A thermodynamic perspective on food webs: Quantifying entropy production within detrital-based ecosystems

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Abstract

Because ecosystems fit so nicely the framework of a "dissipative system", a better integration of thermodynamic and ecological perspectives could benefit the quantitative analysis of ecosystems. One obstacle is that traditional food web models are solely based upon the principles of mass and energy conservation, while the theory of non-equilibrium thermodynamics principally focuses on the concept of entropy. To properly cast classical food web models within a thermodynamic framework, one requires a proper quantification of the entropy production that accompanies resource processing of the food web. Here we present such a procedure, which emphasizes a rigorous definition of thermodynamic concepts (e.g. thermodynamic gradient, disequilibrium distance, entropy production, physical environment) and their correct translation into ecological terms. Our analysis provides a generic way to assess the thermodynamic operation of a food web: all information on resource processing is condensed into a single resource processing constant. By varying this constant, one can investigate the range of possible food web behavior within a given fixed physical environment. To illustrate the concepts and methods, we apply our analysis to a very simple example ecosystem: the detrital-based food web of marine sediments. We examine whether entropy production maximization has any ecological relevance in terms of food web functioning.
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1. Introduction

The biological components within ecosystems engage in a complex process of self-organization so that food webs emerge (Solé and Bascompte, 2006). A fundamental question in ecology is whether these food webs are shaped by (1) the interplay of internal interactions, or (2) external thermodynamic constraints, or (3) a combination of both. Up to now, the ecological literature has primarily explored the first option, looking at architecture, topology, complexity etc.—see reviews in de Ruiter et al. (2005); Montoya et al. (2006). Roughly speaking, one could say that the ecological perspective primarily emphasizes the "inside" of the food web (network organization of the food web, the role of trophic interactions), and because of this, the abiotic environment receives a very crude description.

Thermodynamics offers a different, complementary perspective on food web functioning. Thermodynamic approaches focus on the various process rates induced by the food web, and this requires a detailed description of the communication with the "outside" environment.

To examine whether thermodynamic constraints are relevant for food web operation, one clearly needs a proper thermodynamic description of food webs. This marriage between ecology and thermodynamics continues to be a true challenge. Although the need for a thermodynamic perspective has long been recognized (Schroedinger, 1944), these two disciplines have shown little integration over the past 50 years. This dichotomy between ecology and thermodynamics is nicely illustrated by the distinct model currencies that are in use within different research communities. In the field of ecological modeling, the default state variables are mass and energy, of which the associated conservation equations form the central heart of food web and ecosystem models (Lindeman, 1942; May,

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1981; Grover, 1997; Loreau and Holt, 2004). The theory of non-equilibrium thermodynamics basically extends this mass/energy toolbox with the entropy, the central concept to the Second Law of thermodynamics. A principal focus in thermodynamic analysis is therefore the proper quantification of entropy production within various model systems (Glansdorff and Prigogine, 1971; Nicolis and Prigogine, 1977; Kondepudi and Prigogine, 1998). Nonetheless, the term "entropy" does usually not feature in ecological textbooks (e.g. May, 1981; Begon et al., 1996; Case, 2000). The application of non-equilibrium thermodynamics in biology is classically restricted to the subcellular level, where metabolic processes are cast within the formalism of chemical thermodynamics (Sandler and Orbey, 1991; Kurzynski, 2006). Yet, when moving to the community or ecosystem level, these concepts and methods are no longer invoked. The concept of entropy remains highly enigmatic to most ecological modelers, while thermodynamicists have not applied their entropy production calculations to actual ecosystems.

In recent years, there are a growing number of publications that specifically aim to close the gap between ecology and thermodynamics (see reviews in Jorgensen, 2000; Jorgensen and Svirezhev, 2004; Schneider and Sagan, 2005). Given its central role in physical applications of non-equilibrium thermodynamics, one would expect the entropy concept to play a dominant role in this emerging field of "thermodynamic ecology". With some notable exceptions (Aoki, 1995; Svirezhev, 2000; Aoki, 2006), this is surprisingly not the case. Instead, the prevalent idea is that the standard mass/energy/entropy toolbox of non-equilibrium thermodynamics is not sufficient to describe ecological processes (Jorgensen, 2000; Jorgensen and Svirezhev, 2004). In this view, ecology is inherently more complex than the dissipative phenomena usually considered in "abiotic" non-equilibrium thermodynamics, so that additional constructs and new rules must be introduced to fully describe an ecosystem's functioning. As a result, a number of novel "ecological" concepts have been forwarded as essential complements to the standard entropy concept, including emergy (Odum, 1983), exergy (Schneider and Kay, 1994), eco-exergy (Susani et al., 2006), and ascendancy (Ulanowicz and Abarca-Arenas, 1997). However, the use of these newly defined properties does not come without problems. The first problem is the loose and verbal use of thermodynamic language, and the highly qualitative way in which these concepts are used (e.g. see discussions in Mansson and McGlade, 1993; De Wit, 2005). Secondly, each of these concepts has its proponents, but the exact interrelation between them remains unclear. Thirdly, and more fundamentally, the question remains whether the standard mass/energy/entropy toolbox of non-equilibrium thermodynamics is really insufficient to analyze ecosystem functioning?

Despite some pioneering work (e.g. Aoki, 1995, 2001; Svirezhev, 2000), believe that the theory of non-equilibrium thermodynamics has not been explored to its full potential within an ecological context. This communication has therefore two central goals. The first goal is to illustrate how this theory can be applied in a strict "orthodox" fashion to the analysis of resource processing within ecosystems (i.e. without invoking any "ecological" additions). To this end, we need to correctly translate thermodynamic concepts (e.g. dissipation, thermodynamic gradient, distance from equilibrium) into an ecological context. As noted above, entropy is the central variable in the analysis of dissipative systems, and hence, a prime concern will be to develop a consistent procedure to calculate the entropy production within an ecosystem. The second goal is to examine whether the entropy production rate has any ecological relevance in terms of food web functioning. In recent years, a number of propositions have been made along this line, in which the notion of 'maximal entropy production' surfaces in relation to ecosystem operation (Ulanowicz and Hannon, 1987; Schneider and Kay, 1994; Svirezhev, 2000; Fath et al., 2001; Schneider and Sagan, 2005). Between these studies, there is however considerable difference in the actual implementation of this entropy production maximalization, and its subsequent interpretation. Moreover, the treatments often remain conceptual and vague, and propositions have not been convincingly tested against actual data. To examine whether and how entropy production is relevant to food webs, we will perform a case study of the detrital-based ecosystem of the ocean floor. This ecosystem has the advantages that (1) it is chemotrophic, and so it can be fully described with the standard chemical thermodynamics (and hence we do not need to revert to radiation thermodynamics as in phototrophic systems), (2) suitable data are available from past biogeochemical studies to test thermodynamic constraints, and (3) the procedure can be generalized to other chemotrophic ecosystems (such as chemo-autotrophic vent systems and terrestrial soils).

2. An ecosystem model of the ocean floor

2.1. Mass balance formulation

The ocean floor covers nearly 75% of the earth surface, and apart from some notable but localized exceptions (thermal vent systems, coral reefs, seagrass beds, coastal phototrophic mats), the bulk of the ocean floor harbors a detrital-based, chemo-heterotrophic ecosystem (Burdige, 2006). This system is fueled by organic carbon that is fixed by photosynthesis within the upper ocean, settles through the water column, and rains down on the sediment surface. Within the sediment, part of this organic matter input is taken up by the food web, and converted into biomass and metabolic end products. A small fraction (~5%) of the incoming flux escapes degradation and is buried into deeper layers (Middelburg and Meysman, 2007).

To arrive at a suitable model description of the carbon dynamics within the ocean floor ecosystem, the conceptual scheme of Fig. 1a is used. This scheme reduces sedimentary
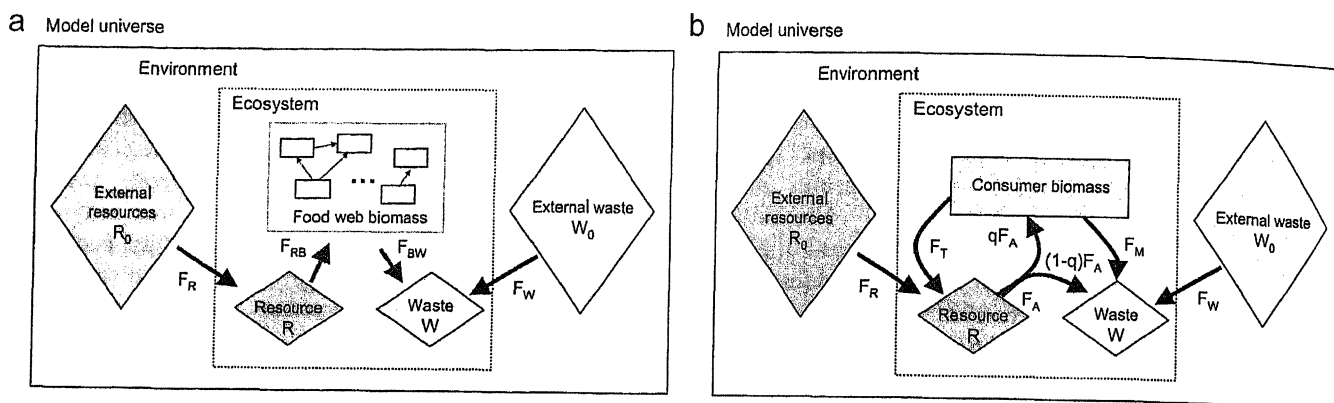
a   Model universe

b   Model universe

Fig. 1. (a) Idealized flow scheme of the detrital-based ecosystem of marine sediments. The ecosystem features an arbitrary complex food web, which is treated as a black box. The direction of the arrows specifies the convention by which flows are taken positive. (b) Specific example of the general scheme depicted on the left: In this basic food web, one consumer is feeding on a single resource. See text for an explanation of the different flows.

organic matter processing to its barest essentials. The principal goal is to illustrate the quantification of entropy production within ecosystems, rather than providing a detailed model of ocean floor biogeochemistry. Our model universe contains two compartments, termed 'ecosystem' and 'environment'. The *ecosystem* refers to the bioturbated zone of the ocean floor, which is a relatively thin sediment layer of thickness L (typically around 10–30 cm), characterized by biological sediment reworking and intensive processing of organic matter (Boudreau, 1998; Middelburg and Meysman, 2007). This intense biogeochemical activity results from an interplay between microbial decomposition and the reworking activity by sediment dwelling invertebrates (Kristensen et al., 2005). All resident organisms (viruses, microbes, meiofauna, invertebrates) are collectively referred to as the food web, which is treated as a black box in Fig. 1a. The *environment* refers to all external surroundings, which includes both the overlying water as well as the deeper lying sediment. Temperature effects are ignored, and so both ecosystem and environment remain at the same temperature T. In our model analysis, we assume that the operation of the food web is only limited by the availability of organic food resources. In other words, organic matter processing is not constrained by the availability of electron acceptors used in respiration, which is a typical assumption in biogeochemical model studies of marine sediments (e.g. Berg et al., 2003; Meysman et al., 2003). As a result, we do not need to consider the mass balance dynamics of the electron acceptors explicitly (e.g. O_2, SO_4). Instead, we only track the behavior of two carbon compounds, termed resource (R) and waste (W). These can be respectively identified as the organic matter food substrate, represented by the simplified stoichiometry $CH_2O|_R$, and CO_2, the metabolic end-product of respiration.

The model ecosystem consists of three carbon reservoirs: one resource reservoir, one waste reservoir, and one reservoir that pools all biomass of the food web (at respective concentrations C_R, C_W and C_B). The environment is abstracted as two separate reservoirs with which

the ecosystem exchanges matter: one resource reservoir at concentration C_R^0, and one waste reservoir at concentration C_W^0. For simplicity, we assume that the exchange of organic matter takes place with a single reservoir (instead of incorporating the buried organic matter into a separate external reservoir). This broad-brush 'pooling' of all external organic matter suitably simplifies the derivations, but does not fundamentally change the thermodynamic analysis or the conclusions arrived upon.

The principal difference between the internal ecosystem reservoirs and those of the environment is their size. The external reservoirs are considered 'infinite', so that the concentrations C_R^0 and C_W^0 are fixed model parameters. Consequently, the operation of the ecosystem is constrained by a fixed physical environment. In contrast, the internal ecosystem reservoirs have a finite size, and are governed by following mass balances

$$\frac{dC_R}{dt} = F_R - F_{RB}, \tag{1}$$

$$\frac{dC_W}{dt} = F_W + F_{BW}, \tag{2}$$

$$\frac{dC_B}{dt} = F_{RB} - F_{BW}, \tag{3}$$

where t represents time, and the flows F_i are expressed as mass per unit of volume and time. The flow F_{RB} represents the net uptake of resource by the food web, while F_{BW} is the net release of CO_2 by the food web. The constitutive expressions for these flows will depend on the structure of the resident food web, and so one needs an explicit food web representation (as shown below). The flows F_R and F_W, respectively, denote the net exchange of resource and waste with the environment, and are parameterized as

$$F_R = \alpha_R(C_R^0 - C_R), \tag{4}$$

$$F_W = \alpha_W(C_W^0 - C_W). \tag{5}$$

This linearized transfer is the standard way of modeling the exchange with the environment in ecological models (Tilman, 1982; Loreau and Holt, 2004). We assume that

the transport coefficients α_R and α_W are not dependent upon food web activity. Although it is known that fauna can significantly influence the exchange between sediment and external environment (Meysman et al., 2006), such feedbacks are not considered here. Accordingly, the coefficients α_R and α_W can be directly calculated from the dominant physical transport processes that are operating in the sediment. The flow F_R represents the difference between the deposition flux of organic matter F_D, and the burial flux F_B (Boudreau, 1997; Burdige, 2006). The deposition flux can be written as $F_D = (\phi\omega/L)C_R^0$, with ϕ the porosity, ω the burial velocity sediment and C_R^0 the organic carbon content of the incoming material. The export to deeper layers can be parameterized as $F_B = (\phi\omega/L)C_R$, which now features the organic carbon concentration within the sediment. The exchange of CO_2 with the overlying water is parameterized by the diffusive exchange $F_W = (3\phi D/L^2)(C_W^0 - C_W)$, where D is the pore water diffusion coefficient of CO_2. Accordingly, one finds that $\alpha_R = \phi\omega/L$ and $\alpha_W = 3\phi D/L^2$.

2.2. Example: a simple single-consumer food web

In the above model formulation of the ocean floor ecosystem, the food web structure was treated as a black box, and the mass balances (1)–(3) hold for any (arbitrarily complex) food web. This black box perspective will be a cornerstone of our thermodynamic analysis. However, as an example illustration, we now analyze an explicit representation of the food web. To this end, we consider the simplest possible ecosystem: only a single consumer is feeding upon the available resource R. This is not meant as a realistic representation of the actual food web in marine sediments, and in fact, it hardly deserves the name food web, as only a single organism is present. Still, because of its simplicity, it didactically illustrates concepts. For reference, one could think of the microbial community in marine sediments that is treated as a single population. Fig. 1b shows the transformations. We assume that the consumer's biomass $CH_2O|_B$ is simply assembled from elementary building blocks of resource $CH_2O|_R$. The synthesis of biomass does not occur spontaneously, and must always be coupled to respiration. This coupling between anabolism and catabolism can be formally represented via the chemical transformation

$$CH_2O|_R + (1 - q)O_2$$
$$\rightarrow qCH_2O|_B + (1 - q)CO_2 + (1 - q)H_2O. \qquad (6)$$
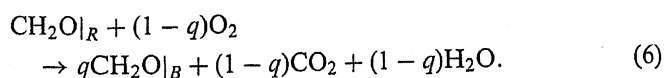
The associated reaction rate F_A represents the assimilation rate. In reaction (6), O_2 generically represents the electron acceptor, while CO_2 and H_2O stand for the end-products of respiration. The yield factor q specifies the amount of biomass that results from the assimilation of one unit of resource. Or equally, $1 - q$ denote the respiration costs associated with biomass synthesis (activity respiration). Obviously, this reaction provides a very simplified picture

of metabolism. Yet, for the present purpose, it is sufficient, as it incorporates those features that are important from a thermodynamic perspective. Basal maintenance refers to energetic costs to 'stay alive', and is described by the transformation

$$CH_2O|_B + O_2 \rightarrow CO_2 + H_2O, \qquad (7)$$
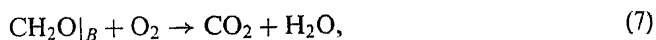
where the associated rate F_M refers to maintenance respiration. The turn-over of biomass due to mortality (from predation, accident, disease, ageing) is described by

$$CH_2O|_B \rightarrow CH_2O|_R, \qquad (8)$$

with associated turnover rate F_T. Biomass turn-over thus means that biomass simply disassembles into basic building blocks, which become again available for biomass synthesis or respiration. Together this implies that $F_{RB} = F_A - F_T$ and $F_{BW} = F_M + (1 - q)F_A$, and so the mass balances for this very simple one-consumer food web become

$$\frac{dC_R}{dt} = F_R - F_A + F_T, \qquad (9)$$

$$\frac{dC_W}{dt} = F_W + F_M + (1 - q)F_A, \qquad (10)$$

$$\frac{dC_B}{dt} = qF_A - F_M - F_T. \qquad (11)$$

In the next sections, we will introduce the necessary theoretical tools to calculate the entropy production associated with this particular food web. This will confront us with the yet unresolved conceptual problem of assigning chemical potentials to organisms.

2.3. Quantifying entropy production

In the standard formulation of non-equilibrium thermodynamics, the entropy production σ_i associated with a given flow F_i is calculated as the product of that flow with a corresponding thermodynamical force X_i (Nicolis and Prigogine, 1977; Kondepudi and Prigogine, 1998)

$$\sigma_i = F_i X_i. \qquad (12)$$

Accordingly, we need to calculate the proper forces X_i that are associated with each of the five flows F_i in our example ecosystem model (Eqs. (9)–(11)). The resource and waste exchange essentially describe a mixing process between two reservoirs A and B at different concentrations. The associated thermodynamic force can be directly calculated from the difference in the chemical potential μ of these reservoirs via the relation $X_{mix} = -\Delta G_{mix}/T = (\mu_A - \mu_B)/T$, where ΔG_{mix} is the Gibbs free energy of mixing and T is temperature (Kondepudi and Prigogine, 1998). If we treat resource and waste as ideal solutes, their chemical potential scales with the logarithm of the concentration, i.e. $\mu = \mu^{ref} + RT \ln(C/C^{ref})$, where R denotes the universal gas constant, and the concentration C^{ref} refers to some reference state. As a result,

we obtain

$$X_R = (\mu_R^0 - \mu_R)/T = R\ln(C_R^0/C_R), \tag{13}$$

$$X_W = (\mu_W^0 - \mu_W)/T = R\ln(C_W^0/C_W). \tag{14}$$

Accordingly, the associated entropy production rates become

$$\sigma_R = F_R R\ln(C_R^0/C_R), \tag{15}$$

$$\sigma_W = F_W R\ln(C_W^0/C_W). \tag{16}$$

The biotic flows F_A, F_M and F_T are in essence rates associated with a given chemical reaction. The thermodynamic force associated with a chemical reaction can be calculated from the relation $X_{reac} = -\Delta G_{reac}/T$, where ΔG_{reac} denotes the Gibbs free energy of the reaction. This quantity is calculated from the difference in chemical potential between reaction products and reactants (Kondepudi and Prigogine, 1998), and so we obtain

$$X_A = -((1-q)\mu_W + q\mu_B - \mu_R)/T, \tag{17}$$

$$X_M = -(\mu_W - \mu_B)/T, \tag{18}$$

$$X_T = -(\mu_R - \mu_B)/T, \tag{19}$$

where μ_B, μ_R and μ_W, respectively, denote the chemical potential of biomass, resource and waste. Note that the assimilation force simply forms a linear combination of the other two forces, i.e., $X_A = (1-q)X_M - X_T$. When the flows F_A, F_M and F_T are known, one can multiply them with the force expressions (17)–(19) to calculate the associated entropy production rates. Together, the five entropy production rates σ_R, σ_W, σ_A, σ_M and σ_T fully quantify all 'dissipation' that occurs within our model universe, where the term *dissipation* is thus simply synonymous to entropy production.

2.4. Two entropy production rates

Two composite rates of entropy production can be derived that are of particular interest. Firstly, the 'ecosystem entropy production' accounts for the entropy production that occurs *within the ecosystem alone*, i.e., the entropy production exclusively associated with the functioning of the food web. Summation of the entropy production rates associated with the biotic flows results in

$$\sigma_{EM} \equiv \sigma_A + \sigma_M + \sigma_T. \tag{20}$$

where the subscript 'EM' refers to ecosystem metabolism. Secondly, we can calculate the entropy production that occurs *within the complete model universe (both ecosystem and environment)*. Summation of all five entropy production rates leads to

$$\sigma_{tot} \equiv \sigma_R + \sigma_W + \sigma_A + \sigma_M + \sigma_T = \sigma_R + \sigma_W + \sigma_{EM}. \tag{21}$$

This 'total entropy production' encompasses the dissipation that occurs within the ecosystem (σ_{EM}), as well as the dissipation that results from the communication with the external surroundings (σ_R and σ_W).

2.5. Entropy balance formulation

The Second Law of Thermodynamics requires that for each independent flow F_i the associated entropy production σ_i should be positive (Nicolis and Prigogine, 1977; Kondepudi and Prigogine, 1998). A given flow is 'independent' when it is not coupled to any of the other flows. In our model, all five flows are independent, and so the associated entropy production rates should all be positive. Note that a proper linkage of anabolism to catabolism through the yield factor q must ensure that σ_A becomes positive.

Accordingly, we also find that $\sigma_{EM} > 0$ and $\sigma_{tot} > 0$ because their individual components are all positive. To provide further insight into the issue of entropy generation, we can write an entropy balance for the model universe as a whole. We can always decompose the total entropy of the universe S_{uni} into separate contributions of ecosystem ("sys") and environment ("env"), $S_{uni} = S_{env} + S_{sys}$. The resulting entropy balance thus becomes

$$\frac{dS_{uni}}{dt} = \frac{dS_{env}}{dt} + \frac{dS_{sys}}{dt} = \sigma_{tot}. \tag{22}$$

Because the model universe is isolated as a whole, no entropy export occurs across its boundaries, the entropy change is only due to internal entropy generation σ_{tot}. Moreover, because $\sigma_{tot} > 0$, Eq. (22) assures that the entropy of our model universe as a whole can only increase, in line with the classical Second Law statement for isolated systems.

2.6. The chemical potential of biomass?

Although theoretically valid, the entropy production expressions (17)–(19) require an explicit expression for the chemical potential of the biomass μ_B. Here we are confronted with one of the real challenges in thermodynamic ecology. To our knowledge, the issue of how to calculate the chemical potential for a population of living organisms has not yet been properly resolved. In general, the chemical potential can be written as $\mu_i = h_i - Ts_i$ where h_i is the specific enthalpy and s_i is the specific entropy (where 'specific' means per mole or kg of substance). Theoretically at least, the specific enthalpy of an organism can be determined by standard calorimetric methods (by putting a suitable number of the organisms in a bomb calorimeter, and measuring the resulting heat of combustion—although this may cause practical/ethical problems). Yet, no theoretical procedure exists to calculate the specific entropy of an organism at a given population density. Three basic obstacles prevent this. Firstly, there is the question whether it is possible at all to attribute a well-defined entropy to a complex, highly-organized, far-from-equilibrium entity such as an organism? Some authors argue that this is possible (Battley, 1999; Aoki, 2001), but the debate has not been convincingly settled. Assuming that it is possible, a second obstacle is that biomass

comprises a complex mixture of different compounds, which also comes in 'biomass packages' of different size (i.e. organisms). Bottom-up approaches have been proposed that start from the basic entropy properties of the different molecules (lipids, sugars, proteins), to calculate the entropy change that corresponds to the formation of 1 g of biomass starting from a dilute aqueous solution of inorganic nutrients (Morowitz, 1968; Battley et al., 1997). However, such procedures are typically based on intracellular conditions in micro-organisms, and whether they apply to macro-organisms such as rabbits or tigers remains to be proven. More importantly, bottom-up procedures seem to ignore that organisms come in different sizes and form populations of different densities. To see this, consider two hypothetical prey populations, i.e. a zebra population at a certain biomass density (kg biomass per m^{-2}), and a rabbit population at exactly the same biomass density. In a first approximation, one can assume that zebras and rabbits consist of roughly the same type of biomass (composition in terms of lipids, sugars, proteins). If so, then the bottom-up procedure would predict about the same specific entropy for both species. Thermodynamically, there would be no distinction between zebra and rabbit populations, although the allocation of organic matter in space is very different. Effectively, the organic matter in the zebra population is 'concentrated' into in a few large packages, while the organic matter in the rabbit population is distributed as many small packages. We believe this crucial difference should also be reflected in the specific entropy.

3. Steady state analysis

The above analysis of the simple single-consumer model has exposed the key problem with entropy production in food webs. The mass balances (1)–(3), the entropy expressions (12)–(21), and the entropy balance (22) are valid both in steady as well as transient regimes. Unfortunately, the inability to calculate the chemical potential of biomass μ_B prevents the use of these expressions to obtain the entropy production associated with food web operation. Here, we propose a way to circumvent this difficulty. This is done by only considering the steady-state, which refers to the situation where the properties of the ecosystem no longer vary with time. In the steady-state, the μ_B quantities will drop from the equations (as shown below). This "trick" forms the cornerstone of our thermodynamic analysis of food webs. This trick not only applies to the specific food web of the previous section, but is generally valid for any food web.

3.1. Steady state mass and entropy balance

Consider an arbitrarily complex food web, whose functioning is governed by some internal dynamics. We do not put any constraint on this internal complexity: many trophic compartments may be present and the

interactions can be highly non-linear. The only assumption we make is that for some fixed boundary conditions C_R^0 and C_W^0, the ecosystem will eventually reach a steady state, thus making abstraction of the possibility of oscillatory and chaotic dynamics. For simplicity, we also assume that a single stable state is reached, thus ignoring the possibility of multiple stable states. To make a distinction with transient properties, steady state values are denoted by an asterisk superscript *. Because we treat the food web as a black box, we cannot say anything about its internal state (e.g. the distribution of biomass over various trophic levels). Yet, we do know that in a steady state, the inputs and outputs must cancel each other, while the total food web biomass must remain constant $dC_B/dt = 0$. Consequently, Eq. (3) directly reveals that

$$F_{RB}^* = F_{BW}^*. \tag{23}$$

In other words, biomass synthesis should match the sum of maintenance and turn-over, and the net metabolic activity of the food web only consists of respiration

$$CH_2O|_R + O_2 \rightarrow CO_2 + H_2O. \tag{24}$$
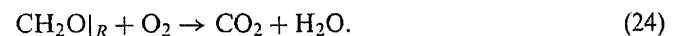
Effectively, this reaction symbolizes the core dissipative process within our ecosystem: high-quality resources (CH_2O, O_2) are converted into low-grade waste products (CO_2, H_2O). The associated reaction rate is referred to as the "ecosystem metabolism" F_{EM}^*. Imposing the steady-state constraint onto the resource and waste balances (1) and (2), we find that the ecosystem metabolism must equal the other flows

$$F_{EM}^* = F_{RB}^* = F_{BW}^* = F_R^* = -F_W^*. \tag{25}$$

Because $\mu_R = \mu_R^{ref} + RT \ln(C_R/C_R^{ref})$ and $\mu_W = \mu_W^{ref} + RT \ln(C_W/C_W^{ref})$, the associated thermodynamic force of the respiration reaction (24) becomes

$$X_{EM} = -(\mu_W^* - \mu_R^*)/T = R \ln(K_{eq} C_R^*/C_W^*), \tag{26}$$

where $K_{eq} = \exp((\mu_R^{ref} - \mu_W^{ref})/(RT))$ is the equilibrium constant of the respiration reaction. For a given reference state, this quantity is a constant. Combining the above relations with expressions (20) and (21), we obtain following steady-state entropy production rates

$$\sigma_{EM}^* = F_{EM}^* R \ln(K_{eq} C_R^*/C_W^*), \tag{27}$$

$$\sigma_{tot}^* = F_{EM}^* R \ln(K_{eq} C_R^0/C_W^0). \tag{28}$$

These expressions do no longer contain the quantity μ_B, and so, we have circumvented the previously discussed difficulty of defining the chemical potential of the biomass. The total entropy production depends on the external boundary conditions imposed upon the ecosystem (via C_W^0 and C_R^0) and on the internal structure of the food web (via F_{EM}^*). In contrast, the ecosystem entropy production depends on the internal 'abiotic' state of the ecosystem (via C_W^* and C_R^*) and on the internal 'biotic' structure of the food web (via F_{EM}^*).

Note that the term "steady-state" should be interpreted with caution: *the time invariance only applies to the*

ecosystem, and not the environment. In the non-trivial situation where there is a food web operating, and so $F_{EM}^* > 0$, the environmental reservoirs do change their mass (the resource reservoir loses mass at rate F_{EM}^*, the external waste reservoir gains mass at rate F_{EM}^*). The assumption that C_W^0 and C_R^0 are fixed is nothing but a suitable approximation for large reservoirs with a slow relaxation time. Also, when applying the steady-state condition to the entropy balance (22), only the term dS_{sys}/dt related to the ecosystem vanishes, and so one obtains

$$\frac{dS_{env}}{dt} = \sigma_{tot}^* > 0. \tag{29}$$

This illustrates that in the "steady-state", the properties of the environment should *not* remain constant in time. Effectively, the Second Law requires that $\sigma_{tot} > 0$, and so the entropy balance (29) necessitates that the entropy of the environment should always increase. In other words, when the ecosystem resides within a steady-state, all the entropy that is generated (i.e. within the ecosystem or through interactions between ecosystem and environment), will ultimately 'accumulate' within the environment.

3.2. Ecosystems as far-from-equilibrium entities

One frequently encountered quote in texts on ecological thermodynamics is that "ecosystems operate far-from-equilibrium". However, a rigorous quantitative interpretation of this "distance from equilibrium" is typically not given. In the classical interpretation, the far-from-equilibrium connotation refers to the thermodynamically 'improbable' state of living organisms (Jorgensen and Svirezhev, 2004). In this view, organisms represent a highly self-organized form of matter, which resides in a low entropy state as compared to their surroundings. This intuitive idea can be formally expressed as

$$\Delta\mu = \mu_B^* - \mu_{ref}^*, \tag{30}$$

where μ_{ref}^* denotes some reference potential, usually introduced as "the chemical potential that biomass would have if it were brought in equilibrium with its surroundings" (e.g. Jorgensen, 2000). Although intuitively appealing, there are two major problems with this definition. First, as explained above, a major roadblock in thermodynamic ecology is the impossibility to calculate the chemical potential μ_B of an organism. This renders the definition (30) of little use in actual calculations. Second, and more fundamentally, there is also a problem with the reference state. In real world situations, neither the ecosystem, nor the environment can reside in a state of thermodynamic equilibrium (see below). As a consequence, it is not possible to "bring biomass in equilibrium with its surroundings", because the surroundings are not in thermodynamic equilibrium themselves. Consequently, there is no "natural" equilibrium state that can serve as a logical reference to define μ_{ref}^*.

A more meaningful interpretation of the distance from equilibrium is possible when looking at the disequilibrium between resource and waste products. For the chemotrophic ecosystems studied here, the term 'thermodynamic equilibrium' refers to the chemical equilibrium of the respiration reaction (28). Two situations can be distinguished, depending on whether thermodynamic equilibrium applies to the environment or to the ecosystem

$$\Delta\mu_{env} = \mu_R^0 - \mu_W^0 = RT \ln(K_{eq} C_R^0 / C_W^0), \tag{31}$$

$$\Delta\mu_{sys} = \mu_R^* - \mu_W^* = RT \ln(K_{eq} C_R^* / C_W^*). \tag{32}$$

Note that both these distances are defined in terms of abiotic state variables (i.e. resource and waste concentrations), and that they are expressed in units of energy. For convenience, we can also define corresponding quantities that are expressed in units of mass (by linearly expanding the logarithm in (31) and (32)). The mass-based analogue of $\Delta\mu_{env}$ thus becomes

$$\Delta = C_R^0 - \frac{C_W^0}{K_{eq}}. \tag{33}$$

This quantity expresses how far the external environment is from thermodynamic equilibrium. In the vocabulary of non-equilibrium thermodynamics, Δ is referred to as the "thermodynamic gradient" that is imposed as a boundary condition upon the (eco)system. Obviously, the environment is in thermodynamic equilibrium when $\Delta = 0$, and in this "ultimate state", no resource conversion can take place and no food web can exist. In a similar fashion, we can introduce the mass-based analogue of $\Delta\mu_{sys}$ as

$$\delta = C_R^* - \frac{C_W^*}{K_{eq}}. \tag{34}$$

This quantity expresses the internal disequilibrium, or how far the ecosystem operates from thermodynamic equilibrium in steady-state. The ecosystem is in thermodynamic equilibrium when $\delta = 0$. The physical interpretation of Δ and δ is further discussed below.

3.3. The ecosystem resource processing regime

Intuitively, it is clear that—at least in theory—many different food webs can operate within a given physical environment. However, to test this statement in a true quantitative sense, we need a rigorous mathematical infilling of both the terms "food web operation" and "physical environment". This can now be done by the tools introduced in the previous sections. In our model universe, the specification of the "physical environment" comes down to the specification of a set of five abiotic parameter values: the concentrations in the external resource reservoirs C_R^0 and C_W^0 (and so the thermodynamic gradient $\Delta > 0$ is fixed), the transport coefficients α_R and α_W, and the equilibrium constant K_{eq}.

Now assume that (1) the physical environment remains constant in time, (2) a certain (arbitrary complex) food web

has established itself within this environment, and (3) this food web operates in a steady state. This state will always be characterized by a particular value for the ecosystem metabolism F_{EM}^*. Now suppose one knows F_{EM}^* (e.g. by measuring CO_2 accumulation in a closed incubation system). This sole quantity is now sufficient to completely characterize the resource processing by the food web, provided the external environment is fully characterized (C_R^0, C_W^0, α_R, α_W, and K_{eq} are known). Indeed, one can directly calculate the associated resource and waste concentrations from the mass balances (1)–(2) as

$$C_R^* = C_R^0 - F_{EM}^*/\alpha_R, \tag{35}$$

$$C_W^* = C_W^0 + F_{EM}^*/\alpha_W. \tag{36}$$

From these concentrations, the disequilibrium distance δ, the flows (F_{EM}^*, F_R^* and F_W^*) and the entropy production rates (σ_{EM}^*, σ_R^* and σ_W^*) can be subsequently calculated using the expressions of the previous sections. We will refer to this particular set of variables as the "ecosystem resource processing regime" (ERPR). The ERPR completely describes the overall effect of the food web on resource processing, but does not specify any "internal" food web characteristics (biomasses, trophic flows). In essence, the ERPR adopts a black box approach to the resource processing of food webs.

A crucial question is then how fast resources are converted? By combining the quantities F_{EM}^*, C_R^* and C_W^*, we can define the *resource conversion rate parameter of the ecosystem* as

$$\kappa_{EM} = F_{EM}^* \delta^{-1} = F_{EM}^* \left(C_R^* - \frac{C_W^*}{K_{eq}} \right)^{-1}. \tag{37}$$

The inverse of κ_{EM} specifies the time scale over which resources are degraded within the ecosystem. Expression (37) can be used to calculate κ_{EM} from F_{EM}^*, but one can also work the other way round. To show this, we first introduce the auxiliary rate constant

$$\kappa_c = \left(\frac{1}{\alpha_R} + \frac{1}{\alpha_W K_{eq}} \right)^{-1}. \tag{38}$$

The parameter κ_c defines the characteristic time scale at which material is exchanged between ecosystem and environment. The value of κ_c will be dominated by the rate limiting transfer (note the analogy with the formula for two serial resistances in an electrical network). When $\alpha_R \ll K_{eq}\alpha_W$ one obtains $\kappa_c \approx \alpha_R$. Upon substitution of the concentration expressions (35) and (36) into (37), one directly finds

$$F_{EM}^* = \frac{\kappa_{EM}}{1 + \kappa_{EM}/\kappa_c} \Delta. \tag{39}$$

Accordingly, there are two equivalent ways to fully characterize the ERPR: either by specifying F_{EM}^* or by fixing κ_{EM}. Both quantities serve as master parameters that suitably summarize the resource processing associated with a particular food web. Note that the ERPR is not a unique identifier of a given food web. Each food web will show a certain value for F_{EM}^* or κ_{EM}. Yet, different food webs can show the same value of F_{EM}^* or κ_{EM}, and hence, different food webs can correspond to the same ERPR.

3.4. The ERPR of the single-consumer food web

The calculation of κ_{EM} is functional, as it condenses all information on the resource processing of a given food web. This enables a straightforward comparison of the operation of different food webs (see below). Yet, it is crucial to understand that κ_{EM} is not a true "kinetic constant", as in general, it shows a complex dependency on the (non-linear) internal dynamics of the food web. To illustrate this, we can revisit the simple food web above with one consumer. To use the mass balances (9)–(11), we need explicit rate laws for the biotic flows F_A, F_M and F_T. The assimilation rate is given a Holling type I response $F_A = r_A(C_R - C_W/K_{eq})C_B$, where r_A is the assimilation rate parameter. This is a classical ecological rate law but for the factor C_W/K_{eq}, which is added for thermodynamic consistency. Free energy constraints require that the synthesis of new biomass should stop when the ecosystem is at chemical equilibrium, i.e., when $C_R = C_W/K_{eq}$. Maintenance respiration and biomass turnover are simply taken linear in the biomass, i.e., $F_M = d_M C_B$ and $F_T = d_T C_B$, where d_M and d_T are rate constants. The values of C_R^*, C_W^* and C_B^* then can be determined from the steady state versions of the mass balances (9)–(11). A bifurcation occurs when the thermodynamic gradient exceeds the threshold value $\Delta_c = (d_T + d_M)/(qr_A)$. This critical threshold is only dependent on the biotic parameters of the food web (here, the consumer parameters q, r_A, d_M and d_T). Effectively, this point serves as 'threshold for life'. When the thermodynamic gradient is too small ($\Delta < \Delta_c$), one obtains the trivial solution $C_R^* = C_R^0$, $C_W^* = C_W^0$, and $C_B^* = 0$. In other words, no stable consumer population can be established, and no resource conversion occurs within the ecosystem. Beyond the threshold value ($\Delta > \Delta_c$), the food web starts operating, and the ecosystem properties take the values

$$C_R^* = C_R^0 - \frac{\kappa_c}{\alpha_R}(\Delta - \Delta_c), \tag{40}$$

$$C_W^* = C_W^0 + \frac{\kappa_c}{\alpha_W}(\Delta - \Delta_c), \tag{41}$$

$$C_B^* = \frac{q\kappa_c}{(1-q)d_T + d_M}(\Delta - \Delta_c). \tag{42}$$

If one substitutes the expressions for C_R^* and C_W^* into the definition (34) of the internal distance from equilibrium, one finds $\delta = \Delta_c$. Accordingly, the internal distance from equilibrium is independent from the external thermodynamic gradient, and is solely dependent on the properties of the consumer. The ecosystem metabolism in steady state becomes

$$F_{EM}^* = (1-q)F_A^* + F_M^* = \kappa_c(\Delta - \Delta_c) = \kappa_{EM}\Delta_c. \tag{43}$$

From this, the resource conversion parameter can be calculated as

$$\kappa_{EM} = \kappa_c \left(\frac{\Delta}{\Delta_c} - 1 \right). \tag{44}$$

This shows how κ_{EM} is ultimately dependent on both the physical environment (through κ_c and Δ) and the internal details of the food web (via Δ_c). The external environment is characterized by a parameter set (C_R^0, C_W^0, α_R, α_W, and K_{eq}). Similarly, the food web is characterized by a parameter set (q, r_A, d_M and d_T). Both parameter sets together thus determine the value of κ_{EM}. Accordingly, this simple example clearly shows that κ_{EM}, and hence the ERPR, is intrinsically dependent on the food web structure.

This simple food web also illustrates the connection between the two disequilibrium distances δ and Δ introduced above. In economic terms, the thermodynamic gradient can be seen as a measure of potential activity. The conversion of resources into waste products can only take place when the thermodynamic gradient is sufficiently large, i.e. when $\Delta > \Delta_c$. When Δ is large, there a large potential for resource transformation within the ecosystem (good 'business opportunities' for the consumer). When Δ becomes small, the opportunities to benefit from the dissipation reaction (24) become smaller and smaller (poor 'business climate'). Whether any resource processing actually occurs, and how fast it proceeds, depends on the details of the food web. Hence the use of the term 'potential'. The external thermodynamic gradient effectively constrains the potential range of the internal disequilibrium distance, i.e., $0 \leqslant \delta \leqslant \Delta$. The disequilibrium distance δ that is effectively realized depends on the particular food web structure (in our case on the consumer properties q, r_A, d_M and d_T). The food web essentially determines how fast resources are processed as compared to transport processes that supply resources and remove waste products. When resources are rapidly processed, the ecosystem is poised close to thermodynamic equilibrium ($\kappa_{EM} \to \infty$ and $\delta \to 0$). In contrast, when resources are slowly processed, the internal disequilibrium approaches the maximal value ($\kappa_{EM} \to 0$ and $\delta \to \Delta$). Note than when $\Delta \to 0$ one automatically obtains $\delta \to 0$: when the environment resides in thermodynamic equilibrium, one automatically obtains that the ecosystem also must be in thermodynamic equilibrium (in this trivial situation nothing happens at all).

4. Thermodynamic analysis of ecosystems

4.1. A comparison of three marine sediment ecosystems

Equipped with the thermodynamic concepts and modeling tools introduced in the previous sections, we can now take up the actual thermodynamic analysis of ecosystems. To illustrate concepts and techniques, we will examine three different marine sediment ecosystems: (1) Aarhus Bay (AB), a temperate coastal site in Denmark characterized by

intense organic matter processing, (2) Young Sound (YS), an arctic site in Northeast Greenland, and (3) the Santa Barbara Basin (SBB), an anoxic basin off the coast of California. These three sites are selected because they are very different in terms of sediment type, geochemistry, and resident food web. A second reason is that their biogeochemistry has been recently studied in great detail (AB: Fossing et al., 2004; YS: Berg et al., 2003, SBB: Meysman et al., 2003). Due to these detailed biogeochemical studies, the physical environment is well characterized, which allows us to directly calculate the parameters of the physical environment in our model (C_R^0, C_W^0, α_R and α_W).

Moreover, these studies provide detailed quantitative information on in situ organic processing. For our purpose here, it is particularly relevant that reliable values for the deposition flux F_D and the resource processing rate κ_{data} have been estimated. The biogeochemical studies referenced above distinguish between three types of organic matter, and hence report three separate values of F_D and κ_{data}. (1) A fast decaying fraction, which is rapidly degraded and disappears within the top mm of the sediment; (2) A slow decaying fraction, which disappears within the top 20 cm; (3) Refractory material, which only shows reactivity over geological time scale (this material only decays on a scale of meters to hundredths of meters of sediment depth). As our study concerns organic matter processing in the bioturbated zone (10–20 cm), we selected the slowly decaying fraction as the relevant type of organic matter for our analysis.

A compilation of parameters is given in Table 1. All but two parameters are constrained by measurements at all three sites, and parameter values are directly taken from the references. This availability of sufficient parameter data was exactly the reason why the three sites were selected. No data are available for the thickness L of the sediment, and the equilibrium constant of respiration K_{eq}. Accordingly, these latter two parameters were given 'best estimates', and afterwards, an uncertainty analysis was performed to check how the results were dependent on these estimates. To constrain the sediment thickness, we used for all three sites the global average thickness of the bioturbated zone, i.e., $L = 10$ cm (Boudreau, 1998). The value of the equilibrium constant K_{eq} is difficult to precisely constrain under natural conditions. However, we know that it is very high for the aerobic degradation of organic matter (reaction 24). Under standard thermodynamic conditions (298.15 K, 1 atm pressure, 1 molar concentrations), and using glucose as the organic substrate, one finds a standard free energy of reaction $\Delta G^0 = -532$ kJ per mole of carbon (Canfield et al., 2005), leading to a value of $K_{eq} = \exp(-\Delta G^0 / RT) \approx 10^{93}$. In actual sediment environments, organic matter will consist of a mix of substrates that release less free energy than glucose, and so K_{eq} will be lower. Still, the value of K_{eq} will remain high, and we employed $K_{eq} = 10^8$ for all three sites as an initial estimate.

Table 1
Parameter set for three marine sediment ecosystems: Aarhus Bay (AB) in Denmark, Young Sound (YS), and Santa Barbara Basin (SBB)

Input data			AB	YS	SBB
Burial velocity	ω	$cm\,yr^{-1}$	0.32	0.12	0.26
Porosity	ϕ		0.80	0.65	0.87
Temperature	T	°C	10	0	6
Diffusion coefficient CO_2	D	cm^2	263	160	270
Deposition flux carbon	F_D	$mol\,m^2\,yr^{-1}$	5.3	1.8	0.6
CO_2 bottom water	C_W^0	$mol\,m^{-3}$	2.5	2.2	2.45
Sediment thickness	L	cm	10	10	10
Model parameters					
Resource exchange	α_R	yr^{-1}	25×10^{-3}	8×10^{-3}	23×10^{-3}
Waste exchange	α_W	yr^{-1}	6.3	3.1	7.0
External resource	C_R^0	$mol\,m^{-3}$	2084	2265	263
External waste	C_W^0	$mol\,m^{-3}$	2.5	2.2	2.45
Equilibrium constant	K_{eq}	–	10^8	10^8	10^8
Resource conversion rates					
Critical value	κ_c	yr^{-1}	0.026	0.008	0.023
Reported value	κ_{data}	yr^{-1}	0.379	0.095	0.056
MEP value	κ_{mep}	yr^{-1}	0.509	0.159	0.442
Resource conversion efficiency	η	%	94	93	72

The input data are taken from detailed biogeochemical studies at these sites: AB (Fossing et al., 2004), YS (Berg et al., 2003), and SBB (Meysman et al., 2003). The model parameters are directly calculated from these input data based on the formulas in the text. The data value κ_{data} is the resource conversion parameter as reported in the above references. The characteristic value κ_c is calculated from the model parameters through Eq. (38). The value of κ_{mep} is found by implementing the constraint of maximal entropy production Eq. (45).

As detailed above, each food web will be associated with a certain ecosystem resource processing regime (ERPR). The ERPR describes the operation of the food web in a black box fashion, and is completely determined when the value of resource processing parameter κ_{EM} is specified. However, within the same physical environment an infinite number of ERPR are possible. In theory, the value of κ_{EM} can range from zero to infinity, and the ERPR of the resident food web will lie somewhere in between these two endpoints. In the next sections, we will proceed in two steps. Initially, we make no assumption on the feasibility of a certain ERPR for each of the three sites examined. So in a first step, we will only use the available data on the physical environment of the sites. For each site, we will scan the whole range $0 < \kappa_{EM} < \infty$, and for each κ_{EM} value, we will calculate the corresponding ERPR. In a second step, we will examine where the actually observed ERPR (i.e. the ERPR corresponding to κ_{data}) lies on this scale $0 < \kappa_{EM} < \infty$.

4.2. Slow and fast food webs

As noted above, the rate constant κ_c provides a characteristic time scale for the physical transport between ecosystem and environment. It also serves as a threshold to distinguish between two broad classes of ERPR, which we refer to as fast and slow food webs. Fig. 2 illustrates this for the Aarhus Bay site (the two other sites show a similar pattern). When $\kappa_{EM} \ll \kappa_c$, the internal resource conversion within the ecosystem is slow compared to physical

exchange with the environment. In this scenario, the ERPR is said to be under "reaction control" and the associated food web is categorized as "slow". Expression (39) reveals that $F_{EM}^* \approx \kappa_{EM}\Delta$, and so the ecosystem metabolism linearly scales with the resource processing parameter (note that the semi-logarithmic plotting in Fig. 2a obscures this linearity). As expected, under reaction control, the resource piles up within the ecosystem, while waste levels are low (Fig. 2b). Oppositely, when $\kappa_{EM} \gg \kappa_c$, the internal resource conversion proceeds much faster than the physical exchange with the environment. In this scenario, the ERPR is said to be under "transport control", and the associated food web is categorized as "fast". When the resource processing rate parameter increases, the ecosystem metabolism rapidly approaches a constant value $F_{EM}^* \approx \kappa_c\Delta$ (Fig. 2a). Under transport control, the resource is depleted by the high food processing activity within the food web, while waste products accumulate (Fig. 2b).

When taken to the extreme, the slow and fast food webs give rise to two end-member situations. The "minimal" end-member is attained when there is no biological activity at all, and so $\kappa_{EM} \to 0$, we find that $F_{EM}^* \to 0$. In this limit also, the resource and waste concentrations will simply match those of the external reservoirs, i.e. $C_R^* \to C_R^0$ and $C_W^* \to C_W^0$ (Fig. 2b), and so, the distance from equilibrium becomes maximal and equals the thermodynamic gradient, i.e. $\delta \to \Delta$. Oppositely, the "maximal" end-member is attained when biological activity is very high: resources are immediately processed by the food web the moment they become available, and so $\kappa_{EM} \to \infty$. Note however that

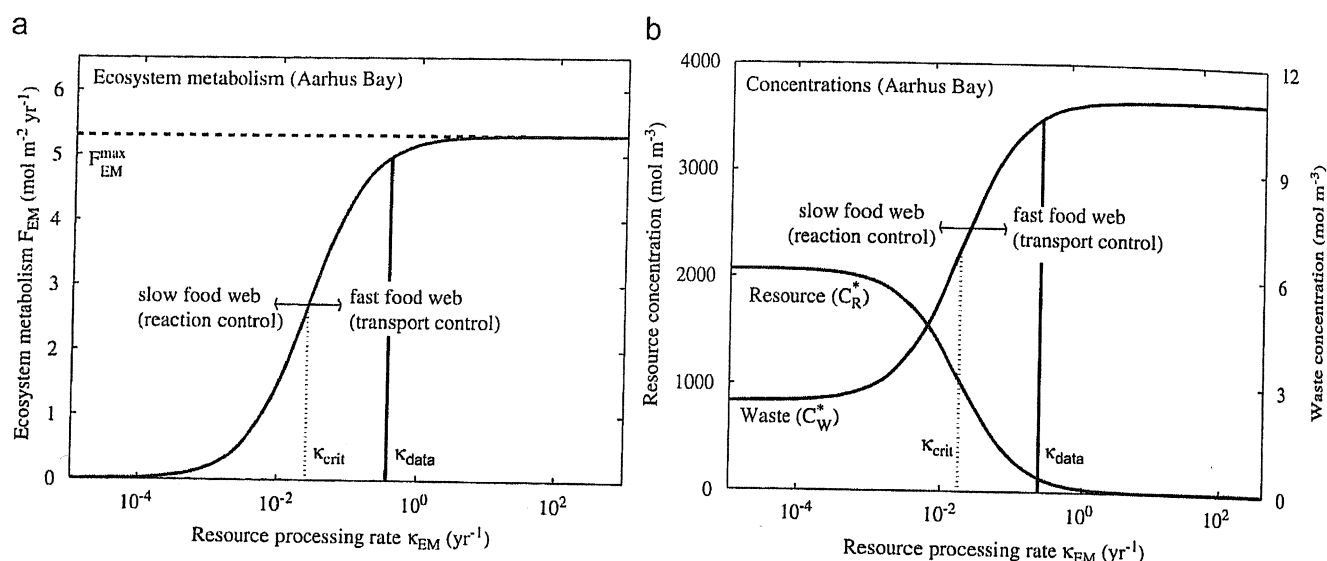Fig. 2. (a) The ecosystem metabolism F_{EM}^* plotted as a function of the specific metabolic rate κ_{EM} for the Aarhus Bay site. (b) The resource C_R^* and waste C_W^* concentrations plotted as a function of the specific metabolic rate κ_{EM} for the Aarhus Bay site. In each panel the actually observed ERPR is plotted as κ_{data}.

the associated ecosystem metabolism still reaches a finite value $F_{EM}^* \to \kappa_c \Delta$ (Fig. 2a). In the "maximal" end-member, the ecosystem effectively operates at thermodynamic equilibrium, i.e. $C_R^* = C_W^*/K_{eq}$ and $\delta \to 0$. In summary, when the resource processing parameter κ_{EM} varies over the semi-infinite range $[0, \infty]$, we find that the ecosystem metabolism F_{EM}^* varies over a finite range $[0, \kappa_c \Delta]$, and the corresponding disequilibrium distance δ varies over the finite range $[0, \Delta]$.

Table 1 shows that all three sites are characterized by fast food webs. For Aarhus Bay and Young Sound, the observed resource processing parameter κ_{data} is an order of magnitude higher than the threshold value κ_c. In these two sites, the actual ecosystem metabolism F_{EM}^{data} is only slightly lower than the limiting value $F_{EM}^{max} = \kappa_c \Delta$. To show this, we calculated the resource conversion efficiency, defined as $\eta = F_{EM}^{data}/F_{EM}^{max}$ where F_{EM}^{data} is derived from κ_{data} via Eq. (39). We find values of respectively 94% and 93% for AB and YS (Table 1). Note that these resource conversion efficiencies are remarkably similar despite the very different setting (a temperate coastal bay versus an arctic sound). The resource processing in the Santa Barbara Basin is markedly "slower", as the observed resource processing parameter κ_{data} is only twice as high as the threshold value κ_c, while the associated resource conversion efficiency attains 72%. The strong difference between the Santa Barbara Basin on the one hand, and the Aarhus Bay and Young Sound sites on the other hand, presumably reflects the intrinsic differences in food web structure and organic matter processing at these sites. The Santa Barbara Basin is an anoxic basin, where most of the time, the bottom water experiences suboxic to anoxic conditions (less than 0.01 mM O_2, Reimers et al., 1990). Due to this oxygen deficiency, no macrofauna are present within the sediment and so the benthic food web is entirely microbial (bacteria,

archaea, viruses). Organic processing in SBB is dominated by the sulfate reduction pathway, where the end products of mineralization (H_2S, NH_4) are not re-oxidized within the sediment (Reimers et al., 1990; Meysman et al., 2003). In contrast, the bottom water in Aarhus Bay and Young Sound is well oxygenated. As a result, the sediment is inhabited by a diverse macrofaunal community, and the associated organic processing within these two sites is governed by an interplay between macrofaunal sediment reworking and microbial metabolism. Although sulfate reduction is still the dominant pathway, the reduced by-products (H_2S, NH_4) are now re-oxidized with O_2, and thus the food web extracts more free energy out of the available organic matter.

4.3. Total and ecosystem entropy production

By scanning the full range $0 < \kappa_{EM} < \infty$, we have examined all resource processing regimes that are possible for each of the three sites. We can now examine whether among these many possible regimes, there are any "remarkable" ones from a thermodynamic perspective. To this end, we can use Eqs. (27) and (28) to calculate the entropy production rates σ_{EM}^* and σ_{tot}^* associated with a certain ERPR. These relations are plotted in Fig. 3 for the three sites. The characteristic shape of the two entropy production rates are very different. The σ_{tot}^* curves monotonically increase with increasing κ_{EM}. This contrasts strongly with the unimodal σ_{EM}^* curves, which start at zero, go through a maximum, and subsequently decrease again to zero.

The monotonic increase of σ_{tot}^* is readily explained by expression (28). The logarithmic factor remains constant, and so, the total entropy production rate simply scales with the ecosystem metabolism F_{EM}^*. The origin of the extremum in the σ_{EM}^* curve is explained by "minimal" and "maximal"
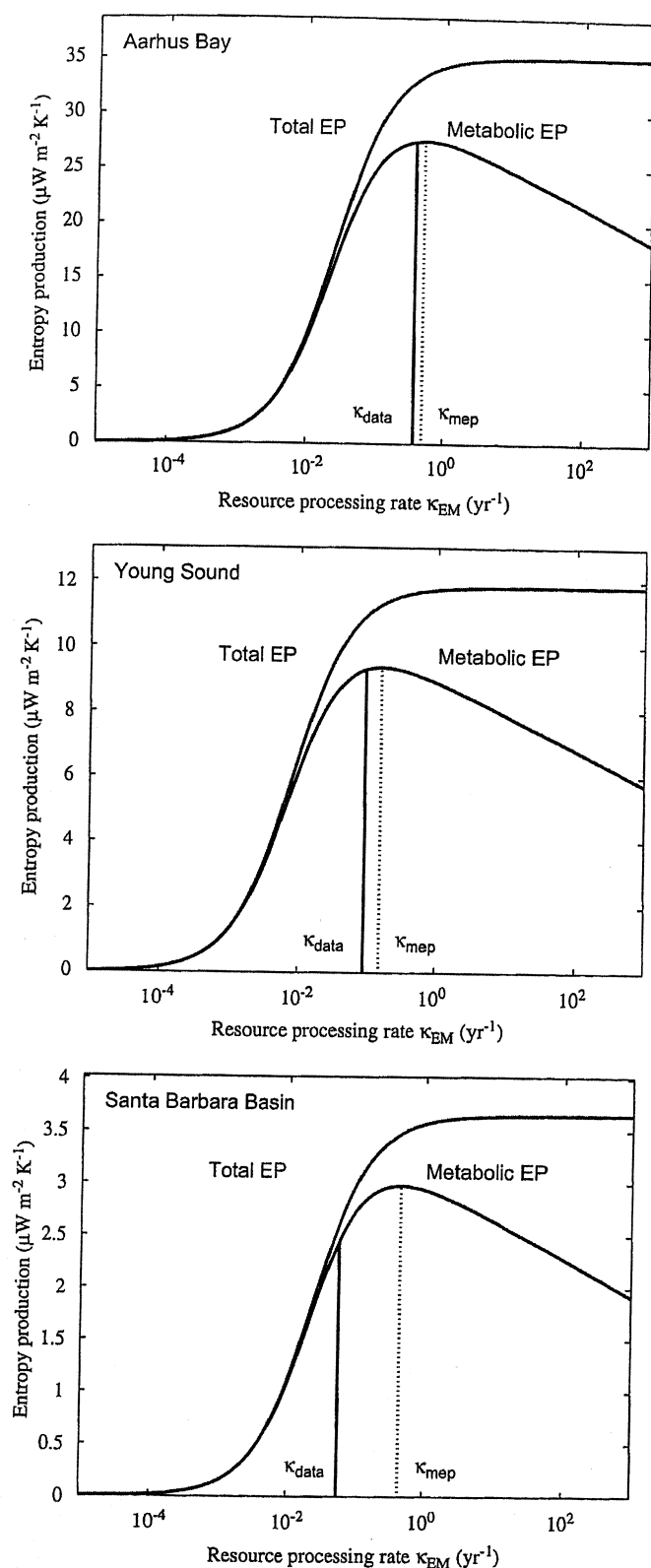
Fig. 3. The total entropy production σ_{tot}^* and the metabolic entropy production σ_{EM}^* as a function of the specific metabolic rate κ_{EM} for three marine sediment sites (Aarhus Bay, Young Sound, Santa Barbara Basin). The κ_{data} value indicates the observed decay constant of organic matter, κ_{data} indicates the value predicted by entropy production maximization.

end-member situations discussed above. In both end-members the entropy production σ_{EM}^* vanishes because the flow F_{EM}^* acts oppositely to the thermodynamic force X_{EM}^*. In the "minimal" end-member (slow food web situation), the concentration difference between the internal ecosystem reservoirs is greatest (large but finite force), but the ecosystem's metabolism vanishes (zero flow). In contrast, in the "maximal" end-member, the ecosystem metabolism is maximal (large but finite flow), but concentration difference between the internal reservoirs vanishes (zero force). In both situations, the product of force and flow makes that σ_{EM}^* vanishes. In between the end-member regimes, the entropy production associated with ecosystem metabolism is positive, and hence, it goes through a maximum.

This state of "maximum ecosystem entropy production" forms a characteristic ERPR in the possible range $0 < \kappa_{EM} < \infty$. To calculate the associated κ_{mep}, we can first rewrite σ_{EM}^* from expressions (35) and (36), to obtain

$$\sigma_{EM}^* = \frac{\kappa_{EM}\Delta}{1 + \kappa_{EM}/\kappa_c}$$

$$\times R \ln\left(\frac{K_{eq}\alpha_W}{\alpha_R} \frac{\alpha_R C_R^0(1 + \kappa_{EM}/\kappa_c) - \kappa_{EM}\Delta}{\alpha_W C_W^0(1 + \kappa_{EM}/\kappa_c) + \kappa_{EM}\Delta}\right).$$

(45)

This expression has a single maximum, and hence, it shows that the ecosystem entropy production σ_{EM}^* is unimodal in the parameter κ_{EM}. The resource processing parameter κ_{mep} at maximal entropy production (MEP) is obtained by solving the non-linear equation $d\sigma_{EM}^*/d\kappa_{EM} = 0$. The resulting values are listed in Table 1 for the three sites. These values of κ_{mep} are compared to the reported value κ_{data} in Fig. 3a–c. Quite intriguingly, the actual values of the resource processing parameter closely match the MEP values for the Aarhus Bay and Young Sound sites. Again, the Santa Barbara Basin shows a distinct response, where the actual resource processing κ_{data} is considerably smaller than the theoretical MEP value. Accordingly, one can ask why this difference between SBB and the two other sites? One assumption in our calculations is that the same equilibrium constant K_{eq} and the same thickness L applies to all sites. There is however no a priori reason why these two parameters should be constant across sites. In contrast, from a biogeochemical perspective, one would expect the Santa Barbara Basin to be different. The value $K_{eq} = 10^8$ was based upon the aerobic respiration reaction (24). But as discussed above, the free energy extracted for organic matter decomposition should be lower in the Santa Barbara Basin, due to the absence of O_2-mediated re-oxidation reactions. Biogeochemically, one thus would expect a lower K_{eq} value in the SBB (sulphate reduction) when compared to the other two sites (aerobic respiration). Moreover, the value of $L = 10\,cm$ was based on the global average thickness of the bioturbated zone. However, the SBB does not experience bioturbation, and intense microbial activity seems still present at greater depth into the sediment (Meysman et al., 2003). To test these aspects, we
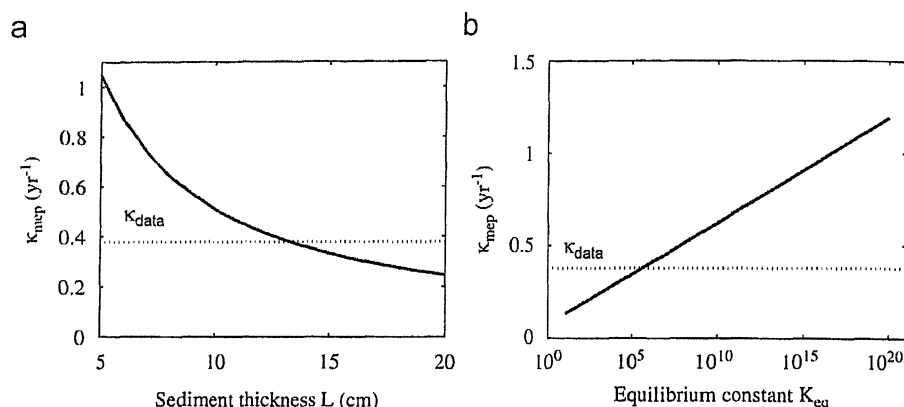
a

b

Fig. 4. Uncertainty analysis. The baseline simulation uses the Aarhus Bay setting with $L = 10$ cm and $K_{eq} = 10^8$. (a) MEP resource processing parameter as a function of the sediment thickness. (b) MEP resource processing parameter as a function of the equilibrium constant. The dashed line indicates the observed decay constant κ_{data}.

conducted an additional simulation for the Santa Barbara Basin with modified parameters $K_{eq} = 10^2$ and $L = 20$ cm. This provided a new value of $\kappa_{mep} = 0.073$, which is now only slightly larger than the observed value $\kappa_{data} = 0.056$.

The parameter adjustment of the Santa Barbara Basin remains to some extent arbitrary: although the direction of the parameter adjustment can be biogeochemically justified (lowering K_{eq} and increasing L), the magnitude of the adjustment remains arbitrary. As noted above, there are no strict data constraints on the parameters L and K_{eq}, and as a consequence, there is substantial uncertainty on the associated values that were used in the above simulations. To investigate how sensitive κ_{mep} is to these two parameters, we performed an uncertainty analysis, where L was varied over the depth range $[5, 20]$ cm and the equilibrium constant was varied over 20 orders of magnitude. Fig. 4 provides the resulting plots for the Aarhus Bay site settings. The MEP resource processing κ_{mep} decreases with sediment thickness, and increases with higher equilibrium constant. For both ranges, the variation in the κ_{mep} is about 1 order of magnitude. Accordingly, the uncertainty on the κ_{mep} values in Fig. 3 is about a factor of 10 higher or lower than the values depicted. This uncertainty is substantial, but is far less than the natural variability κ_{data}. In oceanic sediments, κ_{data} ranges over more than eight orders of magnitude from 10^{-6} to 10^2 yr^{-1} between coastal and deep sea sediments (Boudreau, 1997; Middelburg and Meysman, 2007). Accordingly, we estimate the uncertainty connected to κ_{mep} at about 15% of the possible natural range of κ_{EM}. The fact that the observed values κ_{data} fall within the uncertainty range of κ_{mep} for all three sites is therefore an intriguing observation.

5. Discussion and conclusion

5.1. A thermodynamic perspective on the ocean floor ecosystem

We have developed a thermodynamic approach for the chemotrophic, detritus-based ecosystem of the ocean

floor. This approach makes abstraction of all internal details of the food web, and principally focuses on the interaction of the food web with the external surroundings. Our analysis shows that in the steady-state, an arbitrarily complex food web can be treated as a black box, represented by the parameter κ_{EM}, which condenses all information on resource processing by the food web. This analysis in terms of κ_{EM} provides a generic way to assess the thermodynamic functioning of food webs, resulting in a gradient from slow food webs ($\kappa_{EM} \rightarrow 0$) to fast food webs ($\kappa_{EM} \rightarrow \infty$). If one specifies a specific food web structure, one effectively selects a certain point along the axis $0 < \kappa_{EM} < \infty$. In a case study of three marine sediments, we found that actual resource processing all fell with in the fast food web category, with oxic sediments showing faster resource processing than anoxic environments. Further research needs to determine whether this trend is as general as it appears from this three site sample. If confirmed, natural oceanic sediments emerge as transport-limited systems, where natural selection would favor various ways of enhancing the exchange of resource and waste products with the environment (i.e. biological feedbacks on α_R and α_W). Such transport enhancing activities are actually omnipresent within the marine benthos, in the form of filter-feeding and bio-irrigation (Meysman et al., 2006). Our analysis thus could provide a thermodynamic perspective on the evolutionary development of such transport enhancing strategies.

5.2. Conceptual problems in thermodynamic ecology

The idea that thermodynamic constraints could play a role in ecosystem development, has recently instigated considerable research into the use of thermodynamic principles in ecosystem analysis (Jorgensen, 2000; Jorgensen and Svirezhev, 2004). Yet, some concerns have been issued about the quantitative rigor, the consistency, and the heuristic nature with which thermodynamic concepts are employed within thermodynamic ecology (Mansson and

McGlade, 1993; Wilhelm and Bruggemann, 2000; De Wit, 2005; Gaucherel, 2006). Therefore, in our analysis, we devoted a lot of attention—almost fanatically—to a rigorous mathematical definition of thermodynamic concepts (e.g. thermodynamic gradient, disequilibrium distance, entropy production, physical environment, ERPR) and to their correct translation into ecological terms. Every concept that was employed, was also defined in a strict mathematical sense.

Our analysis provides two clear examples of where past treatments have been confusing. A first issue is the often quoted statement that "ecosystems are far-from-thermodynamic-equilibrium". The classical interpretation of the distance from equilibrium is based on the difference in the chemical potential between biomass and some reference state. We show that this interpretation is troublesome, because (1) no procedure exists yet to define the chemical potential of biomass, and (2) no proper "natural" reference state can be defined. To resolve this situation, we propose two alternative measures for the distance from equilibrium (Δ and δ), which are based upon the disequilibrium between resources and waste products in respectively environment and ecosystem.

A second problem concerns the use of the term "entropy production" in the context of ecological goal functions. Such goal functions are extremal principles, which have been proposed as relevant indicators for ecosystem development—see Muller and Leupelt (1998) for a critical review of the predictive capabilities. In connection to such ecological goal functions, the notion of "maximal entropy production" has surfaced a number of times in recent years (Ulanowicz and Hannon, 1987; Schneider and Kay, 1994; Svirezhev, 2000; Fath et al., 2001; Schneider and Sagan, 2005). Unfortunately, the term "entropy production" has always been used without a proper definition of what this rate actually encompasses. In other words, it is not specified which interactions are included in the entropy production rate. Our analysis shows that such an unconstrained use of the term "entropy production" is problematic. Multiple entropy production rates can be defined, depending on what interactions are accounted for in the entropy production budget (σ_R, σ_W, σ_A, σ_M, and σ_T are the possible contributions in steady-state for a single-consumer ecosystem). These various entropy production rates may show different extremal behavior.

5.3. Entropy production as an ecological goal function?

Given previous propositions along this line (Ulanowicz and Hannon, 1987; Schneider and Kay, 1994; Svirezhev, 2000; Schneider and Sagan, 2005), it is logical to question whether entropy production serves as a useful ecological goal function? And if so, which entropy production rate should be maximal? Among the many possibilities, we have identified two entropy production rates that could be relevant for ecosystem functioning: (a) the entropy production σ_{EM} associated with resource conversion within the ecosystem,

and (b) the total entropy production σ_{tot} within both ecosystem and environment. Our analysis (Fig. 3) shows that only the ecosystem entropy production σ_{EM} has the proper mathematical form of a consistent goal function. The total entropy production σ_{tot} strictly increases with the resource conversion rate κ_{EM}, and hence, it does not show a maximum. In the real world, maximizing σ_{tot} would select a state of maximal resource processing that would have a finite value for κ_{EM}. However, any other monotonic function in κ_{EM} would select the same state, and therefore, σ_{tot} cannot be regarded a proper discriminatory goal function.

In contrast, the metabolic entropy production σ_{EM} does show a clear maximum when the resource processing rate varies from zero to infinity. Because σ_{EM} has the right mathematical form, this does not mean that the ecosystem entropy production also acts as a true ecological goal function. Whether σ_{EM} means something for ecosystem development, has to be verified from experimental observations on ecosystem functioning. To this end, we quantified entropy production in three marine sediment ecosystems. More specifically, we compared values for the resource processing metric κ_{data} as reported from biogeochemical studies with the value predicted by the maximization of the ecosystem entropy production σ_{EM}. The κ_{mep} values approach the κ_{data} within one order of magnitude, which is intriguing, given that κ_{data} in sediments can vary over eight orders of magnitude (Middelburg and Meysman, 2007). However, based on our limited sampling of three sediments, and given the uncertainty on κ_{mep} due to uncertain estimates for L and K_{eq}, this study does not provide unequivocal evidence that ecosystem entropy production σ_{EM} does function as a goal function. The correspondence between κ_{data} and κ_{mep} could be a mere coincidence. Still, our results are intriguing enough to stimulate further investigation into the link between entropy production and resource processing in food webs. Such investigations should focus on more marine sediment sites to see whether the pattern holds, and preferable, very different ecosystems as well (e.g. terrestrial soils).

5.4. Thermodynamic analysis of other ecosystems

Our analysis shows that a proper investigation of "gradients" is needed to calculate the entropy production within ecosystems. Such gradients exist within the ecosystem (δ), and between system and environment (Δ). Once a consistent calculation procedure for the entropy production is established, one can examine whether or not the entropy production is a relevant measure for the behavior of food webs. Accordingly, a pertinent question is whether and how our thermodynamic model analysis of detrital-based ecosystems can be extended to other ecosystem types.

In our description, the ecosystem operation depends on three basic interactions: (1) the supply of resources from a high-quality reservoir in the environment to the ecosystem, (2) the conversion of resources into waste products within

the ecosystem, and (3) the discharge of waste products into a low-quality reservoir in the environment. Each of the three steps is "dissipative" in the sense that each step leads to a corresponding positive entropy production. The true dissipative effect of the food web is the entropy production σ^*_{EM} associated with step (2), i.e., the resource conversion that allows the food web to maintain its self-organization. Our analysis of ocean floor sediments indicates that from all entropy production rates, σ^*_{EM} surfaces as the only candidate that could have ecological significance.

If one is able to properly map resources and waste, the above three-step-mechanism could apply to chemo-auto-trophic and photo-autotrophic ecosystems as well, and so it could provide a road map to eventually calculate σ^*_{EM}. In the case of chemo-autotrophy, one can think of a marine hydrothermal vent system, where (1) reduced chemical compounds (e.g. H_2S) percolate out of the sea floor (the high-quality reservoir in the environment), (2) these reduced species are then oxidized ($H_2S \rightarrow SO_4$), and the free energy of this redox reaction is used to build and maintain the food web of the vent system, and (3) the oxidized products (SO_4) are then mixed within the over-lying water column. The gradients Δ and δ that character-ize the hydrothermal vent ecosystem are based on free energy difference between reduced and oxidized species. Just like the heterotrophic ecosystems studied here, chemo-autotrophic ecosystems fit within the framework of standard chemical thermodynamics, and so we expect that descriptions will be rather similar.

However, things appear more complicated in photo-autotrophic ecosystems. This is because one needs to invoke the more complex thermodynamics of radiation, in addition to chemical thermodynamics. Still, the general three-step scheme also holds for ecosystems that are driven by photosynthesis. In this case, (1) radiation energy is derived from a high quality reservoir (the sun at 5800 K), (2) short-wavelength solar radiation is converted to long-wavelength heat radiation in photosynthesis, (3) the resulting heat is subsequently radiated back to a low-quality reservoir (deep space at 3 K). At first sight, the thermodynamic gradient Δ in photo-autotrophic ecosystem should involve the wavelength difference between the radiation emitted by the sun and deep space. However, the infilling of δ is less obvious. Clearly, there is some analogy between chemotrophic and phototrophic systems, but how far this analogy stretches must be resolved in future studies.

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