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Thermodynamics and Optimality of the Water Budget on Land: A Review

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The water balance on land plays a critical role in connecting key hydrological processes with climate and ecology. Over the last few years, several advances have been made in applying thermodynamic and optimality approaches to better describe Earth system processes in general, and the water balance on land in particular. Both concepts relate to the proposed principle of Maximum Entropy Production (MEP), which states that complex systems far from thermodynamic equilibrium organize in a way such that the rate of entropy production – a measure of irreversibility – is maximized in steady state. MEP provides a foundation to understand optimality in hydrology at a fundamental, thermodynamic level that is applicable across a wide range of Earth systems beyond hydrology. This review describes the foundation of the water balance far from thermodynamic equilibrium and potential applications of MEP. Some of the objections to optimality and thermodynamics are discussed as well as its potential implications.

1. Introduction

The terrestrial water balance links the partitioning of precipitation (P) into evapotranspiration (E) and runoff (R) with the surface energy balance, and thereby plays a critical role for the climate system over land. It can be expressed as:

$$\frac{dW_s}{dt} = P - E - R \qquad (1)$$

where the term dW_s/dt represents the change in soil water storage. At the small scale of a catchment, the details of eqn. (1) depend on a large number of details, such as soil properties, surface slope and orientation, and vegetation cover. This would seem to imply that a vast amount of small-scale information is required to predict the water balance at larger scales. Optimality principles provide a potential means to simplify the task of scaling up hydrologic fluxes with less detailed information.

Budyko's (1974) analysis of the relationship between rainfall and runoff provides a first justification for such principles. On climatic time scales, $dW_s/dt \approx 0$, thus reducing eqn. 1 to $P \approx E + R$. When E/P is plotted against the radiative index of dryness R_{net}/LP (net radiation R_{net} divided by the energy required to evaporate all precipitation, LP, with L being the latent heat of vaporization), observations are close to the maximum possible value of E/P. This upper limit is set by the amount of energy available by net radiation in humid regions and water availability (i.e. precipitation) in arid regions.

Another justification is found in thermodynamics and its foundation in statistical physics. Statistical physics deals with the scaling of microscopic properties to the macroscopic scale and is able to derive simple macroscopic relationships. The common example is the scaling of the nearly chaotic motion of individual

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molecules to the macroscopic properties of the ideal gas. While the microscopic scale is characterized by the position and velocity of each individual molecule, the macroscopic properties of the gas are described by properties such as temperature, pressure, density. The scaling is achieved by the assumption that the ideal gas is found in the most probable state (i.e. a state of maximum entropy), that is, in the state that represents the vast majority of microscopic states. Statistical mechanics has been extremely successful in deriving relationships such as the ideal gas law and the Boltzmann distribution simply from the assumption of maximum entropy and the constraints of the energy and mass balance.

Thermodynamic arguments have been applied in the past to describe hydrologic fluxes (e.g. *Leopold and Langbein* [1962], *Rodriguez-Iturbe et al.* [1992], *Rinaldo et al.* [1996], *Rodriguez-Iturbe and Rinaldo* [2001]). *Leopold and Langbein* [1962] compared the flow of water along topographic gradients to temperature conversions of a heat engine, where the heat flow is directed towards lower temperatures. They compared this to the drainage of land where gradients in topography drive the water flux towards lower elevations. However, they used thermodynamics mainly as an analogy.

To apply non-equilibrium thermodynamics to hydrology, two difficulties need to be addressed: First, the water balance is an open thermodynamic system. It exchanges energy and mass of different entropies with its surroundings, and these exchanges need to be formulated in terms of their chemical potentials (*Kondepudi and Prigogine* [1998]). Secondly, it is a system far from thermodynamic equilibrium (TE). The corresponding principle to the maximum entropy assumption in equilibrium thermodynamics is still an open issue. The principle of Maximum Entropy Production (MEP) has been proposed to address this deficiency (*Ozawa et al.* [2003], *Kleidon and Lorenz* [2005], *Martyushev and Seleznev* [2006]). Recent theoretical work by *Dewar* [2003], *Dewar* [2005a], and *Dewar* [2005b] has attempted to prove the generality of MEP using a similar approach to the one used to derive equilibrium thermodynamics. The MEP principle holds the promise to provide a very general and fundamental understanding of optimality and macroscopic behavior in a wide range of complex systems far from thermodynamic equilibrium and has recently gained interest (*Whitfield* [2005]).

In this review we first provide an overview of non-equilibrium thermodynamics and how it relates to the hydrologic cycle within the Earth system and the water balance on land. The MEP principle is briefly described and its application to poleward heat transport is used to illustrate its application. A simple model is set up to demonstrate possible applications of MEP to land surface hydrology. This example is used to discuss why, how, and at what spatial and temporal scales the MEP principle should apply to land surface hydrology. We close with a discussion, relating potential applications of MEP to previously suggested optimality approaches, potential limitations and implications.

2. Thermodynamics and the hydrologic cycle

2.1. Thermodynamics far from equilibrium

The second law of thermodynamics governs the direction of processes in an isolated system (i.e. no exchange of energy and mass with the surroundings). This is expressed as:

$$\frac{dS}{dt} = \sigma \quad (2)$$

where dS/dt is the change of entropy with time and $\sigma \geq 0$ is the rate of entropy production associated with irreversible processes within the system, such as diffusion. Over time, S will increase to a state of maximum entropy while $\sigma \to 0$, thus approaching

TE.

In a non-isolated system the exchange fluxes of entropy associated with energy and mass exchange across the system boundary need to be taken into account (e.g. *Kondepudi and Prigogine* [1998]):

$$\frac{dS}{dt} = \sigma - NEE \tag{3}$$

where NEE stands for the net entropy exchange associated with energy- and mass exchange across the system boundary.

A steady state is reached when $\overline{dS/dt} = 0$. Entropy production σ within the system is then balanced by the net entropy export to the surroundings, so that $\sigma = \vec{\nabla} \cdot \vec{F_s}$. Entropy production σ is generally expressed as a product of a thermodynamic force and flux. Entropy production by a heat flux F_{heat} from a warm reservoir of temperature T_{warm} to a cold reservoir of temperature T_{cold} can be expressed as

$$\sigma = F_{heat}(1/T_{cold} - 1/T_{warm}) \tag{4}$$

For mass exchange, entropy production by a mass flux F_{mass} from a higher chemical potential μ_{high} to a lower potential μ_{low} is expressed similarly as

$$\sigma = F_{mass}(\mu_{high} - \mu_{low})/T \tag{5}$$

with T being the temperature at which the process occurs. Eqns. 4 and 5 can be used to derive an entropy budget. Note that these equations are simplified expressions (see e.g. *Kondepudi and Prigogine* [1998] for details).

2.2. The hydrologic cycle within the Earth's entropy budget

The processes of the hydrologic cycle, like most processes within the Earth system, are irreversible and produce entropy. To understand where this irreversibility stems from, we consider the state of TE as a reference state. Atmospheric water vapor is in TE with a water surface when its relative humidity is 100 %. At TE, net evaporation balances net condensation with no net exchange of moisture. The evaporation of water into an unsaturated atmosphere is irreversible and produces entropy, bringing the atmosphere closer to TE. Unsaturated conditions are being produced through atmospheric motion, which acts as a dehumidifier (*Pauluis* [2005]). When air is lifted by motion, it cools and water vapor is brought closer to saturation. The condensation of supersaturated vapor is again irreversible and produces entropy, as does diffusion of water vapor. Irreversibility of the hydrologic cycle is therefore intimately linked to the strength of the atmospheric circulation.

The contribution of the hydrologic cycle to the Earth's entropy budget is estimated from the mean latent heat flux $F_{lh} = 79$ W m^{-2} and the temperatures at which evaporation ($\approx$ 288K) and condensation ($\approx$ 266K) occurs (*Peixoto et al.* [1991], *Kleidon and Lorenz* [2005]). The total entropy production of $\sigma = 23$ mW m^{-2}K^{-1} originates from several irreversible processes, including evaporation, condensation of supersaturated vapor, water vapor diffusion and expansion, as well as re-evaporation and frictional dissipation of raindrops (*Goody* [2000], *Pauluis et al.* [2000], *Pauluis and Held* [2002]). *Kleidon* [2008] estimates that entropy production associated with evaporation into an unsaturated atmosphere contributes about 8 mW m^{-2} K^{-1} with strong geographic and seasonal variations. The remaining part would be related to irreversible hydrologic processes in the atmosphere.

2.3. Thermodynamics of the water budget on land

Hydrologic processes on land are formulated in thermodynamic terms using the chemical potential of water vapor in air and of bound water in the soil. Since all water fluxes take place in the gravitational field of the Earth, modified chemical potentials are used (*Kondepudi and Prigogine* [1998], *Kleidon et al.* [in press]). For simplicity we will refer to these simply as chemical potentials. We set the chemical potential of free water at mean sea level to zero and express height z in relation to height above mean sea level.

The chemical potential of water vapor with partial pressure e is calculated from the expansion work of vapor from saturation e_{sat} to e (e.g. *Campbell and Norman* [1998]), and the gravitational field:

$$\mu_a = R_v T \ln(RH) + gz \quad (6)$$

where R_v is the gas constant of water vapor, $RH = e/e_{sat}$ is the relative humidity, and g is the gravitational acceleration.

The chemical potential of water in the soil μ_s accounts for the binding energy of water with the soil matrix (essentially proportional to the matric potential of the soil Ψ_m) and the gravitational field:

$$\mu_s(z) = \Psi_m(\theta(z)) + g(z - z_{msl})\theta(z) \quad (7)$$

where $\theta(z)$ is the volumetric soil moisture content.

Thermodynamic equilibrium applies as follows: (i) water vapor in air is in TE with a saturated surface when $RH = 100\%$; (ii) bound soil moisture is in TE with soil air when the chemical potential of soil water is equal to the chemical potential of water vapor in soil air, i.e. $\mu_s = \mu_a$. (iii) the distribution of soil moisture in the soil profile is in TE when $\nabla\mu_s = 0$ for a given, total amount of soil water.

The water balance on land is moved away from TE when precipitation wets the soil (Fig. 1). This corresponds to a phase transition from free to bound water, and the associated decrease in internal energy is released as heat ("heat of immersion", e.g. *Hillel* [1998]). Soil wetting is only reversible if the soil is saturated. The entropy production associated with wetting of unsaturated soil is $\approx$ 0.01 mW m^{-2} K^{-1} or less (*Kleidon et al.* [in press]).

After wetting, redistribution of moisture depletes gradients in chemical potential $\nabla\mu_s$, bringing the soil water distribution closer to TE. The entropy produced by the redistribution of soil moisture is in a similar range as that of wetting.

Evapotranspiration is driven by the gradient $\mu_s - \mu_a$. It brings the near-surface air closer to TE with the soil moisture content up to the point where $\mu_s = \mu_a$. It produces entropy when the nearly saturated air from the surface (or the canopy) mixes with the drier air of the atmospheric boundary layer. Entropy production depend on E and RH, and ranges from 0.2 - 10 mW m^{-2} K^{-1} (*Kleidon et al.* [in press]). Included in this estimate is entropy production associated with transpiration, which depletes the gradient $\mu_s - \mu_v$ as well, where μ_v is the chemical potential of leaf water.

Runoff generation and groundwater drainage are driven by gradients in the gravitational part of μ_s. Entropy production associated with runoff can be estimated from the gradient in z. When this potential energy gradient is converted into kinetic energy and dissipated into heat by friction, this results in entropy production of $\approx$ 0.01 - 1 mW m^{-2} K^{-1}, depending on R and ∇z.

3. Maximum Entropy Production and potential applications to land surface hydrology

The proposed MEP principle states that thermodynamic systems maintain steady states at which entropy production is maximized. The MEP state generally emerges from a trade-off between the thermodynamic flux and force, that is, the force (e.g. a gradient in temperature) causes the flux, but the flux depletes the force. This trade-off applies to many hydrologic processes on land, where the fluxes generally deplete gradients in chemical potential (Fig. 1). We first review previous applications of MEP to illustrate its use, and then develop a simple model to demonstrate potential applications of MEP to land surface hydrology.

3.1. Previous examples of MEP in the climate system

The common application of MEP is poleward heat transport in the climate system (*Paltridge* [1975], *Paltridge* [1978], *Paltridge* [1979]). Due to the latitudinal variation in solar radiation, the radiative difference between the tropics and polar regions result in uneven heating and a temperature gradient, which generates motion. The more heat is transported by atmospheric motion, the more this temperature gradient is depleted (Fig. 2a). Hence, an intermediate temperature gradient and heat flux result in MEP. The associated temperature gradient corresponds largely to observations. A detailed review of MEP in the climate system is given by *Ozawa et al.* [2003].

Lorenz et al. [2001] demonstrated that MEP makes better predictions for other planetary atmospheres than conventional scaling assumptions of atmospheric properties. *Kleidon et al.* [2003] and *Kleidon et al.* [2006] used sensitivity simulations with an atmospheric general circulation model to show that MEP predicts semi-empirical parameters that describe boundary layer friction. These latter studies show important progress in demonstrating the validity of MEP and point out deficiencies in existing models that could be improved by using MEP.

3.2. An example of MEP and hydrologic fluxes on land

We illustrate the flux-force tradeoff and MEP for soil hydrologic fluxes using a simple setup (Fig. 3). Precipitation P completely infiltrates into the soil, resulting in some chemical potential of soil moisture μ_s. This flux is partitioned into E and R. Both fluxes are gradient-driven, i.e. they are expressed as $E = k_e \cdot (\mu_s - \mu_e)$ and $R = k_r \cdot (\mu_s - \mu_r)$, where μ_e is the chemical potential at which water evaporates (e.g. the permanent wilting point of plants) and μ_r is the chemical potential of the water when it reaches the river channel. Once the fluxes leave the soil system, they continue to be driven by gradients with associated entropy production: E by the difference $\mu_e - \mu_a$ (see Fig. 1), and R by the difference $\mu_r - \mu_{msl}$. The latter two aspects are not considered here.

Using the above expressions of E and R and the constraint $P = E + R$, we obtain an expression for μ_s of:

$$\mu_s = \frac{P + k_e\mu_e + k_r\mu_r}{k_e + k_r} \quad (8)$$

Entropy production associated with E and R are:

$$\sigma_e = k_e(\mu_s - \mu_e)^2/T \quad (9)$$

$$\sigma_r = k_r(\mu_s - \mu_r)^2/T \quad (10)$$

We take E as an example to demonstrate the existence of a MEP state of σ_e with respect to k_e for given values P and k_r. At the limit of $k_e = 0$, $E = 0$ and hence $\sigma_e = 0$. At the other extreme of $k_e \to \infty$, $\mu_s \to \mu_e$ and hence $\sigma_e = 0$. Consequently, this trade-off leads to a MEP state and an optimum value for k_e and E (Fig. 4). Similarly, a maximum in σ_r can be demonstrated for given P and k_e.

Since σ_e is generally higher than σ_r, we would expect that optimisation of both k_e and k_r would lead to the domination of E over R in the partitioning of P in the absence of other limitations. This is qualitatively consistent with the findings by Budyko (Section 1), but it remains to be tested whether the simple model used above would be able to reproduce the Budyko curve if supplemented by an energy constraint and applied to real catchment conditions.

3.3. The role of boundary conditions

The example illustrates some critical factors that result in MEP. The MEP state is found because the gradient can respond to the flux, i.e. μ_s responds to the partitioning between E and R. In other words, we allow for flexible boundary conditions. If we had prescribed the flux from μ_p to μ_s with a fixed conductivity k_p (cf. Fig. 4), then μ_s would be fixed to a value of $\mu_s = \mu_p - P/k_p$ and the gradient $\mu_s - \mu_e$ no longer responds to E. If we consider the flux partitioning of the whole system, we cannot identify a MEP state because we fixed the potentials at the boundary (μ_p, μ_e, and μ_r) as well as the flux ($P = E + R$), so that there is no trade-off between flux and force.

This issue of fixed boundary conditions is, however, also a result of the setup. It neglects feedbacks that take place outside the system and that affect boundary conditions, so that these would no longer be fixed. However, a different value of E will alter RH (thereby μ_a) and eventually P, especially at larger spatial scales. Such larger-scale atmospheric feedbacks have been demonstrated by sensitivity simulations with climate models (*Shukla and Mintz* [1982], *Kleidon et al.* [2000]). At long time scales, the flux partitioning also alters soil texture and slope, e.g. through sediment transport, which would affect $\mu_s = f(\theta)$ and ∇z, so that these conditions are not fixed either. Hence, feedbacks outside the system under consideration are important for shaping MEP states in that these act to make boundary conditions more flexible, allow for the flux-force trade-off and therefore for a wider range of possible steady states to be selected from.

MEP may still be applicable to systems where parts of the boundary conditions are fixed. If the potential gradient at the boundary is fixed, but the flux is allowed to vary, a flux-force trade-off can form within the system. MEP then results in a maximization of the flux (e.g. *Ozawa et al.* [2001]). An example is Bernard convection, which is driven by fixed temperatures at the boundaries of a convection cell. The heat flux within the system is maximized by creating steep gradients at the system boundary and relatively large areas within the system with little gradients where the heat transport is achieved by convective flow.

3.4. Discussion

The simple example illustrates the potential use of MEP for hydrologic fluxes at the land surface. There is some support to assume that hydrologic fluxes indeed maximize entropy production. For instance, *Wang et al.* [2004] and *Wang et al.* [2007] successfully tested the hypothesis that E is maximized under given environmental constraints in the field. This work would support the applicability of MEP under the assumption of fixed boundary conditions.

There are several challenges faced by the application of MEP. MEP considers entropy production in steady state, although the time interval on which a steady state is achieved in the hydrologic cycle may be difficult to quantify. Furthermore, variability of the exchange fluxes and gradients is not considered here either, even though *Porporato et al.* [2004] showed that different variability regimes can result in different hydrologic flux partitioning.

Another issue is that hydrologic fluxes interact with other dissipative processes. This is particularly evident in the strong coupling of hydrological processes on land with vegetation processes. Vegetation properties such as stomatal conductance, leaf area, root biomass and depth substantially affect E and thus the partitioning of fluxes. Vegetation activity, the combined processes of carbon uptake by photosynthesis (which converts low entropy solar radiation into chemical free energy associated with carbohydrates), and respiration of carbohydrates into heat are also dissipative processes, but of biogeochemical nature. MEP applied to vegetation activity would imply maximization of mean gross carbon uptake (*Kleidon* [2004a], *Kleidon* [2004b]). Since both maximizations interact – hydrologic fluxes are affected by vegetation activity and vegetation activity depends on water availability – this seems to result in conflicting predictions of MEP to hydrological and biogeochemical fluxes. This conflict could be addressed by considering the different time scales at which these processes are optimized. While redistribution of soil moisture takes place at a time scale of days, maximization of vegetation activity likely takes place through adaptation processes in ecophysiological functioning at a much longer time scale of years or longer. Hence, ecophysiological behavior could be prescribed as fixed for the optimization of hydrologic fluxes, and then subsequently optimized given optimal hydrologic fluxes. This interaction of slow and fast processes in the application of MEP has, however, not been applied or tested yet.

MEP has also faced criticisms. *Rodgers* [1976] (also *Goody* [2007]) criticized MEP as applied to poleward heat transport because it does not account for the important role of planetary rotation rate. However, the lack of conservation of angular momentum in the simple energy balance models used by *Paltridge* [1975] and *Lorenz et al.* [2001] are a deficiency of the models, not of MEP per se. MEP has been tested within an atmospheric general circulation model that explicitly accounts for the constraint imposed by the planetary rotation rate (*Kleidon et al.* [2003], *Kleidon et al.* [2006]), demonstrating that MEP is compatible with other constraints on the system.

4. Synthesis and Outlook

This review provided a brief introduction to the application of non-equilibrium thermodynamics and the proposed principle of Maximum Entropy Production to the water budget on land. Compared to other optimality approaches, MEP has clear advantages: (i) it is grounded in fundamental physics (even if its theoretical base is still in the process of getting established); (ii) it is universal in scope, that is, it should be applicable to purely physical exchange processes of heat and matter (such as turbulence), but also to many chemical and biogeochemical processes as these are thermodynamic in their nature; and (iii) it is relatively objective regarding the choice of the goal function, i.e. the aspects of systems that should be maximized, why these should be maximized, and under which conditions.

In terms of implications, non-equilibrium thermodynamics and MEP provide us with a perspective of how we should think about the hydrologic cycle within the Earth system. While the terms "system" and "systems perspective" are commonly used, they usually do not refer explicitly to the system's thermodynamic nature. The thermodynamic nature, however, tells us how these systems should be coupled (by their thermodynamic fluxes at their boundaries), and how the fluxes within these systems should be optimized (MEP). While the small-scale complexity that we find in hydrological systems (e.g. with respect to spatial heterogeneity in catchments) may overwhelm us, MEP provides a relatively simple way out by telling us that the more complex the system under consideration becomes, the more likely MEP should be able to describe its large-scale function. This follows directly from MEP being rooted in statistical physics, which is valid if a sufficiently large number of objects are considerd.

MEP should enable us to improve prediction of hydrologic fluxes by avoiding the need for scaling up small-scale, heterogeneous processes to the larger scale. It should help us at a more theoretical level to build better simple models that can advance our understanding. For example, entropy fluxes and MEP provide additional information and constraints that should help us to better understand Budyko's (1974) analysis.

In conclusion, MEP shows great promise to provide us with a better, holistic, and more fundamental understanding of the organization of hydrologic processes within the Earth system. In order to achieve progress, we need to construct models based on non-equilibrium thermodynamics and test cases for demonstrating the applicability and limits of MEP.

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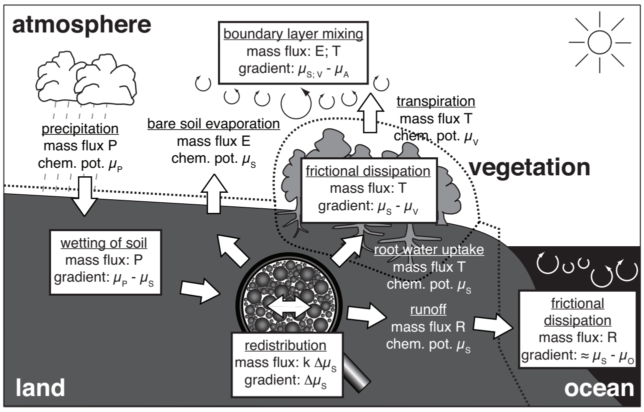

Figure 1. Schematic diagram illustrating the land surface as a thermodynamic system, with boundaries shown as dotted lines. The arrows show the mass fluxes across system boundaries in terms of their rates and chemical potentials μ (with subscripts: P = precipitation, S = soil, V = vegetation, A = atmosphere, O = ocean) and the boxes denote dissipative processes.

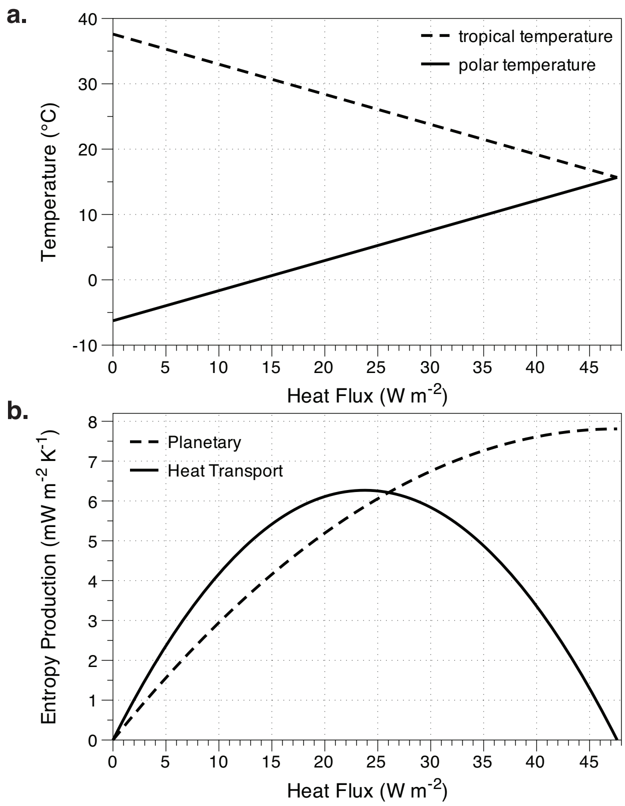

Figure 2. Diagram to illustrate a MEP state for poleward heat transport. a: Temperature difference as a function of heat flux. b: Entropy production associated with poleward heat transport and the increase in planetary entropy production as a function of poleward heat transport. After *Kleidon and Lorenz* [2005].

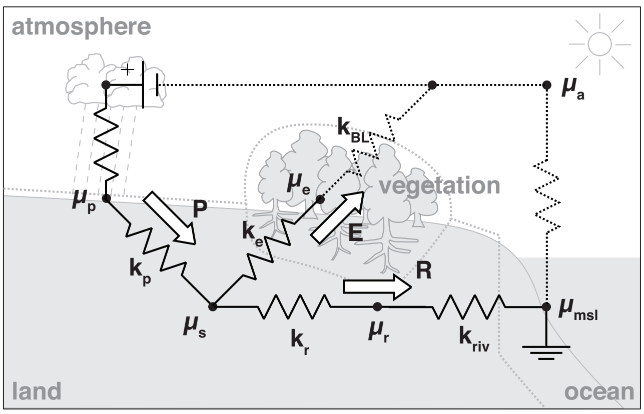

Figure 3. Simplified representation of the land system of Fig. 1 in terms of an electric circuit analogy. The solid lines represent flow of liquid water, the dashed line flow of water vapor.

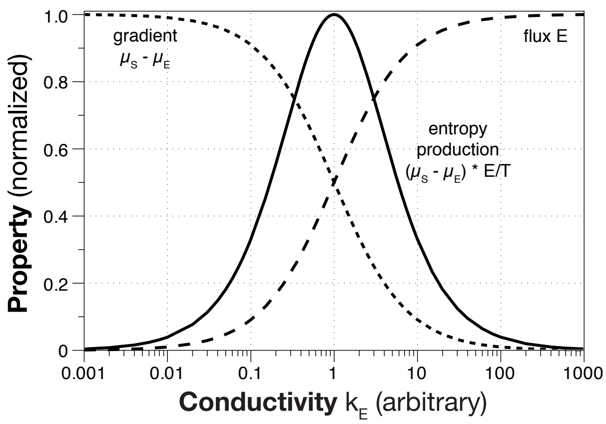

Figure 4. Existence of an MEP state as a result of flux-force trade-off associated with evapotranspiration E and conductivity k_e (cf. eqn. 8). For demonstration, values shown have been normalized by their maximum value.