Differences and implications in biogeochemistry from maximizing entropy production locally versus globally
by J. Vallino

Reviewer's Comments

The author examines one of the most fundamental questions facing practitioners of the maximum entropy production principle: under what circumstances can it be applied, and at what scale is it applicable. This goes to the heart of current arguments over the different formulations of MEP given by Dewar (2003, 2005) and Niven (2009). The author therefore considers a critical problem, using a very useful case study. However, the manuscript is marred by **serious** errors, in (1) its theoretical and mathematical formulation, (2) its omission of key entropy production or flux terms from the calculations, and (3) in the inconsistent and (in some cases) completely incorrect handling of units. A major rewrite of the manuscript, and a reanalysis of the model systems, is essential before the manuscript can even be considered for publication. At such time, it must undergo a further episode of peer review.

Acronyms used below: EP = entropy production; MEP = maximum entropy production.

Comments

1. Like many studies on MEP, the actual system (control volume) under examination is not properly specified:

   - Definition 1: Is it the totality of the two boxes, two reservoirs and three flows in Figure 1?

   or

   - Definition 2: by a crude analogy with studies of planetary climate systems, is it simply the two boxes plus the flow $F_{1,2}$? - i.e., should the two reservoirs and the boundary fluxes $F_{0,1}$ and $F_{2,3}$ be excluded?

   Note that at steady state, the EP of a system is given *either* by (a) the sum of EPs due to internal flows between compartments plus the internal EP production within each compartment, *or* (b) by the sum of EPs through the external boundary (Ozawa et al., 2001). It is not permissible to count the EPs due to both internal and external flows. It is therefore critical that the system boundary be specified clearly.

   It appears in (14)-(15) that the author wishes to adopt two variants of Definition 2 above, but this is not stated explicitly, and it is not explained why this definition should override Definition 1. What is it about the EP in the two reservoirs, and/or the flows $F_{0,1}$ and $F_{2,3}$, which require that they be excluded from the system ? (The author's system, in some respect consistent with the many 2-box planetary MEP models, involves its own "local" rather than "global" calculation of EP). Alternatively, should the system really encompass definition 1, since the flows $F_{0,1}$ and $F_{2,3}$ are not necessarily constant?

2. (p10-11) It is not at all clear why the author omits the entropy flux between boxes 1 and 2 from his models (14) or (15). This term may be small, but unless this is clearly demonstrated, the calculation is incomplete and may have led to a false conclusion. In

the extreme cases of either a high gradient between boxes 1 and 2, or a high flux between them, the conjugate variable will diminish to zero and so the EP will be low; but for moderate gradient and flux, this EP may well be quite high. It is **essential** to examine the effect of this term, since it may explain the reported discrepancy between models (14) and (15).

Similar arguments apply to fluxes $F_{0,1}$ and $F_{2,3}$, if these are to be included within the system.

3. There are many inconsistencies and/or errors in the use of units in the manuscript, some quite serious:

(a) (p7) There appear to be two serious problems with the equation for EP in each compartment (8):

- It is given in units of entropy flux, J K^{-1} m^{-2} s^{-1}, rather than the overall entropy production, J K^{-1} s^{-1}. It therefore cannot be used to determine the entropy production within a compartment due to a chemical reaction. Also, note that the total EP must be computed, J K^{-1} s^{-1}, not merely the EP per unit volume J K^{-1} s^{-1} m^{-3}, to allow the comparison of boxes of different volumes.

- There also appears to be a unit imbalance in (8), unless ΔG_{ri} is given in units of J m^{-3} instead of the usual units J mol^{-1}. It would be preferable to give ΔG_{ri} in standard form, and explicitly show the dependencies on density (concentration) and molecular mass.

(b) (p10) The mass balances (13) also have two problems:

- The first terms are calculated by dividing the fluxes (kg m^{-2} s^{-1}) by h, a unit length, to give $dC_k[i]/dt$ in kg m^{-3} s^{-1}. This depends on the flux area and so is not a true mass balance. The fluxes should instead be multiplied by the unit area of flow, to give the total $dC_k[i]/dt$ in kg s^{-1}.

- Since the units of parameters ν_i and hence r_i are specified as d^{-1}, but those of the stoichiometric coefficients are unspecified (normally they are mol of species/mol of reaction), the units of the $\mathbf{\Lambda}_k[i]\mathbf{r}[i]$ terms in (13) are not clear, nor whether they are compatible with the first term in (13).

(c) (p 12) Although the author does not yet do this (see comment 2), the EP flux terms (12) cannot simply be added to the EP productions within each box (8), due to their different units. Consideration must be made of the cross-sectional area of each box, normal to the flux. (Alternatively, calculate flow rates rather than fluxes.) Similarly, different symbols **must** be used for entropy fluxes and production rates, so their meaning is absolutely clear.

(d) The author deviates from standard SI or CGS chemical units in a number of places, e.g. the measurement of concentrations in mmol m^{-3}, or the ideal gas constant in J $mmol^{-1}$ K^{-1}, or chemical potentials (presumably) in J $mmol^{-1}$. These could cause confusion to many readers and should be avoided.

4. (p5) The chemical reactions (1) and (2) are not in stoichiometric balance, and/or the stoichiometry of the biochemical structures $\$_1$ and $\$_2$ (I do not have the author's symbols) is not specified. By my reckoning, the first structure is $\$_1 = C_{\varepsilon_1} H_{\varepsilon_1(3\rho+2)} O_{\varepsilon_1} N_{\rho\varepsilon_1}$, and the second is much more complicated. The stoichiometry of the biological structures should be discussed and justified.

5. (p6) Concerning the biological growth curve, the rate coefficient (4) is assumed to be (pseudo) first-order, without inclusion of a respiration rate constant k_d or carrying capacity K, and indeed, contains a range of other assumptions which are uncommon in microbiology. Chemically, it does not contain any Arrhenius-like connection to an activation energy or other thermodynamic energy term. The assumptions used may or may not be justifiable, and the author does attempt to explain them; this is a small concern. Of greater importance is the question: would it be preferable to actually try to derive (4) on the basis of some fundamental principle, perhaps even MEP? Alternatively, could the free parameters such as ν^* be interpreted as adjustable parameters in the MEP context, to be optimised using MEP?

6. (p8) I do not understand the changes in Gibbs free energy (9) and (10), in particular the presence of the two leading terms on the right. Surely the ΔG_{ri}'s are completely expressed by the $RT\ln(..)$ terms? Perhaps this problem arises from the lack of specification of stoichiometry in (1) and (2), which the author wishes to correct by adding other reactions to (1) and (2)?

Due to the above serious problems, I did not examine the findings in §3. I would like to do so, once I have more confidence in the author's theoretical framework and methodology used.

Minor Comments

7. It is not stated explicitly that each compartment in Fig. 1 is considered a "well mixed tank" or "completely mixed flow reactor" (CMFR). This assumption is important. Biological organisms may contain domains of different biochemical conditions, and larger scale structures may produce conditions of altered local equilibrium. The author assumes all such effects are negligible.

8. (pp5-7) The symbols r_1, r_2 are used to name the chemical reactions (1) and (2), and then later are used for their rate constants (6) and (7).

9. (pp7-8) The chemical rate equations and Gibbs free energies should, of course, depend on the chemical *activities* of each species, not their concentrations; only at low concentrations can it be assumed that concentrations = activities. Arguably, these should also be included in the biochemical growth rate equations (4). The distinction could be extremely important, especially in a background electrolyte of seawater, even though the activity coefficients of neutral species and biochemical structures are not well understood or easily modelled. The author mentions activity effects briefly (p9), but does not provide any detail on whether or how they were computed for the model.

10. (p7) The extra ε_i term in (5) appears to be omitted from the equations (7). Surely they depend on ε_i^3 ? It would be preferable to specify the actual first-order rate equations, so that the reader can understand the distinction between ν_i and μ_i.

11. (p9) The β term in (11) is omitted from (12).

12. (p11) The author mentions the possibility of optimisation for the transient problem. Please note that there is no theory or even any viable hypothesis for a transient MEP principle, only some evidence for the existence of MEP at steady state.

References

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