamic function acts to influence evolution on all scales. Probability of selection on all scales is based on global entropy production. However, in general, selection of processes on small scales is difficult to delineate since they are thermodynamically coupled to many other irreversible processes, making division of the system into parts difficult. Under the particular conditions where the processes operate on vastly different time scales, the selection of parts based on their own entropy production can be validated. There are many advantages to the thermodynamic view of evolution; 1) this characteristic ability to act on all scales, 2) avoiding the tautology, 3) explaining the co-evolution of the biotic with the abiotic, and 4) new insights into the evolutionary dynamics of coupled biotic-abiotic systems.

Plants do indeed limit water loss through stomata closing, but this happens precisely when no high energy photons are present to dissipate (at night), or when they are at risk of drying and dying. Some water loss does occur at night through the xylem and some open stoma. In very water-scarce areas CAM plants only open their stoma at night. I suggested in the manuscript that this is consistent with my hypothesis since photons from the near infrared (shortest wavelength) part of the black-body spectrum emitted by the Earth's surface at night may be dissipated further. Indeed, chlorophyll has an important absorption peak at these wavelengths. Conditions conducive to the opening of stoma are high light conditions and high humidity, just those conditions promoting entropy production through photon dissipation. The closing of stomata is completely consistent with the proposed thesis of the manuscript. It is not water loss which is important, but the dissipation of photons through transpiration. The coupled water cycle also contributes to the entropy production by dissipating further still the energy.

CAM and C4 plants do exist, but this metabolism has not displaced the heavily transpiring C3 metabolism. Instead, new niches for these plants have opened up in water scarce areas such as deserts. This was mentioned in the original text.

In the context of the proposed hypothesis, the variety of life can be explained, analogously as in traditional Darwinian Theory, by the variety of environments, both biotic and abiotic, and life's utility to global entropy production in being able to cover as much area of Earth's varied surface as possible with photon dissipating organic molecules and water. Traditional evolutionary theory has trouble explaining why CAM and C4 metabolism has not displaced C3 metabolism, whereas thermodynamic theory does not. In my opinion, at least this variety (in metabolism) is better explained from a thermodynamic perspective. Although the photon gradient is certainly the most important potential, and was probably the first potential utilized by life, life has evolved to produce entropy through the dissipation of other potentials, such as chemical potentials. Each potential, or new environment, requires a particular variety of organism optimized for dissipation. Varieties also exist to promote the dispersal of nutrients and seeds, allowing the photon-dissipating varieties to flourish.

The water cycle is an integral part of life and life's ability to produce entropy. I have mentioned in the text that there is no known life that can exist without water. I have also mentioned that life has probably played a crucial role in maintaining the existence of water on Earth (this is a Gaia hypothesis). I have mentioned, particularly in the cited references, but now directly in the revised version, that the chlorophyll molecule and other pigments must be surrounded by water molecules in order to dissipate efficiently their photon-induced excitation energy. It is this dissipation (the conversion of a high energy photon into many low energy ones with the aid of water) that produces the greatest amount of entropy in the biosphere. Transpiration is one component of the water cycle. Another component is the diffusion and convection of water vapor to the cloud tops where it condenses at approximately -14°C and the latent heat of condensation is eventually given off to space in an approximately black-body spectrum of

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this temperature. Entropy is produced in both parts of the cycle, but predominantly in the first. I have also mentioned the work of Makarieva and Gorshkov and (2007) whom have described a biotic pump for transporting water inland. Finally, I have included new paragraphs describing new evidence of how bacteria floating in the atmosphere act as seed of water condensation due to a particular enzyme on their outer surface. I have made numerous re-arrangements throughout the text to emphasize the integral role of life in the water cycle. In particular I have created 3 new subsections entitled "Life and Water", "Life and Transpiration" and "Life and Condensation" which explain how life is involved in every part of the water cycle.

In general, I have improved the structure of the article at all levels, incorporating most of the suggestions made by the referee. The entropy production calculations are move to the beginning and now associated information is collected in new sections and subsections. I have also avoided giving information about the water cycle without directly associating it with my thesis of life's involvement. I thank the referee for this request to re-structure; it has improved greatly the transparency and flow of the article.

Specific Comments

p. 1095 If the "environment" were fixed then it might seem plausible that life adapts to the environment in such a manner so as to improve its survivability. Note, however, that there is nothing in Darwinian Theory to explain why life would do that. One might answer that "if it doesn't it will cease to exist". Well, that is fine, all life disappears, so what? One might explain that there is some inherent (unexplained) force within every individual, species, clade, ecosystem, biosphere, imploring it to survive. This is our human experience. However, "this will to survive" must ultimately have a physical (I would say "thermodynamic") basis. Without this, Darwinian Theory is incomplete, even tautological.

The situation becomes even more difficult to reconcile, however, if it is found that life is actively transforming its "environment". Then it is not adapting to anything, it is

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co-evolving along with its environment. But, co-evolving towards what? There is no answer forthcoming from Darwinian theory, but there is from thermodynamics; "existing and co-evolving with the rest of the irreversible processes occurring in the ecosphere to increase the global entropy production of Earth in its solar environment". The thermodynamic view avoids the tautology of Darwinian theory (irrespective of Popper's recanting on the subject).

p. 1096 I have now defined "available energy" and "free energy" as "Gibb's free energy" (at constant temperature and pressure) in this section. This is the free energy most easily measured as most biological processes occur at constant temperature and pressure. Besides a change in entropy, a change in enthalpy may affect the change in Gibb's free energy, or, in other words, the change in entropy is affected by a change in the Gibb's free energy plus a change in the enthalpy (e.g. heat brought into, or taken out of, the system). I have used "free energy dissipation" in the text when referring to confined biological irreversible processes such as photosynthesis only because I feel that the phrase "entropy production" is less familiar. I have clarified the definition of "free energy" in the revised text. The most general potentials, valid under all conditions, for all irreversible processes, are the entropy and entropy production.

I wanted to emphasize that plants facilitate the absorption of sunlight in water by transforming visible and UV light (where water is transparent) into infrared light (where water absorbs strongly). I have included a parenthesis in the revised text to make this point clear.

The three-fold increase in evaporation due to zooplankton comes from a reference that I have not been able to re-locate. I believe that it comes from Lapov's "Traces of Bygone Biospheres" but I could not find it. I have opted to simply leave it out.

p. 1099, line 14 to 15; It is my understanding that the difference in buoyancy resulting from the difference in densities of dry air and water vapor gives rise to the powerful upward water-laden air currents that promote hurricanes and tornados. It is also gener-

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ally believed that this same buoyancy gives rise to the upward convection found under storm clouds. There is not a complete separation of air and water vapor, but neither is the mixture completely homogeneous, especially over heavily transpiring areas, as Makarieva and Gorshkov (2007) have pointed out. I have re-worded the text to avoid any confusion.

p. 1099, line 16; I have re-worded the text.

p. 1100; The question of the referee of the effect of clouds on global evaporation is similar to one asked by Prof. Schymanski. I will simply repeat my answer here. Unfortunately, it appears to be too complicated to sort out all factors and risk a premature answer. This is particularly because the effect of clouds on a global scale may be very different from that on a local scale. I have not found anything in the literature with respect to the effect of clouds on evaporation at a global scale. My response to Prof. Schymanski:

1. "Prof. Schymanski's question concerning the effect of clouds on evaporation rate is very interesting but very difficult to answer. Local clouds certainly reduce local evaporation by cooling the surface (this has been confirmed in numerous studies) but the effect on global evaporation has not, to my knowledge, been studied. Here I give a few indications suggesting that a partially clouded Earth may, counter-intuitively, be beneficial for global evaporation;

a) Clouds, by providing both local cooling and local heating, produce wind currents that help to mix atmospheric layers and thus reduce relative humidity directly over the wet surface.

b) The condensation of water vapor into clouds reduces the absolute amount of water vapor in the atmosphere, meaning reduced humidity at the surface.

c) Clouds bring water to inland regions which allow plants to grow and thus increment land evapotranspiration and thus the size of the water cycle over land.

However, the important question within the context of the hypothesis presented in my manuscript is not the evaporation rate, but rather the global entropy production rate under a partly cloudy sky as compared to a clear sky. This is a much more complex issue because we have to take into account all irreversible processes operating in the biosphere. For example, even Lambertian reflection of light produces entropy. Most importantly, however, the potential for entropy production is biased towards dissipation in the visible and UV regions so strong absorption by clouds in the infrared will have a reduced effect on entropy production in the biosphere. Finally, as the referee noted, clouds are a necessary part of the hydrological cycle and without them there would be no plants growing on land, and therefore less global photon dissipation. These are very complex issues and this manuscript only begins to address them. I have re-written the paragraph containing the reference to clouds to reflect these complexities.

p. 1101 to 1102; Please see my third paragraph under General Comments. The referee is correct, the comparison of entropy production among planets is not conclusive to life's involvement, but I maintain that it may be suggestive, and has information content, since Earth is the only planet not following the tendency to decrease entropy production per unit area with distance from the Sun and, of the planets with an atmosphere, it is the one of greatest entropy production per unit area (see revised version of text, and also Aoki, 1984). I have reworded the relevant text accordingly.

It certainly would be interesting to calculate the entropy production of Earth before the advent of life and compare it to that of today. However, I cannot imagine a reliable estimate coming out of such an attempt given our very uncertain knowledge of Earth's characteristics during the Archean, not to mention our very poor understanding of all irreversible processes occurring on Earth. We have no emitted spectra of the Earth, nor incident spectra of the Sun, during the Archean – it is not only Earth's effective temperature that is important (even taking into account the albedo and emissivity), but more accurately, the exact wavelength dependent incident, radiated, and reflected spectra of Earth. What could perhaps be possible, and I will set to work on determining its feasibility, is to determine a small, perhaps detectable, shift towards longer wavelengths of Earth's emitted spectrum over some small number of years for which there exists satellite data. If the biosphere is indeed evolving to greater entropy production then, in principle, a small yearly shift in the emitted spectrum should exist. However, such a shift may be too small to measure with today's technology (for example, if Earth with life has been augmenting global entropy production for 4 billion years, a change in the last decade would be of the order 0.25x10ˆ-8 times the entropy production difference today between Earth and its neighbors). The effect that we measure over a decade may also be only local in time due to astronomical effects. We would need very accurate satellite data for such a determination. I thank the referee for stimulating thought on the possibility of such a test of the hypothesis.

p. 1101; I thank the referee for the Wu and Liu reference. It is the most recent (2010) and complete treatment I have seen on the entropy production calculation of Earth. I have reworked completely my corresponding section, using now the Planck equation given in the Wu and Liu (2010), and taken into account an expansion factor for the incident entropy flux as given in Wu et al. (2011), instead of the Ulanowicz equation. (Note also that Wu and Liu's (2010) result for the reflected entropy flux should also be corrected by this factor.) This should satisfy all the referees who have criticized this section.

p. 1105; Correct. The sentence has been changed.

p. 1106; I have re-written the second half of the paragraph.

p. 1108; As mentioned in my response to Prof. Schymanski (point 15), dissolved salts and other inorganics absorb very little in the visible and UV and almost all attenuation due inorganics is thus attributable to particulate scattering, which is at least an order of magnitude less than that due to absorption on dissolved organic material and chlorophyll in turbid costal waters (Liew, 2002). I am using the absorption coefficient of costal turbid water as a proxy for the same of the ocean surface layer since, the density of organic material in costal turbid water is a factor of 103 that of deep ocean water. The ocean surface layer has an organic density of at least 104 that of deep ocean water (Grammatika and Zimmerman, 2001). This absorption coefficient proxy is therefore a lower limit to the real one for the surface layer. This proxy is used for only the visible and UV (all water absorbs very strongly the infrared). I, therefore, maintain that this is a reasonable underestimate for an absorption coefficient that has still to be measured. The new reference has been included.

p. 1108 I agree with the referee that a rigorous calculation of the energy deposited in the surface skin layer of the ocean is important. This would require a convolution of the direct and sky light spectra at the Earth's surface with the absorption coefficient for water, with and without organic material, and for clear and cloudy skies, and an integration of the solar spectrum over the entire day. However, this requires not only accurate knowledge of the incident spectra on a clear and cloudy day, as well as knowledge of the wavelength dependent absorption coefficients of water, with and without the organic material of the surface skin layer, but also the wavelength dependence of absorption and reflection by the atmosphere, and reflection by the ocean surface. Using the proxies, such as that of costal turbid waters, would probably cancel all rigor gained by the convolution over wavelength. Such a rigorous calculation is certainly doable, and I will set out to do it. However, all this would postpone too long my response. What I can assure the referee is that the first row of the two tables, the total energy incident in each wavelength region, were obtained by graphical integration of the plots by Gates (1980). I estimate the errors of this technique to be less than 5%. The sum of the separate wavelength regions corresponds well to the total integration.

What is important, however, is to emphasize roughly how the different wavelength regions contribute. The tables 2 and 3 (revised version) show that dissipation of UV and visible photons due to the organic material in the surface skin layer is a very important part of the total. The actual values may change somewhat if a convolution is performed over all wavelengths and if an integration is made over the entire day, however, I am convinced that main conclusions that have come out of my approximate calculation will remain; 1) that organic material floating on the ocean surface increases the entropy production of Earth through UV and visible dissipation, 2) that in the surface skin layer (1 mm), UV absorption contributes more than visible light absorption (perhaps providing a thermodynamic relevance for mycosporines), 3) that UV and Visible light absorption on the surface skin layer augments the hydrological cycle through increased evaporation. I have endeavored to make the limitations of this calculation more evident in the revised text.

p. 1108, line 20 The Martin Chaplin web page is complete and well maintained. In any case, this light absorption data on pure water can be found on many web pages by making a simple search with Google. I have not found a published article including the full spectrum, probably because the website is a compilation of data from many sources covering different wavelength regions.

p. 1109, line 18; I have made a very rough calculation of the increase in the evaporation rate expected due to absorption of UV and visible light on organic material at the ocean surface skin layer by assuming that the evaporation rate is proportional to the vapor pressure deficit and assuming an exponential relation between saturation vapor pressure and temperature (see revised version of text for details). This calculation depends on various assumptions that may eventually be shown to be incorrect. In any case, I believe that it will serve as a first approximation for more refined future calculations.

p. 1109, line 21-22; I am not sure as to what text the referee was referring to as the page number and line numbers quoted by the referee are incorrect, and I can't find accommodating ones. If the referee is referring to the statement that the latent heat is transmitted to space, then I have two comments; 1) nitrogen and oxygen molecular gas absorb very little in this wavelength region, 2) if some energy is absorbed, then it goes to the surrounding air, but this air then emits it to space in a quasi-black-body spectrum (including emissivity) corresponding to the air temperature of about -14 °C.

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The Earth's outgoing emitted energy must balance the incoming energy.

p. 1110; I have now made a much more careful calculation of the relative entropy production due to photon dissipation in each wavelength region. This new calculation takes into account the full black-body spectrum of the radiated radiation, although still using average energy deposition values for each region. A new section, 5.2, has been dedicated to this calculation.

p. 1114; Any absorption, or Compton scattering (non-elastic) of a photon will produce entropy.

p. 1116; I have mentioned in the text that photosynthesis accounts for the utilization of only 0.1% of all the Gibb's free energy arriving at the leaf and that transpiration accounts for over 90% of its utilization (references were given to Gates, 1980; new references are given in the revised manuscript). It follows that photosynthesis is only a minor contribution to the thermodynamic work performed by life.

Minor Comments

p. 1097; If photosynthesis can be found to be efficiently operating at 70 °C and higher in certain bacteria, then it is surprising that plants would not also have taken advantage of this possibility and avoided the tremendous free energy costs required in cooling the leaf through its complicated water flow and transpiration systems, and, instead, used this free energy for greater biomass production through photosynthesis. I have also mentioned that there are studies showing that the leaf temperature is optimized for maximizing transpiration, not photosynthesis (Wang et al., 2007). I have re-worded the text and used the words "at odds" in replace of "inconsistency".

All other minor corrections have been attended to.

I sincerely thank the referee once again for his/her very through and useful review which has led to a much improved paper.

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