Is Spatially Integrated Entropy Production Useful to Predict the Dynamics of Ecosystems?

Juan C. Quijano^a, Henry Lin^{a,*}

^a*The Pennsylvania State University, 116 Agricultural Sciences and Industries Building,
University Park, PA 16802*

Abstract

Production of entropy by macroscopic systems in far from equilibrium as estimated from the spatial integration of the entropy production density have been considered as an important concept that could help understand and predict the evolution of open systems. In this study we have used an extensive dataset of energy fluxes recorded in Ameriflux sites to compute the entropy production across different climates and ecosystems in order to analyze whether there are clear patterns showing a higher entropy production in more vegetated sites or in more developed stages. The entropy budget has been defined over a conceptualized system defined by the Earth Critical Zone. Based on previous studies we have recognized four different formulations for the estimation of entropy production in macroscopic systems: (i) a total entropy production that accounts for all the energy fluxes including radiation fluxes, (ii) an entropy production that includes only those fluxes of energy absorbed within the open system, (iii) an entropy production that includes only living systems and accounts for the biochemical energy absorbed during photosynthesis and its further dissipation in the form of heat, and (iv) an entropy production that includes only incoming and outgoing heat fluxes into the open system that occurs at different temperatures. We quantified these entropy productions at different sites and stages of ecosystem development using available information recorded in 36 Ameriflux sites. We observed rather different magnitudes and patterns in all these formulations of the entropy productions. Therefore, these formulations can not be compared or considered as the same concept as has been done previously because they represent different scales and processes. In addition, we did not find a clear

*Corresponding author. Tel.: +1 814-865-6726, henrylin@psu.edu

evidence of a maximum entropy production in more vegetated sites and at more mature stages of development, for any of these four entropy production formulations. These results suggests that hypotheses based on a maximum entropy production estimated from spatial integration over macroscopic systems in far from equilibrium should not be considered as a fundamental principle to understand or predict the evolution of these systems.

Keywords: Entropy production, Critical Zone, Thermodynamics

1. Introduction

Since thermodynamic entropy (hereafter entropy) was proposed initially by Clausius in 1865 it has been considered as a promising concept that could lead us to the understanding of the evolution of different kind of open systems. In particular, the production of entropy has been considered as a major concept that could provide important information of a system and predict its behavior. Today, more than two centuries after it was developed many different hypotheses have been proposed in the light of entropy production. However, none of these hypotheses have been fully proven. In particular, a major difficulty lies in the implementation of entropy related principles to areas that are dealing with macroscopic scales where different assumptions including temporal thermal equilibrium and spatial integration of entropy production are considered. In this study we analyze the production of entropy in the Earth Critical Zone, and in order to compute the entropy production over this domain we use an extensive database of energy fluxes that allow us to compare the entropy production across different climates and at different stages of ecosystem development.

The most important hypotheses defined in the light of entropy production are the minimum entropy production principle (MinEnt) by *Prigogine* (1947) and the maximum entropy production principle (MEPP) proposed initially by *Ziegler* (1963, 1983). On the one hand, MinEnt suggests that systems in the linear non-equilibrium regime reach a steady state at which the entropy production from the system is constant and attains a minimum value (*Kondepudi and Prigogine*, 1998). Previous studies have questioned the validity of MinEnt (*Martyushev and Seleznev*, 2006; *Martyushev*, 2013; *Jaynes*, 1980; *Pálffy-Muhoray*, 2001; *Danielewicz-Ferchmin and Ferchmin*, 2000; *Hoover*, 2002). In particular, *Martyushev and Seleznev* (2006); *Martyushev* (2013) showed that MinEnt could be conceptualized as an special case of MEPP.

29 On the other hand, MEPP as proposed initially by *Ziegler* (1983) suggests
 30 that when thermodynamic forces are preset the fluxes are such that there is a
 31 maximization of the entropy production density (*Martyushev and Seleznev*,
 32 2006). It is important to keep in mind that MEPP implies a maximization
 33 of the entropy density δ defined over a fundamental spatial domain where
 34 the thermal equilibrium assumption remains valid. Different fields, includ-
 35 ing atmospheric sciences, hydrology, ecology, pedology, and geomorphology,
 36 have looked at MEPP as an alternative to predict the evolution of systems.
 37 However, these fields deal with macroscopic domains where the definition of
 38 such a fundamental scale is challenging. As a result, previous studies (*Lucia*,
 39 2014; *Ozawa et al.*, 2003; *Kleidon et al.*, 2010) in these fields have modified
 40 the MEPP. This modified version, here we call *ModMEPP*, suggests that
 41 evolution of open macroscopic systems in far from equilibrium conditions is
 42 guided toward a maximum entropy production σ that is defined over the
 43 entire domain by spatial integration of the entropy production density:

$$\sigma = \int \delta \quad (1)$$

44 where δ is the entropy production density. This formulation involves an
 45 integration of the entropy production density over domains where the thermal
 46 equilibrium assumption is not longer valid. Therefore, some previous authors
 47 such as *Martyushev* (2013) claim that maximization of σ as suggested in
 48 *ModMEPP* may not be valid.

49 Although the validity of *ModMEPP* is still under debate, it could have
 50 a significant contribution in areas dealing with macroscopic systems. Com-
 51 putation of σ by spatial integration could be attained with measurements
 52 of energy fluxes and temperature performed in macroscopic domains. Dif-
 53 ferent examples of macroscopic systems where such an approach has been
 54 performed to compute the entropy production include a cell (*Lucia*, 2014),
 55 a leaf (*Aoki*, 1989), an ecosystem (*Aoki*, 1995; *Holdaway et al.*, 2010), the
 56 global water cycling (*Porada et al.*, 2011; *Westhoff et al.*, 2014), a portion
 57 of the atmosphere (*Paltridge*, 1975; *Pauluis and Held*, 2002), or even the
 58 entire planet (*Ichiro*, 1983-03-15; *Lorenz*, 2002). As a result validation of
 59 *ModMEPP* is more doable than MEPP. In fact, while there are still no clear
 60 methodologies to validate MEPP, many previous studies have performed val-
 61 idations of *ModMEPP*. For instance, in atmospheric sciences different studies
 62 trying to understand the exchange of heat fluxes within the atmosphere and
 63 to the ocean have found that *ModMEPP* is able to reproduce observed pat-

terns (see *Ozawa et al.* (2003)). Similarly studies with FLUXNET towers in ecosystems found that entropy production increases in the more developed ecosystems supporting ModMEPP (*Holdaway et al.*, 2010). However, more recent studies in ecological networks (*Meysman et al.*, 2010) claimed that the evolution of such systems is not always guided by a maximum production of entropy. In addition, studies performed on different atmospheric conditions show that rather different conditions and dissipation of energy could attain the same magnitude of entropy production by different mechanisms (*Pauluis and Held*, 2002), which indirectly disprove ModMEPP.

ModMEPP has also been proposed as a leading hypothesis to understand the evolution of terrestrial ecosystems. Previous studies have suggested a connection between life and higher production of entropy (*Schneider and Kay*, 1994; *Ulanowicz and Hannon*, 1987), and according to *Kleidon* (2004) the presence of vegetation in different parts of the Earth support this hypothesis. In addition, *Holdaway et al.* (2010) compared σ at different stages of ecosystem development and found that σ increases in the more developed ecosystems, which in turn support ModMEPP. However, some of previous studies have been supported on deductions based on expected patterns, instead of actual quantifications of σ . On the other hand, the studies that have quantified σ have analyzed few ecosystems and have used different periods throughout the year that has been selected arbitrarily. Therefore, it is important to perform a more comprehensive comparison, that includes different ecosystems and climates. In this study we used an extensive database of energy fluxes over different sites spanning climates, to bring more evidence into the patterns of the entropy production σ in terrestrial ecosystems, and in particular analyze whether these patterns support ModMEPP. The system under study is the Earth Critical Zone (CZ), which according to NRC (2001), is defined as the *heterogeneous, near surface environment in which complex interactions involving rock, soil, water, air, and living organisms regulate the natural habitat and determine the availability of life-sustaining resources*. The definition of this system allows us to take advantage of the extensive dataset recorded in FLUXNET Towers (Ameriflux Sites) to analyze the budget of entropy in different sites and at different developmental stages.

An important consideration that most studies have overlooked is the actual formulation that is implemented for the estimation of the entropy production. Previous studies have used different formulations for σ , and the outcomes from different formulations may result in different patterns. Based

on previous studies we recognized the next formulations that have been considered for the estimation of σ : (i) some approaches include all the sources of energy that reach the system under analysis, including the incoming radiation, heat and chemical energy, (ii) other approaches neglect radiation fluxes because they claim most of radiation is dissipated instantaneously by the surface and include only the energy fluxes in the form of heat and chemical energy that goes into the system of analysis, and (iii) other approaches consider that the most interesting component to analyze are the fluxes with the highest levels of specific exergy and include only the chemical energy (neglecting heat) that is absorbed by the system under analysis. These different formulations for the estimation of σ are defined on different scales and included different processes. Thus, it is unclear whether all of them lead to similar patterns, and even more if all of them support ModMEPP.

The main goals of this study are: (i) to quantify the production of entropy σ in the CZ for the formulations of entropy production that have been discussed above, (ii) to analyze whether computed σ from these formulations have the same patterns across climates and stages of development, and (iii) to analyze whether these patterns support ModMEPP as a leading hypothesis for terrestrial ecosystems.

2. Theory

2.1. Formulations for Entropy Production

Previous studies have implemented different formulations for the computation of entropy. In this section we define these formulations and explain how these approaches are applied to the CZ.

2.1.1. Total Entropy Production σ

Previous studies (Aoki, 1987; Holdaway *et al.*, 2010) have conceptualized the production of entropy by considering all the fluxes that reach the domain under analysis. As a result, the production of entropy in these approaches is quantified by including the exchanges of radiation, heat, and chemical entropy fluxes with the environment.

In order to analyze the budget of entropy and energy in the CZ it is important to define the boundaries that delineate the CZ. According to Kleidon *et al.* (2012) and Quijano and Lin (2014), the lower boundaries of the CZ are defined by the bottom of the regolith, and the upper boundary as an imaginary limit right above the canopy. In this study we use the same

conceptualization (Figure 1). The delineation of the lateral boundaries associated with the CZ is more subjective. They may range from a soil profile, an ecosystem, to a geographic cell, a watershed, or an entire continent (*Quijano and Lin, 2014*). In this study the spatial delineation of the CZ is given by the ecosystem scale defined by the footprint of the FLUXNET tower. Figure 1 shows a schematic representation of the control volume used for the CZ in this study. Neglecting energy fluxes due to mass transport, and horizontal and bottom fluxes of heat (these fluxes are significantly lower compared with the other fluxes in Equation 2) (*Quijano and Lin, 2014*), the energy balance of the control volume as defined in Figure 1 is given by:

$$\frac{dE_{cz}}{dt} = E_{SW,in} - E_{SW,out} + E_{LW,in} - E_{LW,out} - E_{LE} - E_H \quad (2)$$

where dE_{cz} is the rate of change of energy within the CZ per unit area, E_{SW} , E_{LW} , E_{LE} , and E_H are the fluxes of energy related to shortwave (SW) radiation, longwave (LW) radiation, latent heat (LE), and sensible heat (H) fluxes, respectively. Using the same formulation we can define the production of entropy by the CZ as:

$$\sigma_{cz} = \frac{dS_{cz}}{dt} + \left(S_{SW,out} - S_{SW,in} + S_{LW,out} - S_{LW,in} + S_{LE} + S_H \right) \geq 0 \quad (3)$$

where dS_{cz} is the rate of change of entropy within the CZ per unit area, S refers to fluxes of entropy associated with the different terms in Equation 2, and σ_{cz} is the total production of entropy by the CZ.

2.1.2. Internal Production of Entropy σ_{int}

A significant fraction of the radiation that is coming to the surface is dissipated instantaneously. As a result, the fluxes of radiation and heat used in this dissipation are significantly higher than the fluxes of energy that are absorbed by the surface. As a result, previous studies in Earth Sciences (*Rasmussen et al., 2011*) have neglected the fluxes of radiation and heat dissipated by the surface, and consider only the fluxes of energy, entropy,

162 and exergy that are absorbed by the system under analysis. The rationale is
 163 that fluxes absorbed by the system are directly responsible for the alteration
 164 of the internal structure of it and therefore will provide more explanation for
 165 its evolution.

166 The CZ is experiencing a continuous exchange of radiation fluxes with its
 167 environment. However, incoming radiation (SW and LW) is dissipated in-
 168 stantaneously by the surface in the form of outgoing radiation (SW and LW),
 169 LE and H heat. The fraction of energy that is absorbed by the CZ is mostly
 170 in the form of heat and chemical components, in particular photosynthetic
 171 compounds. Considering only photosynthetic compounds and heat, we can
 172 express the energy balance in the CZ as:

$$\frac{dE_{cz}}{dt} = E_{SW,pho} + E_{Q,G} + E_{Q,A} \quad (4)$$

173 where $E_{SW,pho}$ refers to the SW radiation flux that is captured through pho-
 174 tosynthesis, and $E_{Q,G} + E_{Q,A}$ are the net heat fluxes to the below and above-
 175 ground regions of the CZ, respectively. Both $E_{Q,G}$ and $E_{Q,A}$ can be decom-
 176 posed in incoming and outgoing fluxes of heat. Also, note that some fraction
 177 of the outgoing heat fluxes come from the dissipation of work and respiration
 178 of living systems within the CZ ($E_{Q,resp}$), thus we can express Equation 4 as:

$$\begin{aligned} \frac{dE_{cz}}{dt} = & \underbrace{E_{SW,pho} - E_{Q,resp}}_{\text{Biochemical } (E_{bio})} + \\ & \underbrace{\underbrace{E_{Q,G,in} - E_{Q,G,out}}_{\text{Below-ground}} + \underbrace{E_{Q,A,in} - E_{Q,A,out}}_{\text{Above-ground}} + E_{Q,resp}}_{\text{Heat } (E_Q)}, \quad (5) \end{aligned}$$

179 where the energy into the CZ is divided into two main components, *(i) net*
 180 *biochemical* (E_{bio}) fluxes that refer to the uptake of SW radiation by photo-
 181 synthesis and its subsequently dissipation in the form of heat after respiration
 182 and work, and *(ii) net heat* (E_Q) fluxes that refer to incoming and outgoing
 183 fluxes of heat energy in the CZ.

184 Based on the energy balance in Equation 5 it is possible to define the pro-
 185 duction of entropy that includes only the fluxes of energy that are absorbed
 186 by the CZ, as:

$$\sigma_{cz,int} = \frac{dS_{cz}}{dt} + \underbrace{\left(S_{Q,resp} - S_{SW,pho} \right)}_{\sigma_{bio}} + \underbrace{\left(S_{Q,A,out} - S_{Q,A,in} \right) + \left(S_{Q,G,out} - S_{Q,G,in} \right) - S_{Q,resp}}_{\sigma_Q} \geq 0 \quad (6)$$

where S refers to exchange fluxes of entropy, and $\sigma_{cz,int}$ is the instantaneous production of entropy within the CZ. According to Equation 6 the internal production of entropy in a system delineating the CZ has two main components: (i) σ_{bio} , which is the entropy produced by the transformation of SW radiation to chemical energy stored in reduced carbon compounds, and its further conversion to heat (after oxidation and work performed), and (ii) σ_Q , which is the entropy produced by fluxes of heat that enter and leave the system at different temperatures.

In addition, note that $\sigma_{cz,int}$ is embedded in σ_{cz} , and:

$$\sigma_{cz} = \sigma_{cz,int} + \sigma_{rad} \quad (7)$$

where σ_{rad} is the production of entropy caused by the instantaneous transformation of SW radiation at the surface.

2.1.3. Biological Entropy Production σ_{bio}

Previous studies (*Meysman et al.*, 2010; *Bendoricchio and Jorgensen*, 1997) have considered only the processes that are directly connected with living systems. These approaches include only the fluxes of energy, entropy, and exergy that are associated with the reduction and oxidation of organic compounds. According to these studies, the exergy that is stored in living systems is by far the most important source of exergy stored in ecosystems. Also, this production of entropy is important because it is directly related to the work performed by living systems, and this work is the base of ecological interactions and ecosystem dynamics. The production of entropy associated with living systems is originated by the oxidation of photosynthetic products with low entropy (high exergy), and subsequently dissipation of heat with higher entropy (lower exergy). Note that the definition of σ_{bio} presented in Equation 6 represents the production of entropy by considering only biological systems as in previous studies.

213 *2.2. Annual Production of Entropy*

214 In previous section we defined different formulations for the instantaneous
 215 production of entropy, σ_{cz} , $\sigma_{cz,rad}$, $\sigma_{cz,int}$, σ_Q , and σ_{pho} , in the CZ based on
 216 different processes that are included. It is worth mentioning that these def-
 217 initions refer to entropy production in a conceptualized macroscopic system
 218 and already involve a spatial integration. Now, if we integrate these in-
 219 stantaneous productions of entropy over a year we obtain the total entropy
 220 produced in a year, which is a more fair quantity to compare the productions
 221 of entropy over different ecosystems:

$$\begin{aligned} \eta_{cz} = & \int_{\text{year}} \frac{dS_{cz}}{dt} + \underbrace{\int_{\text{year}} S_{SW,out} - S_{SW,in}}_{\eta_{SW}} + \\ & \underbrace{\int_{\text{year}} S_{LW,out} - S_{LW,in}}_{\eta_{LW}} + \underbrace{\int_{\text{year}} S_{LE}}_{\eta_{LE}} + \underbrace{\int_{\text{year}} S_H}_{\eta_H} \geq 0 \end{aligned} \quad (8)$$

222 Term η_{cz} is the total production of entropy by the CZ in a year. Terms η_{SW} ,
 223 η_{LW} , η_{LE} , and η_H refer to the different components that are associated with
 224 SW and LW radiation and LE and H heat over a year, respectively. Similarly:

$$\begin{aligned} \eta_{cz,int} = & \underbrace{\int_{\text{year}} S_{Q,resp} - S_{SW,pho} + \frac{dS_{cz}}{dt}}_{\eta_{bio}} \\ & + \underbrace{\int_{\text{year}} S_{Q,G,out} - S_{Q,G,in} + S_{Q,A,out} - S_{Q,A,in} - S_{Q,resp}}_{\eta_Q} \geq 0. \end{aligned} \quad (9)$$

225 where $\eta_{cz,int}$ refers to the total production of entropy within the CZ in a
 226 year. Terms η_{bio} and η_Q refer to the components associated with biological
 227 systems, and heat fluxes, respectively.

228 At the annual scale the storage of energy, entropy, and exergy associated
 229 with heat fluxes is negligible (*Rasmussen et al.*, 2011), thus at the annual scale
 230 the changes in energy and entropy are linked mostly to biomass accumulation,
 231 thus:

$$dE_{cz} \Big|_{\text{year}} \approx \left(E_{\text{SW,pho}} - E_{\text{Q,resp}} \right) \Big|_{\text{year}} \quad (10a)$$

$$dS_{cz} \Big|_{\text{year}} \approx \left(S_{\text{SW,pho}} - S_{\text{Q,resp}} \right) \Big|_{\text{year}} . \quad (10b)$$

232 Therefore, $\frac{dS}{dt}$ is considered as part of η_{bio} in Equation 9.
 233

234 2.3. Exergy Destruction

235 Following the Gouy-Stodola theorem (*Bejan*, 2013; *Lucia*, 2013), the de-
 236 struction of exergy by a system can be computed as:

$$\Gamma \approx T_o \eta \quad (11)$$

237 where Γ is the destruction of exergy, and T_o is the temperature of a hypo-
 238 thetical reference environment to the system. From Equation 11 it is possible
 239 to define the destruction of exergy Γ_{cz} , $\Gamma_{\text{cz,rad}}$, $\Gamma_{\text{cz,int}}$, Γ_{bio} , and Γ_{Q} associated
 240 with the different productions of entropy that have been described above,
 241 η_{cz} , $\eta_{\text{cz,rad}}$, $\eta_{\text{cz,int}}$, η_{bio} , and η_{Q} .

242 However, note that a hypothetical environment for the CZ could be rep-
 243 resented by rather different systems such as the atmosphere, a nearby CZ,
 244 the lithosphere, or even the sun (*Jørgensen et al.*, 2011; *Quijano and Lin*,
 245 2014). Therefore, estimation of the reference temperature of a hypothetical
 246 environment is challenging for the CZ. Although a direct quantification of
 247 exergy destruction is not possible, we see from Equation 11 that the exergy
 248 destruction is proportional to the entropy production, and as a result can be
 249 associated with different processes in the CZ.

250 3. Methods

251 3.1. Sites

252 In this study we have selected 36 Ameriflux sites with available informa-
 253 tion to compute σ_{cz} or $\sigma_{\text{cz,int}}$. Table 1 shows the complete list of selected

254 sites, and Figure 2 shows the location of all these sites. In addition, the On-
 255 line Supplement Section 1 shows the specific years of information that were
 256 utilized for each of the figures generated in this study.

257 3.2. Entropy Calculation with FLUXNET data

258 In this section we introduce the formulations to compute the production
 259 of entropy from information recorded in FLUXNET towers. These equations
 260 are based on previous approaches such as *Aoki* (1987, 1989), *Holdaway et al.*
 261 (2010), and *Quijano and Lin* (2014). The entropy flux associated with an
 262 energy flux of SW radiation (E_{SW}) recorded in a FLUXNET tower is given
 263 by:

$$S_{\text{SW}} = \text{RF}_{\text{SW,dir}} \left(\frac{E_{\text{SW,dir}}}{T_{\text{sun}}} \right) + \text{RF}_{\text{SW,dif}} \left(\frac{E_{\text{SW,dif}}}{T_{\text{sun}}} \right) \quad (12)$$

264 where $E_{\text{SW,dir}}$ and $E_{\text{SW,dif}}$ are the fluxes of direct and diffuse SW radiation,
 265 respectively. The terms $\text{RF}_{\text{SW,dir}}$ and $\text{RF}_{\text{SW,dif}}$ are the radiation factors (RF)
 266 for direct and diffuse SW radiation, respectively. Radiation factors are com-
 267 puted based on *Wu and Liu* (2010) and *Wright et al.* (2001), see Online
 268 Supplement Section 2. Term T_{sun} is the temperature of the Sun (Table
 269 2). Similarly, the entropy flux associated with LW radiation recorded in a
 270 FLUXNET tower is given by:

$$S_{\text{LW}} = \text{RF}_{\text{LW}} \left(\frac{E_{\text{LW}}}{T_{\text{emi}}} \right) \quad (13)$$

271 where RF_{LW} is the radiation factor for LW radiation (see Online Supplement
 272 Section 2), and T_{emi} is the temperature of emission associated with the LW
 273 radiation. For incoming LW radiation T_{emi} is the atmospheric temperature,
 274 while for outgoing LW radiation T_{emi} is an effective temperature of the CZ
 275 (T_{cz}) that is computed as:

$$T_{\text{cz}} = \left(\frac{E_{\text{LW,out}}}{\varepsilon \lambda} \right)^{1/4} \quad (14)$$

276 where λ is the Stefan-Boltzmann constant, and ε is an effective emissivity
 277 of the CZ. The entropy flux due to fluxes of LE and H from the CZ are
 278 computed as:

$$S_{\text{LE}} = \left(\frac{E_{\text{LE}}}{T_{\text{cz}}} \right) \quad S_{\text{H}} = \left(\frac{E_{\text{H}}}{T_{\text{cz}}} \right). \quad (15)$$

279 The flux of energy in the form of photosynthesis captured by the CZ is
 280 computed as:

$$E_{\text{SW,pho}} = h_{\text{BIO}} \text{GPP} \quad (16)$$

281 where GPP is the Gross Primary Production provided by the Ameriflux
 282 network, and h_{BIO} is the specific biomass enthalpy (*Nikolov, 1995; Rasmussen*
 283 *et al., 2011*). Using a similar approach we can compute the flux of energy
 284 that is released as heat after respiration.

$$E_{\text{Q,resp}} = h_{\text{BIO}} \text{Reco} \quad (17)$$

285 where Reco is the net flux of ecosystem respiration. As mentioned above at
 286 the annual scale the rate of energy change in the CZ is mostly associated with
 287 biomass (Equation 10). Therefore, the rate of change of entropy is defined
 288 based only on photosynthetic and respiration fluxes, as:

$$dS_{\text{CZ}} = \begin{cases} \left(dE_{\text{CZ,pho}} \right) \xi_{\text{SW,in,yr}}, & \text{if } dE_{\text{CZ,pho}} \neq 0 \\ 0, & \text{if } dE_{\text{CZ,pho}} = 0 \end{cases} \quad (18)$$

289 where $\xi_{\text{SW,in,yr}}$ is a mean annual ratio between the entropy and energy fluxes
 290 of the incoming SW radiation that is captured through photosynthesis in
 291 the CZ. In other words, we assume that the biomass that is stored, has on
 292 average, a ratio of entropy to energy equal to $\xi_{\text{SW,in,yr}}$, which is given by:

$$\xi_{\text{SW,in,yr}} = \frac{\int_{\text{year}} S_{\text{SW,in}}}{\int_{\text{year}} E_{\text{SW,in}}}. \quad (19)$$

293 The net flux of heat into the CZ is computed as:

$$E_{\text{Q}} = R_{\text{n}} - E_{\text{LE}} - E_{\text{H}} - E_{\text{SW,pho}} + E_{\text{Q,resp}} \quad (20)$$

294 where R_{n} is the net radiation recorded by the FLUXNET tower. If the
 295 ground heat flux $E_{\text{Q,G}}$ is recorded by the tower it is possible to differentiate
 296 the below- ($E_{\text{Q,G}}$) and above-ground ($E_{\text{Q,A}}$) fluxes of heat. The entropy
 297 production associated with heat fluxes absorbed by the CZ is then given by:

$$\eta_Q = \frac{E_Q}{T_{cz}}. \quad (21)$$

Previous studies have reported lack of energy balance closure in most of the FLUXNET towers (*Fisher et al.*, 2007; *Oliphant et al.*, 2004; *Wilson et al.*, 2002). In turn, this may impact the computation of E_Q . In this study we implement an additional correction to E_Q in order to account for this closure. Online Supplement Section 3 shows this correction in more detail.

4. Results

4.1. Total Entropy Production by the Critical Zone σ_{cz}

Figure 3a shows a plot of η_{cz} vs $E_{SW,in}$ for 24 different sites with available information to compute η_{cz} for at least a year. There is a clear pattern showing that η_{cz} increases with $E_{SW,in}$. These results support the findings obtained by *Aoki* (1987, 1989) who found a linear relationship between the incoming global radiation and the production of entropy in plant leaves. However, here these results are obtained for the entire CZ (See Figure 1) and for many sites in different climates. This pattern is expected as SW radiation is the source of incoming energy with the lowest entropy. Thus, a higher flux of SW radiation would increase the production of entropy.

Surface albedo (α) directly measures the fraction of incoming SW radiation that is transformed to other forms of energy. Therefore, when α is included in Figure 3a it helps to see a clearer representation of the trends that are observed for η_{cz} . Although both $E_{SW,in}$ and α are able to explain some of the trends observed in η_{cz} in different sites, there are some variations that are not completely captured by these two variables (Figure 3). This suggests that spatial variations associated with temperature or emission of LE or H heat also play a role in the production of entropy. Figure 3b shows a plot of η_{cz} vs the effective temperature of the CZ (T_{cz}). Contrary to intuition there is a clear trend showing that η_{cz} increases with T_{cz} . These results also suggests that the total exergy dissipated by the CZ Γ_{cz} (following Equation 11) increases with T_{cz} which is opposite to previous hypotheses claiming that cooler ecosystems will result in higher dissipation (destruction) of exergy (*Kay*, 2000). As we will show in Section 4.1.1 a cooler ecosystem could result in higher η_{cz} if all the ecosystems that are compared are exposed to the same climate; however according to Figure 3b this pattern does not hold anymore if we compare ecosystems experiencing different climates because the amount

of incoming SW radiation as well as the atmospheric temperature impact the entropy production.

Figure 4 shows the annual energy budgets and the production of entropy for the 24 sites presented in Figure 3. The left bar displays the incoming energy reaching the CZ with two main components, SW and LW radiation. The incoming energy in the form of LW radiation is higher than SW radiation in all the sites. The bar in the middle shows the dissipation of energy from the CZ. As expected, the dissipation in the form of LW radiation is the most prominent component. There is an important fraction that is dissipated in the form of LE and H heat, and this fraction varies across the different sites. The bars on the right in Figure 4 show the total production of entropy in the CZ with the respective components of the entropy budget according to Equation 8. Note that component η_{SW} is negative in all the sites. This negative value results from a significantly higher incoming flux of SW radiation when compared with the outgoing flux of SW radiation. However, the total production of entropy by the CZ when all the components are considered is always positive, following the second law of thermodynamics. It can be seen that η_{LW} and η_{LE} are in most of the sites the most important components. As expected, in arid and semi arid climates η_{LE} is significantly lower and the η_{LW} is higher when compared to other climates.

The highest η_{SW} in Figure 4 occurs in sites experiencing semi arid climates (such as sites #2 and 16 in Table 1). Semi arid sites are able to produce more entropy because there is more incoming SW radiation (less clouds), and in addition there is a preference for LW instead of LE for the dissipation of energy. Note that $RF_{LW} > 1$ (see Equation 13) and therefore LW radiation contains higher entropy than heat (Wu and Liu, 2010). Therefore, dissipation of incoming SW radiation in the form of LW radiation instead of LE or H heat would enhance the production of entropy. In addition, the gradients in temperature throughout the day are magnified in arid climates enhancing the production of entropy.

4.1.1. Dynamics of η_{cz} Over Time

Figure 5 shows η_{cz} across different stages of ecosystem development in nine different sites. The value of η_{cz} shown in Figure 5 is the result of an average performed over all historical periods with available records to compute η_{cz} at different stages of development. This approach allows for a fair comparison between the different stages of development. We observe that for all the sites displayed in Figure 5 there is a consistent pattern that shows an inverse

relationship between η_{cz} and α . As α reduces there is a higher η_{cz} . This suggests that when ecosystems under the same climate are compared the trends of η_{cz} can be captured only by α .

In addition, Figure 5 shows that in most of these sites η_{cz} increases with the stage of the ecosystem, and becomes higher as T_{cz} reduces (not shown). The same pattern was reported by *Holdaway et al.* (2010) for different successional stages in the Amazon, and supports ModMEPP. As ecosystems develop there is an increase in the above-ground biomass and leaf area index (LAI) that induces a reduction of α . This explains the general pattern observed in different ecosystems with a higher η_{cz} as they become more mature. However, in some ecosystems such as in sites #6, 30, and 36 such a pattern does not hold. The different patterns observed at these three sites could be explained by different causes. In site #30 the younger site corresponds to a disturbance. This suggests that throughout a disturbance event there could be a transition where α becomes lower and thus increases η_{cz} . In site #36 the the LAI in all the three states of development is significantly low and α is controlled by the soil type rather than the vegetation. Finally, in site #6 the species composition at the different stages of development varies significantly (pines to deciduous), which suggests that transition of species across ecosystem development may cause a reduction (instead of an increase) in η_{cz} .

4.2. Entropy Production Within the Critical Zone $\sigma_{cz,int}$

In this section we examine the production of entropy associated with the internal processes in the CZ ($\eta_{cz,int}$), and analyze whether it shows a similar trend as η_{cz} . We observed that η_{cz} is connected with the total destruction of exergy in the CZ. This destruction in turn is connected to the transformation of SW radiation to other forms of energy that is directly linked to α . It has been observed that more developed ecosystems tends to reduce the albedo resulting in a higher η_{cz} (Figure 5). Figure 6 shows the fraction of the transformed SW radiation that is actually captured through photosynthesis. It can be seen that this fraction is fairly low ($\approx 2\%$). Figure 6 also shows the ratio $\eta_{cz,int}/\eta_{cz}$ for those sites where there is at least one year of information available to compute both η_{cz} and $\eta_{cz,int}$. We observe that this ratio is close to 2-3%, which suggests that about 97-98% of the exergy that is destroyed in the CZ (Equation 11) is due to an instantaneous and irreversible transformation of SW radiation at the top of the CZ ($\sigma_{cz,rad}$). Therefore, as ecosystems mature, they reduce α and increases σ_{cz} , and they become more effective to destroy exergy. However, only a small fraction of this exergy that

is destroyed occurs internally to provide work and sustain different processes within the CZ.

Figure 7 shows the energy balance within the CZ and $\eta_{cz,int}$ for 16 sites where there is available information to compute $\eta_{cz,int}$ for at least a year. We observe that E_Q is significant and represents the most prominent source of energy that is absorbed by the CZ. In those sites where information of $E_{Q,G}$ is available we are able to differentiate the fraction of incoming heat fluxes that are related to $E_{Q,G}$ and $E_{Q,A}$. The bars on the right in Figure 7 shows $\eta_{cz,int}$ and the respective components following Equation 9. There are important facts that should be highlighted. First, there is an important fraction of $\eta_{cz,int}$ that results from the fluxes of heat (η_Q). Although the net annual storage of energy due to heat fluxes is negligible, there are differences in temperature between the incoming and outgoing fluxes that result in production of entropy. In particular, these patterns are more critical in sites experiencing a hot semi arid climate (Bsh) such as site #24 (Table 1) where the gradients in temperature throughout the day in the CZ result in a significant η_Q (See Figure 8). Second, there is also an important production of entropy associated with biological components (η_{bio}). Although the incoming fluxes of energy linked to photosynthesis are considerably lower than those of heat, η_{bio} becomes significant because it involves the absorption of SW radiation (with low entropy) and a further release of heat through respiration. In particular, η_{bio} is more prominent in site #19 located in the tropics where the photosynthetic rate is significant.

4.2.1. Dynamics of $\sigma_{cz,int}$ Over Time

Figure 9 shows five different sites where there is available information to compute $E_{cz,in}$ and $\eta_{cz,int}$ at different stages of ecosystem development. Figure 9a,b,c and d shows $E_{cz,in}$, dE_{cz} , dE_{cz} , and $\eta_{cz,int}$, respectively across different stages of ecosystem development. The dynamics of $\eta_{cz,int}$ are controlled by a trade off between η_{bio} and η_Q . In the following we further analyze these two components independently.

Dynamics of η_{bio}

Analysis of the data recorded in site #20 (Figure 9 I.) shows that η_{bio} is higher in the more developed stages. However in sites #23 (Figure 9 II.), #6 (Figure 9 IV.), and #24 (Figure 9 V.) η_{bio} tends to be lower in the more developed stages. In site #29 (Figure 9 III.) the only site where more than two points with reliable information is available, we observe that

442 η_{bio} fluctuates across different stages following the dynamics observed in the
443 respiration fluxes.

444 Note that η_{bio} relies in the transformation of biochemical energy stored
445 as reduced carbon (with low entropy) into heat (with higher entropy) (see
446 Equation 9). This process is induced by oxidation of stored biochemical
447 energy through respiration. As a result, η_{bio} is strongly regulated by respira-
448 tion fluxes. In Figure 9 we observe that in the more mature ecosystems the
449 storage of energy $dE_{\text{cz,pho}}$ increases. This storage refers to photosynthetic
450 compounds of reduced carbon with low entropy (high exergy), which sug-
451 gests that exergy tends to increase in the more developed stages. However,
452 increase of $dE_{\text{cz,pho}}$ is associated with lower respiration fluxes that in turn
453 hinders η_{bio} . In the end, we observe that in the more developed stages there
454 are higher photosynthetic fluxes ($E_{\text{sw,pho}}$) but there is a preferential trend
455 to increase the storage instead of respiring the entire input biomass, and as
456 a result there is no clear pattern for η_{bio} .

457 Because η_{bio} relies on respiration, η_{bio} could be higher in stages with lower
458 photosynthetic rates if the fluxes of respiration are significant. This pattern
459 is observed in site #6 (Figure 9 II.b and d), and site #24 (Figure 9 V.b
460 and d.) where η_{bio} is higher in the less developed stages and the fluxes of
461 photosynthesis are lower, but the fluxes of respiration are higher and are
462 maintained at the expense of exergy that had been stored previously.

463 From the information analyzed in Figure 9 we observe three consistent
464 patterns across the different stages of ecosystem development:

- 465 - $E_{\text{sw,pho}}$ tends to increase in the more developed ecosystems, with higher
466 photosynthetic fluxes.
- 467 - $dE_{\text{cz,pho}}$ tends to increase in the more developed ecosystems, with higher
468 exergy stored.
- 469 - There is no clear pattern for η_{bio} with the development stage.

470 *Dynamics of η_Q*

471 Figure 9d shows η_Q at five locations where it is possible to compare η_Q
472 during different stages of ecosystem development. In order to provide a fair
473 comparisson, η_Q reported in Figure 9d corresponds to computations per-
474 formed over a common period of time with available records to estimate η_Q
475 at all the different stages of development that are compared within a site.

476 We observe that η_Q tends to decrease in the more developed stages as in sites
 477 #6, #20, #23, and #29. In site #24 we do not observe significant differences
 478 in η_Q between the two stages that are compared. As mentioned above η_Q
 479 is function of the net heat flux into CZ and the gradients in temperature at
 480 which the incoming and outgoing heat fluxes occur. In turn, these variables
 481 are regulated by the released of LE and H fluxes from the surface. Higher
 482 LE and H fluxes enhance the dissipation of heat from the CZ and therefore
 483 they hinder the heat flux that is absorbed by the CZ. We observe that the
 484 variation of η_Q was inversely proportional to the emission of LE and H fluxes.

485 5. Conclusions

486 In this study we have recognized different formulations for the produc-
 487 tion of entropy that have been conceptualized in previous studies and are
 488 associated with different scales and processes in the Earth's Critical Zone
 489 (CZ):

- 490 • η_{cz} is the total production of entropy including all the exchange fluxes
 491 reaching and leaving the CZ, and is regulated by the transformation
 492 of shortwave (SW) radiation to other forms of energy. Around 97%
 493 of η_{cz} is due to an instantaneous transformation of SW at the surface
 494 ($\eta_{cz,rad}$), and as a result η_{cz} is enhanced by the amount of incoming SW
 495 radiation and is mainly controlled by the albedo of the land surface.
- 496 • η_{bio} refers to the production of entropy due to biological processes, and
 497 is associated with the absorption of shortwave (SW) radiation in chem-
 498 ical compounds and its further dissipation in the form of heat after
 499 respiration. η_{bio} is regulated in most part by respiration because it is
 500 the process that triggers the conversion of chemical energy with low
 501 entropy to heat with higher entropy. We observe that higher photosyn-
 502 thetic fluxes do not necessarily imply higher η_{bio} if there is significant
 503 storage of photosynthetic products that hinders respiration. In addi-
 504 tion, as pointed in *Volk and Pauluis (2010)* the highest η_{bio} will occur
 505 during a disturbance such as a fire where the energy stored in chemical
 506 compounds will be transformed to heat in a short period of time.
- 507 • η_Q refers to the production of entropy due to fluxes of heat, and is
 508 related to incoming and outgoing heat fluxes that occur at different
 509 temperatures. Therefore, η_Q is regulated by the magnitude of the heat
 510 fluxes and the gradients in temperature that occur during these fluxes.

- $\eta_{cz,int}$ refers to the production of entropy due to internal processes by considering only the energy that is absorbed, $\eta_{cz,int} = \eta_{bio} + \eta_Q$.

We observed different patterns in the entropy production computed from these formulations. Although all these formulations refer to entropy production they include different processes and refer to different scales of dynamics. Therefore, the conclusions or hypotheses that are extracted from these formulations should be considered and analyzed independently.

In this study we have made an attempt to quantify the production of entropy in the CZ with information recorded in FLUXNET towers. We have taken advantage of the data recorded in the Ameriflux Network to quantify the production of entropy in different climates and at different stages of ecosystem development. Based on the results obtained in this study we did not find a clear evidence that supports a maximization of entropy production in more vegetated areas or an increment across the different stages of development, for any of the entropy production formulations that were considered:

- (i) We computed the productions of entropy in different ecosystems and climates. On the one hand, when the production of entropy including all the energy fluxes (η_{cz}) was compared we observed that different ecosystems with rather different dynamics of energy dissipation could attain similar η_{cz} . This result is similar to previous findings reported by *Volk and Pauluis* (2010) where rather different atmospheric conditions could lead to the same entropy production. In fact, we observed that η_{cz} was highest in the arid and semi arid climates. This is contrary to intuition and the reason is because these ecosystems receive higher incoming SW radiation (less clouds) and dissipate the energy in the form of LW instead of heat (sensible or latent) that enhance the production of entropy. This in turn suggests that dry ecosystems with little vegetation could have a significant production of entropy because they are receiving more SW radiation, and using LW (less latent heat) as a main alternative to dissipate the incoming fluxes of energy. These results disclaim previous studies suggesting that vegetation is a major evidence for the Maximum Entropy Production Principle for macroscopic systems (ModMEPP) because they enhance the production of entropy. On the other hand, when the production of entropy including only the energy fluxes absorbed within the CZ were considered we observed that there is a production of entropy from heat (η_Q) and photosynthetic (η_{bio}) fluxes at all the sites, but their magnitudes vary according to the type of ecosystem and climate. For instance, in

548 site #19 (br-sa) located in the Amazon η_{bio} was dominant, while in dessert
 549 ecosystems such as in site #24 (us-se) η_{Q} was dominant. These patterns
 550 reflect only the presence of vegetation. As expected η_{bio} will be higher in
 551 systems where photosynthetic fluxes are more prominent. Similarly, in the
 552 absence of vegetation (lower latent heat) there is a higher heat absorbed by
 553 the system that in turn enhances η_{Q} . However, there are no clear patterns
 554 for the total internal entropy production ($\sigma_{\text{cz,int}} = \sigma_{\text{bio}} + \sigma_{\text{Q}}$) as different
 555 ecosystems with rather different configurations could attain similar values of
 556 $\sigma_{\text{cz,int}}$.

557 (ii) We also analyzed the production of entropy across different stages of
 558 ecosystem development. In a previous study *Holdaway et al.* (2010) com-
 559 pared η_{cz} across different stages of development in the Amazon and found
 560 that η_{cz} tends to increase in the more developed stages. They claimed these
 561 dynamics support ModMEPP because the ecosystems were converging to-
 562 wards a higher production of entropy. Here, we analyzed η_{cz} across different
 563 stages of development in nine sites exposed to different climates. We ob-
 564 served the surface albedo tends to reduce in the most developed stages and
 565 therefore η_{cz} tends to increase in the more developed stages as suggested by
 566 *Holdaway et al.* (2010). However, we found these dynamics do not hold in
 567 three of the nine sites analyzed where the albedo did not increase in the
 568 more developed stages. This suggests that η_{cz} do not always increase in the
 569 more developed stages as claimed by *Holdaway et al.* (2010). The patterns
 570 for σ_{bio} and σ_{Q} across different stages of development are even less clear. On
 571 the one hand, σ_{bio} varies in time following dynamics in respiration and pho-
 572 tosynthesis. We observed that more developed ecosystems tend to increase
 573 the photosynthetic flux but also they increase the storage of photosynthetic
 574 products. This pattern supports the maximum exergy storage production
 575 principle (*Mejer and Jorgensen*, 1979). However, increase in storage comes
 576 with the cost of hindering respiration that in the end results in no clear pat-
 577 tern for σ_{bio} , which can increase or decrease during the different stages of
 578 development. These dynamics suggest that ModMEPP in the light of σ_{bio} is
 579 not valid for ecosystem development. On the other hand, we observed that
 580 σ_{Q} tends to reduce in the more developed stages because less amount of heat
 581 is going into the CZ, which is opposite to ModMEPP.

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Figure 1: Schematic of the Critical Zone (CZ) showing different entropy productions that are examined in this study. The control volume of the CZ is considered as an imaginary boundary delineated by the footprint of the FLUXNET tower. Horizontal and bottom transfers of heat (i.e., $E_{Q,hor}$ and $E_{Q,bot}$) are neglected. The CZ receives an important source of energy (E_{in}) in the form of shortwave (SW) and longwave radiation (LW). A significant fraction of this energy is dissipated instantaneously in different forms such as SW and LW radiation, latent heat (LE), and sensible heat (H). Transformation of SW radiation to heat accounts for an instantaneous production of entropy at the top of the CZ (σ_{CZ}). A small fraction of the incoming E_{in} is absorbed by the CZ in the form of heat and chemical compounds through photosynthesis ($E_{CZ,in}$). The dissipation of $E_{CZ,in}$ in the form of heat results in a production of entropy that is directly related to internal processes within the CZ ($\sigma_{CZ,int}$). On one hand, the absorption of SW radiation through photosynthesis and further release as heat through respiration produces the most significant entropy production in living components (σ_{bio}). On the other hand, the absorption and dissipation of heat fluxes within the CZ also produce entropy and is denoted as (σ_Q). The inset figure shows a schematic representation of σ_{CZ} , $\sigma_{CZ,int}$, σ_{bio} , and σ_Q .

Figure 2: Map of the Ameriflux sites selected for this study. The background shows the Kö-Geiger climate classification according to *Kottek et al.* (2006).

Figure 3: Top panel shows (a) the relationship between the total production of entropy by the Critical Zone (CZ) in a year (η_{cz}) and the incoming SW radiation ($E_{SW,in}$) for different sites with available information to compute η_{cz} . In this figure we differentiate between grasses (squares), crops (triangles), and forest (circles). In addition, we grouped the sites based on the albedo and perform the fitting for these groups separately. Bottom panel shows (b) the relationship between η_{cz} and the effective temperature of the CZ (T_{cz}).

Figure 4: Energy balance (first two bars) and total production of entropy in the Critical Zone in a year (η_{cz}) (3rd bar) based on records from selected FLUXNET towers in different locations. The numbers above the bars represent the Ameriflux tower as displayed in Figure 2 and listed in Table 1. The code below bars represents the climatic classification as displayed in Figure 2.

Figure 5: Patterns of η_{cz} across different stages of ecosystem development for nine sites where information at all the different stages of development is available. In most cases these records were not available for an entire year. Thus entropy production is presented per day instead of year, and represents the averaged daily entropy generated during the period with available data. Data in this figure is presented in Section 2 in the Online Supplement.

Figure 6: **(Left)** Ratio between the internal ($\eta_{cz,int}$) and total (η_{cz}) entropy production over a year time period (red dots), and **(Right)** ratio between the photosynthetic flux ($E_{SW,pho}$) and the energy flux of incoming shortwave radiation that is transformed to other forms of energy (including longwave radiation, photosynthesis, and heat, blue dots). This figure includes only sites where it is possible to compute both σ_{cz} and $\sigma_{cz,int}$ for at least one year. See Table 1 and Figure 2 for the specifics of the locations indicated.

Figure 7: Energy balance (first two bars) and the production of entropy within the Critical Zone ($\sigma_{cz,int}$) (3rd bar), including only the fluxes of energy that are absorbed by the CZ. The numbers above the bars represent the AmeriFlux tower as displayed in Figure 2 and listed in Table 1. The code below the bars represents the climatic classification as displayed in Figure 2.

Figure 8: Mean annual diurnal temperature at the Critical Zone surface (T_{cz}) computed with Boltzmann Equation from outgoing longwave (LW) radiation records (Equation 14). This figure shows the diurnal temperature for the sites displayed in Figure 7. However, only those sites with available information of outgoing LW radiation are displayed. In particular, we highlight the diurnal patterns in site #24 (us-se) where the amplitude in the mean diurnal temperature is significantly higher when compared with all the other sites. Higher amplitude in surface temperature in site #24 allows a higher production of entropy in the form of heat (η_q) as shown in Figure 7.

Figure 9: Patterns of (a) incoming energy absorbed by the Critical Zone (CZ), (b) rate of change of energy within the CZ (dE_{CZ}), (c) rate of change of entropy within the CZ (dS_{CZ}), and (d) internal entropy production within the CZ ($\eta_{CZ,int}$). There are five different rows - with one row for each independent site- showing the respective dynamics where information at all the different stages of ecosystem development is available. In most cases these records were not available for an entire year. Thus entropy production is presented per day instead of year, and represents the averaged daily entropy generated during the period with available data.

Table 1: List of Ameriflux sites used in this study. See Figure 3 for the specific locations of these sites and the legends of climatic regions.

Number	Code	Location	Climate	Used as *	Number	Code	Location	Climate	Used as *
1.	us-sgp	US-OK	Cfa	1	2.	us-aud	US-AZ	Bsh	1
3.	us-bo	US-IL	Dfa	1	4.	us-bkg	US- SD	Dfa	1
5.	us-br	US-IA	Dfa	1	6.	us-dk	US- NC	Cfa	1,2 a,b
7.	us-ib	US-IL	Dfa	1	8.	us-fm	US- AZ	Bsh	a
9.	us-skr	US-FL	Aw	1	10.	us-dix	US-NJ	Cfa	1
11.	us-fpe	US-MT	Bsh	1	12.	us-fr	US-TX	Cfa	1 a
13.	us-gle	US-WY	Bsk	1	14.	us-goo	US-MS	Cfa	1
15.	us-wrc	US-WA	Dfb	1	16.	us-wkg	US-AZ	Bsh	1
17.	us-los	US-WI	Dfb	1	18.	us-mrf	US-OR	Csb	1
19.	br-sa	BR-PA	Aw	2	20.	us-me	US-OR	Csb	2 a,b
21.	us-moz	US-MO	Cfa	1,2	22.	us-mms	US-IN	Dfa	2
23.	us-nc	US-NC	Cfa	2 a,b	24.	us-se	US-AZ	Bsh	1,2 a,b
25.	us-shd	US-OK	Cfa	1	26.	us-slt	US-NJ	Cfa	1
27.	us-so	US-CA	Csa	2	28.	us-ton	US-CA	Csb	2
29.	ca-ns	CA-MB	Dfc	2 a,b	30.	us-umb	US-MI	Dfb	a
31.	us-var	US-CA	Csa	2	32.	us-wbw	US-TN	Cfa	2
33.	us-wlr	US-KS	Cfa	1	34.	us-wcr	US-WI	Dfb	2
35.	us-bar	US-NH	Dfb	1,2	36.	us-an	US-AK	Dfc	a

*1. Used to compute η_{cz}
*2. Used to compute $\eta_{cz,int}$
*a. Used to compute η_{cz} for at least two stages of development
*b. Used to compute $\eta_{cz,int}$ for at least two stages of development

Table 2: List of parameters used for the computation of entropy.

Property	Symbol	Units	Magnitude
Sun Temperature	T_{sun}	K	5760
Stefan-Boltzmann Constant	λ	$\text{Wm}^{-2}\text{K}^{-4}$	5.67×10^{-8}
Specific Biomass Enthalpy	h_{BIO}	$\text{J } \mu\text{mol}^{-1}$	¹ 0.506
Critical Zone Emissivity	ε	-	² 0.95
¹ <i>Nikolov (1995)</i> ; ² <i>Holdaway et al. (2010)</i> , <i>Campbell and Norman (1998)</i>			

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