A Thermodynamic Approach for Assessing Agroecosystem Sustainability

Ferdouz V. Cochran^{1,*}, Nathaniel A. Brunsell², Andrew E. Suyker³

Abstract

By revisiting theoretical concepts in biogeography and the importance of thermodynamic laws in biosphere-atmosphere interactions, ecological sustainability in agricultural systems may be better defined. In this case study, we employed a multidisciplinary methodology for exploring agroecosystem sustainability by using eddy-covariance data to compute thermodynamic entropy production (σ) and relate it to water, energy and carbon cycling in croplands and grasslands of the Central US. From 2002 to 2012, the biophysical metric of σ was compared across AmeriFlux sites, each with site-specific land management practices of irrigation, crop rotation, and tillage. Results show that σ is most correlated with net ecosystem exchange (NEE) of carbon, and when cropland and grassland sites are close to being carbon neutral, σ values range from 0.51 to 1.0 WK⁻¹m⁻² for grasslands, 0.81 to 1.0 WK⁻¹m⁻² for rainfed croplands, and 0.81 to 1.1 WK⁻¹m⁻² for irrigated croplands. Ir-

*Corresponding Author. Tel.: +1 808 984 3709

Email address: ferdouz@hawaii.edu (Ferdouz V. Cochran)

¹Sustainable Science Management, University of Hawai'i Maui College, 310 W. Ka'ahumanu Ave, Kahului, HI 96732-1617, USA

²Department of Geography and Atmospheric Science, University of Kansas, 1475 Jayhawk Blvd, Lawrence, KS 66045-7613, USA

³School of Natural Resources, University of Nebraska, 3310 Holdrege Street, Lincoln, NE 68583-0968, USA

irrigated maize stressed by hydrologic and high temperature anomalies associated with the 2012 drought exhibit the greatest increase in σ , indicating the possibility of decreased sustainability compared to rainfed croplands and grasslands. These results suggest that maximizing carbon uptake with irrigation and fertilizer use tends to move agroecosystems away from thermodynamic equilibrium, which has implications for ecological sustainability and greenhouse gas (GHG) mitigation in climate-smart agriculture. The underlying theoretical concepts, multidisciplinary methodology, and use of eddy-covariance (EC) data for biophysical indicators in this study contribute to a unique understanding of ecological sustainability in agricultural systems.

Keywords: biophysical indicators, climate-smart agriculture, drought, irrigation, thermodynamic entropy, AmeriFlux

1. Introduction

The role of thermodynamics is inherent in the fields of ecology and physical geography, exemplified through abiotic-biotic or spatial interactions. Discussions concerning non-equilibrium dynamics and irreversible processes are seen in biogeography, climatology, geomorphology, and landscape ecology (Brunsell et al., 2011; Holdaway et al., 2010; Perry, 2002; Phillips, 1999, 2008; Smith, 2005; Steinborn and Svirezhev, 2000; Svirezhev, 2000) and are applicable to all natural and anthropogenic landscapes, including agricultural systems on varying temporal and spatial scales. In this study, we tie together thermodynamic laws, theories of complex ecosystem dynamics, and resilience theory to explore biophysical aspects of sustainability in agroecosystems. We propose that higher thermodynamic entropy production (σ)

indicates higher stress and a move away from thermodynamic equilibrium and adaptive potential.

1.1. Thermodynamics and ecosystem evolution

Thermodynamic entropy has been explored for evaluating sustainability in various disciplines including industrial ecology, resource economics, and mechanical engineering (Gutowski et al., 2009; Hermanowicz, 2007; Krotscheck, 1997; Liao et al., 2012; McMahon and Mrozek, 1997). Different frameworks for evaluating systems and subsystems have been proposed, but complexities in applying these frameworks remain. The major difficulty in conducting and interpreting studies, manifesting in numerous debates and misunderstandings across disciplines and between Nobel Laureates (Gnaiger, 1994), relates to the terminology used in describing the systems studied and in identifying spatial and temporal boundaries. It is through identification of these system boundaries and improved understanding of abiotic-biotic or spatial interactions that the field of physical geography is ideally equipped to contribute to the future of sustainability science.

Based on the laws of thermodynamics, the physical boundaries for interactions between the Universe, the Earth and its ecosystems can be outlined as follows: the Universe is an isolated system that does not have inputs and outputs of energy; the Earth is a closed system that exchanges energy with the Universe but, for our purposes, not matter; and ecosystems are open systems exchanging both energy and mass within the Earth system. The second law of thermodynamics helps us understand ecosystems as open systems with dissipative structures far from thermodynamic equilibrium that evolve to maintain a high level of local organization resulting in a production

of entropy (Schneider and Kay, 1994). Schneider and Kay (1994) argue that ecosystems, and the species that thrive within them, develop an increasing ability to degrade incoming solar radiation, which increases the total dissipation of heat from that ecosystem. This part of energy that is no longer available for work is also known as thermodynamic entropy.

Thermodynamic entropy results from non-equilibrium thermodynamic processes occurring in a system. It is produced by fluxes of heat, matter, and momentum and related to gradients of temperature, pressure, concentration, etc., which maintain systems away from equilibrium. Within the closed Earth system, solar radiation creates a large influx of energy and a gradient that open ecosystems will strive to reduce through all available chemical and physical processes. Ecosystems that are less stressed tend to exhibit a greater ability to degrade solar energy and reduce gradients than stressed ecosystems (Schneider and Kay, 1994).

From an ecosystem development perspective, entropy production may be at a maximum during three developmental stages due to: 1) early successional growth and rapid colonization by fast growing species, 2) sustained production during maturity of longer-growing species, and 3) extended maturity or delay of retrogression by stress-tolerant species (Holdaway et al., 2010). During the growth stage, species with rapid population growth may have a higher initial entropy production than slower growing species. The temporal and spatial scales of biogeochemical and biogeophysical processes involved add to the complexity of evaluating the maximum entropy production (MEP) hypothesis, which suggests that the maximum rate of entropy production in a system occurs when the influence of vegetation productivity

on land surface albedo and the effect of solar radiation absorption on evapotranspiration result in maximizing the energy flux or dissipation from the system (Kleidon, 2009).

Changes in overall entropy of a system result from all the entropy production and entropy transfer processes associated with that system. Brunsell et al. (2011) quantified the overall thermodynamic entropy budget of a land surface, calculating both entropy production and entropy transfer, and found that a higher vegetative fraction results in increased entropy production and a decreased rate of change in overall entropy. It is important to note that the decrease in the overall entropy budget is related to the decrease of the Bowen ratio (the ratio of sensible to latent heat fluxes) or the increase of entropy transfer associated with latent heat flux during the daytime and sensible and soil heat fluxes during the nighttime. Brunsell et al. (2011) also applied their methodology to data from three eddy covariance (EC) flux towers in northeastern Kansas with different land cover types and land use management practices. Results suggest that the overall ecosystem entropy is related most to net radiation at the land surface, and that *entropy production* is driven by land cover and land management.

Land cover disturbance plays an integral role in the structure of ecosystems at multiple scales creating a mosaic where there are interactions between the heterogeneous surface properties or patchiness of the landscape and ecological processes (Perry, 2002). Phillips (1999, 2008) outlines the thermodynamic principles behind numerous theories of ecosystem structure, function, and development, where evolution itself can be thought of as a fundamental irreversible process. Phillips (2008, pg. 56) states that “perhaps

the most robust theory of evolution at the ecosystem and biospheric scale” is one presented by biogeographer Charles H. Smith, an expert on Alfred Russell Wallace.

Smith (2005) interprets Wallace’s view of evolution as one based on spatial interactions between species, versus adaptations within species. In Wallace’s perspective, Smith argues, there is no process of adaptation only the result of being adapted. In this paradigm, evolution of spatial interactions occurs between abiotic and biotic components in a systems framework, which contains both negative and positive feedback loops (Smith, 1986, 2005). “Adaptive structures” are part of a negative feedback loop where “deviation-countering” processes are maintained at the organismal level through biogeochemical cycling and dissipation of energy, hence the production of entropy. “Adaptive potential” and the selection of traits at the ecosystem level entails a positive feedback loop where “deviation-amplifying” processes occur and spatial interactions evolve. The divergence associated with evolutionary change and adaptive potential is a return toward instead of a move away from thermodynamic equilibrium. Using theoretical models, Kostitzin (1934) also described evolution as a series of unlikely events opposing the increase of thermodynamic entropy. Consequently, the energy and directionality that exist in working against change in the negative feedback loop may increase thermodynamic entropy production, and the randomness associated with genetic mutations and probabilistic spatial interactions related to evolutionary change in the positive feedback loop will correspond with lower entropy production (Phillips, 2008; Smith, 1986, 2005).

Organisms and ecosystems may also evolve in directions of lower stress

(Smith, 1986, 1989, 2005). If we consider stress as spatial gradients related to the negative feedback part of the evolution framework described above, more intense gradients will require more work to maintain “deviation-countering” processes resulting in higher entropy production. Thus, thermodynamic entropy production can be an indicator of higher stress where the system is maintained in the negative feedback loop moving away from thermodynamic equilibrium versus entering the positive feedback loop where “deviation-amplifying” processes bring a system back toward equilibrium. It is important to recognize that living systems do not actually reach thermodynamic equilibrium because they are continuously exchanging energy and matter with their environments as open systems, as previously explained. However, it is the move back toward thermodynamic equilibrium that is crucial to Wallace’s evolutionary theory, the result of adaptation, and the metric we propose for evaluating agroecosystem sustainability.

Anthropogenic inputs of fertilizer and irrigation in agricultural systems can force organisms to remain in the negative feedback loop, creating larger gradients with their surroundings corresponding to higher stress and entropy production. Anthropogenic impacts on agroecosystems have previously been quantified with thermodynamic entropy metrics using data on agricultural inputs and outputs related to tillage, fertilization, pesticide use, harvest, etc. (Steinborn and Svirezhev, 2000; Svirezhev, 2000; Patzek, 2008). Energy inputs in agricultural systems can lead to an overproduction of entropy, and the greater the overproduction, the less sustainable a system is said to be (Steinborn and Svirezhev, 2000; Patzek, 2008).

1.2. Biophysical sustainability

With compounding pressures of a growing global population, increased food demand, and changing climatic conditions there is an urgent need to understand the geographic variability of sustainability in agricultural systems. Sustainability in agroecosystems has been defined as the maintenance of productivity over time despite socio-economic pressures and ecological constraints and disturbances (Altieri, 1987; Conway, 1985; Wezel et al., 2009). Recently, the Food and Agriculture Organization (FAO) of the United Nations (UN) has introduced a framework for the management of sustainable agroecosystems and livelihoods given anthropogenic climate change. In climate-smart agriculture, agricultural systems should sustainably increase agricultural productivity and income, build adaptation and resilience to climate change, and contribute to mitigation or removal of greenhouse gases (Lipper et al., 2010). Achieving climate-smart agroecosystems requires a high level of diversity in land cover and species composition, a focus on land-use interactions, and integrated landscape management at a landscape scale (Scherr et al., 2012).

While many still view the triple bottom line for sustainability as parallel pillars that must be addressed equally, Fischer et al. (2007a) prefer to see the ecological, social, and economic components of sustainability as a nested hierarchy. In this approach, ecological or biophysical considerations are primary, for all just societies (secondary) and economic prosperity (tertiary) must rely first on our Earth system. This framework is appropriate when examining sustainability on a global scale. For example, by evaluating our Earth’s energy budget, scientists have concluded that anthropogenic climate

change is a biophysical indicator that our Earth system is moving away from sustainability. In addition, Kleidon (2009) argues that it is useful to consider Earth’s entropy budget, since non-equilibrium thermodynamic entropy production is a measure of dissipative processes and may provide an estimate of climate sensitivity.

At anything less than a global scale, the challenge in evaluating sustainability becomes identifying appropriate spatial and temporal boundaries for the assessment of human-environment systems (Mayer, 2008). The identification of system boundaries is essential for acknowledging leakage effects where resource inflows may or may not be sustainable (Mori and Christodoulou, 2012), and legacy effects where human-environment couplings can vary from decades to centuries (Liu et al., 2007). In addition, the usefulness of sustainability metrics remain uncertain when they do not get at the underlying mechanisms or processes that move systems toward or away from sustainability.

In resilience theory, building and maintaining resilience through the adaptive cycle is an essential part of working toward long-term sustainability. The ability to continue adapting and changing yet remain within critical thresholds makes a system more resilient (Walker and Salt, 2012). Both a system’s resilience and its efficient use of resources/energy contribute to its sustainability (Patzek, 2008; Walker and Salt, 2012).

The adaptive structures in the negative feedback loop and the adaptive potential in the positive feedback loop from Wallace’s evolutionary theory can be combined with the adaptive cycle of resilience theory to relate thermodynamic entropy production, our proposed metric, to biophysical sustainability.

Evolutionary divergence or adaptive potential in the positive feedback loop is characterized by a return toward thermodynamic equilibrium. Hence, our theoretical definition of sustainability states that a move away from thermodynamic equilibrium with higher entropy production indicates less adaptive potential in an open agroecosystem, which corresponds to less resilience and sustainability. At the same time, higher entropy production signals the breakdown of more intense or persistent gradients corresponding to higher stress, which may indicate inefficient energy or resource use in agricultural management also indicating less sustainability.

1.3. Case Study

Given the need for a better understanding of the geographic variability of ecological sustainability in different land use management strategies, the increasing availability of EC tower data through AmeriFlux and other regional networks allows for empirical studies. The micrometeorological data from these networks enables computation of thermodynamic entropy production in ecosystems across the US and other parts of the world. Without the additional calculations related to anthropogenic inputs of energy (Svirezhev, 2000), the methodology provided by Brunsell et al. (2011) may facilitate the use of thermodynamic entropy for assessing sustainability. Therefore, this case study examines agroecosystems from the perspective of thermodynamics and evaluates the use of entropy production as a biophysical metric for agroecosystem sustainability across the geographic region of the Central US.

The overarching question of this case study is: How does thermodynamic entropy production (σ) as a theoretical measure of sustainability in agroecosystems relate to water and carbon cycling in the Central US? It is hypoth-

esized that: Agroecosystems that are stressed by hydrologic anomalies will exhibit increased thermodynamic entropy production indicating decreased sustainability. To test this hypothesis, thermodynamic entropy production is computed using net radiation and individual radiation terms from AmeriFlux site data in select croplands and grasslands in the Central US over a time frame including the extreme drought year of 2012. Variability of thermodynamic entropy production is then compared to changes in soil water content, energy partitioning indicated by the Bowen ratio, and net ecosystem exchange of carbon. While the need for a “standard environment” as a reference level for the evaluation of entropy production and sustainability is debatable (Hermanowicz, 2007; Krotscheck, 1997), we have chosen to include the Kansas grasslands as baseline ecosystems against which to compare entropy production in the Nebraska and Oklahoma agroecosystems.

2. Methods

2.1. AmeriFlux cropland and grassland sites

Thermodynamic entropy production was evaluated for six AmeriFlux sites in Kansas, Nebraska, and Oklahoma (Figure 1) with differences in land cover and land management practices. All sites are within the humid continental Köppen climate classification, though the Oklahoma site is sometimes categorized as humid subtropical. Table 1 provides a summary of site characteristics with average daytime hourly values for incoming solar radiation (Q_S , Wm^{-2}), entropy production (σ , $\text{WK}^{-1}\text{m}^{-2}$), soil water content (SWC , %), the Bowen ratio (β), and net ecosystem exchange of carbon (NEE , $\mu\text{mol C m}^{-2}\text{s}^{-1}$). Further description and land use histories of Kansas grassland sites

Figure 1: AmeriFlux tower locations (not to scale) for grassland and cropland sites in Kansas, Nebraska, and Oklahoma. Colorbar indicates mean hourly σ from monthly day-time (9am-4pm) averages across all years of available data at each site.

are given in Cochran et al. (2013). Details on the Nebraska cropland sites, which are within 1.6 km of each other, are outlined in Verma et al. (2005), and information on the Oklahoma cropland site can be found in Fischer et al. (2007b).

The data obtained at these sites and used in the analysis are from micrometeorological EC towers, which measure fluxes of energy, momentum, water, and carbon dioxide. The footprint of these towers can cover a longitudinal length of 100–2000 m depending on atmospheric conditions and sampling height (Baldocchi et al., 2001), which for this study is assumed to be 3 m at all sites. These specifications provide clear spatial boundaries

Table 1: AmeriFlux EC tower site characteristics, including site years available, International Geosphere-Biosphere Programme (IGBP) class, dominant vegetation, management, mean annual temperature (T), mean annual precipitation (PPT), and average hourly values between 9am-4pm across all available site years of incoming solar radiation (Q_S), entropy production (σ), soil water content (SWC), the Bowen ratio (β), and net ecosystem exchange (NEE).

Sites	ARM	KFS	KON	NE1	NE2	NE3
Years	2003-2012	2008-2012	2007-2012	2002-2012	2002-2012	2002-2012
IGBP Class	Cropland	Grassland	Grassland	Cropland	Cropland	Cropland
Dom Veg	Winter Wheat	C ₃ Grasses	C ₄ Grasses	Maize	Maize/Soy Rot*	Maize/Soy Rot
Management	Rainfed	Rainfed	Rainfed	Irrigated	Irrigated	Rainfed
	Till	5yr Burn/Mow	Annual Burn	Till/Cons Plow	Till/Cons Plow	No Till
Mean Annual PPT	600mm	937mm	835mm	839mm	861mm	697mm
Mean Annual T	15°C	13°C	13°C	11°C	10°C	10°C
Q_S (Wm^{-2})	492.213	448.182	474.511	456.094	462.057	452.909
σ ($WK^{-1}m^{-2}$)	1.072	1.097	1.126	1.169	1.140	1.110
SWC (%)	21.580	33.890	34.492	29.551	33.085	29.417
β	1.501	1.589	2.039	1.098	1.191	1.383
NEE ($\mu mol C m^{-2}s^{-1}$)	-2.204	-2.843	-3.670	-6.120	-5.376	-4.148

* From 2009 to 2012, crop rotation at NE2 changed to continuous maize.

in which sustainability can be evaluated for these ecosystems or agroecosystems. Long-term availability of observational data is a limitation in the broad application of this metric. Most EC tower sites only measure net radiation, which means that the incoming and outgoing shortwave and longwave radiation components have to be estimated using empirical formulations from the net radiation measurement in order to calculate the associated entropy production. Some EC tower sites, such as those selected for this study, measure all radiation terms individually and these data are preferable for calculating entropy production.

Level 2 standardized files with gaps were obtained at the AmeriFlux website (<http://ameriflux.ornl.gov/>) for the above described sites and available years from 2002-2012. Data with gaps were selected in order to eliminate potential errors associated with gap-filling. The reader is referred to the Summary Reports where information is available on percent available data for each variable by year (for example, availability of ARM variables can be found at ftp://cdiac.ornl.gov/pub/ameriflux/data/Level2/Sites_ByName/ARM_SGP_Main/with_gaps/ARM_SGP_Main_SummaryReport.htm). Outliers for all variables at all sites were removed above the 99th percentile and below the 1st percentile. For sites ARM, KFS and KON, half-hourly data were converted to hourly to match the hourly timescale of the NE1, NE2 and NE3 site data.

2.2. Thermodynamic entropy production

Following methodology from Brunsell et al. (2011), thermodynamic entropy production (σ) was calculated for each site across all available site years. Given Earth's energy budget, net radiation at the land surface (R_n ,

Wm^{-2}) is the balance between incoming and outgoing radiation that is partitioned into turbulent transport of sensible heat (H , Wm^{-2}) and latent heat (LE , Wm^{-2}) fluxes and heat conduction into the ground by the soil heat flux (G , Wm^{-2}):

$$R_n = Q_S + Q_{L,in} - Q_{L,out} = H + LE + G + \epsilon \quad (1)$$

where the absorbed solar radiation is represented by Q_S (Wm^{-2}) and the longwave radiation terms are represented by $Q_{L,in}$ (Wm^{-2}) for incoming and $Q_{L,out}$ (Wm^{-2}) for outgoing. A residual of the energy budget (ϵ) accounts for the energy terms that are not considered in the other fluxes, like photosynthesis, and the instantaneous rate of heating. The inclusion of this term is important because energy balance closure rarely occurs with EC measurements (Wilson et al., 2002).

Thermodynamic entropy production can be calculated using R_n or the individual radiation terms, when available. For this study, we computed σ from both R_n for all sites and from the individual radiation terms for all sites except KON, where there is only a net radiometer. To obtain σ using R_n , the incoming and outgoing shortwave and longwave radiation components are derived from the R_n measurement as outlined below. This requires invoking the Monin-Obukhov similarity theory from air temperature, heat flux, and local stability (Foken, 2006) to derive the surface temperature (T_{sfc} , K), which is the temperature at the land surface disregarding any directional aspect of solar radiation (Wu, 2010) and assumed to be identical to the aerodynamic temperature (T_o , K):

$$T_o = T_a + \frac{H}{\kappa \rho c_p u_*} \left(\ln \left(\frac{z-d}{z_m} \right) + \psi_H \right) \quad (2)$$

where T_a is the air temperature at the measurement height (z) assumed to be 3 m at all sites, κ is the von Karman constant (0.4), ρ is the air density, c_p is the specific heat capacity, u_* is the friction velocity, d is the displacement height (2/3 height of canopy), and z_m is the aerodynamic roughness length ((1/10) d). A stability correction ψ_H is applied for unstable atmospheric conditions:

$$\psi_H = -2 \ln \left(\frac{1 + (1 - 16(z/L))^{1/2}}{2} \right) \quad (3)$$

where L is the Obukhov length.

The longwave radiation from the atmosphere ($Q_{L,in}$, Wm^{-2}) is calculated from the measured air temperature (T_a , K) using the empirical formulation of Brutsaert (1975):

$$Q_{L,in} = 0.552e_a^{(1/7)} 5.67e^{-8} T_a^4 \quad (4)$$

where e_a is the actual vapor pressure in millibars.

The outgoing longwave radiation ($Q_{L,out}$, Wm^{-2}) is computed using the Stefan-Boltzmann Law with a constant surface emissivity assumed to be 0.95, and T_o assumed to be equal to T_{sfc} :

$$Q_{L,out} = 5.67e^{-8} 0.95 T_o^4 \quad (5)$$

The absorbed solar radiation (Q_S , Wm^{-2}) can then be computed as the difference between the measured R_n and the incoming and outgoing longwave

radiation:

$$Q_S = R_n + Q_{L,out} - Q_{L,in} \quad (6)$$

with a minimum value of zero. Although the use of the aerodynamic temperature as the surface temperature introduces some complications, the two temperatures are related (Stewart et al., 1994). Any errors in the calculation of the radiation terms will propagate to the calculations of σ .

Values for Q_S and $Q_{L,in}$ that were either derived from R_n as outlined above or measured by a four-way radiometer, were then employed to calculate σ . Entropy production associated with solar radiation (σ_{Q_S} , $\text{WK}^{-1}\text{m}^{-2}$) is computed from the fluxes per unit area by:

$$\sigma_{Q_S} = Q_S \left(\frac{1}{T_{sfc}} - \frac{1}{T_{sun}} \right) \quad (7)$$

where the assumed temperature of 5780 K for the sun (T_{sun}) is constant and T_{sfc} is the same as T_o . The entropy production associated with the absorption of longwave radiation and degradation to heat (σ_{Q_L} , $\text{WK}^{-1}\text{m}^{-2}$) is:

$$\sigma_{Q_L} = Q_{L,in} \left(\frac{1}{T_{sfc}} - \frac{1}{T_{atm}} \right) \quad (8)$$

where the temperature of the atmosphere (T_{atm} , K) is computed by inverting the Stefan-Boltzmann law. To arrive at total entropy production (σ , $\text{WK}^{-1}\text{m}^{-2}$), the entropy terms for solar and longwave radiation are summed:

$$\sigma = \sigma_{Q_S} + \sigma_{Q_L} \quad (9)$$

Entropy production related to mass fluxes of water and carbon are not directly considered in these calculations. In addition, this study focuses only

on thermal entropy production and omits the contribution of radiation pressure, which constitutes one third of the radiative entropy production factor of 4/3 (Goody and Abdou, 1996). A complete review of the entropy budget can be found in (Peixoto et al., 1991).

For all available Level 2 data (with gaps) at each AmeriFlux site between 2002 and 2012, hourly values of measured variables (u_* , T_a , H , LE , G , R_n , Q_S , $Q_{S,out}$, $Q_{L,in}$, $Q_{L,out}$, relative humidity (RH , %), pressure (P , kPa), vapor pressure deficit (VPD , kPa), SWC , and NEE) and calculated variables (ρ , L , ψ_H , T_{atm} , and T_o or T_{sfc}) were averaged across all days in a month to provide a daily cycle for each month. Only seven monthly diurnal cycles were missing across all 54 site years due to missing data and were, therefore, omitted from the analysis.

Thermodynamic entropy production was calculated from the average monthly diurnal cycle from R_n and from individual solar and longwave radiation terms at each site except KON, and the respective values of σ were compared (Figure 2). Since correlations were high, the analysis employed values of σ calculated from R_n in order to include the KON site years. Values from daylight hours of 9:00 a.m. to 4:00 p.m. were selected to analyze σ across sites and within land cover type with variables of SWC , β as an indicator of energy partitioning, and NEE of carbon. These monthly daytime averages, initially for all available years of data at each site and then for 2008-2012, define the temporal boundaries of this sustainability assessment.

Regression tree analysis was used to provide increased understanding of processes and thresholds contributing to entropy production. Using the `rpart` library in R (Therneau et al., 2010), regression models were built recursively

Figure 2: Correlations between σ from R_n and σ from individual radiation terms obtained by a four-way radiometer for (a) ARM, (b) KFS, (c) NE1, (d) NE2, and (e) NE3 using average monthly daytime (9am-4pm) values for all years available at each site.

and represented as binary trees. The regression trees were pruned with the 1 - standard error (SE) rule of Breiman et al. (1984), where the largest value of the complexity parameter (cp) with a cross-validation relative error (xerror) within one standard deviation of the minimum is selected. This value can be identified using the plotcp function and selecting the first cp value that lies below the 1 - SE dashed line. Mean standard error (MSE) values at each node were computed and used to evaluate the error in trees associated with entropy production for rainfed and irrigated cropland sites and grassland sites.

3. Results

Results indicate varying levels of thermodynamic entropy production and sustainability at each site related to interannual, seasonal, or extreme changes in water and carbon cycling given specific land cover and land management practices. The mean value of all monthly daytime observations for all site years is shown in Figure 1. These values indicate that σ varies from lowest to highest at ARM, KFS, NE3, KON, NE2, and NE1. Although this could be related to a latitudinal gradient of incoming solar radiation, it is opposite of what is expected (Peixoto et al., 1991). This is a first indication that σ is not solely determined by incoming solar radiation, but also by how the land surface or vegetation dissipates that energy based on other natural and anthropogenic inputs.

Across the entire time series, the most negative mean value of NEE indicating the largest overall carbon sink occurs at the NE1 site where there is the greatest mean value of σ (Table 1). Likewise, the largest mean value

of NEE or the site which is the smallest carbon sink or greatest carbon source is the ARM site where the mean value of σ is at its lowest. Other values in Table 1 indicate that the rainfed cropland sites of ARM and NE3 have the lowest mean values of SWC , followed by the irrigated cropland sites of NE1 and NE2, and then the grassland sites of KFS and KON with the highest SWC . β values give us an indication of energy partitioning between H and LE at each site. All mean β values are above 1, which signifies that on average H is higher than LE for all sites throughout the daytime hours of the years examined. However, cropland sites have lower β values than grassland sites, indicating the greater role of LE throughout the year and especially during the growing season.

To further explore the differences between sites on a monthly scale, we examined time series of diurnal cycles of daytime hours for years 2008-2012 (Figure 3). The dashed red lines identify key values for each variable which help distinguish between diurnal, monthly, seasonal and annual patterns amongst sites. For example, σ values above $1.5 \text{ WK}^{-1}\text{m}^{-2}$ (75th percentile) occur primarily in the summer months at all sites. SWC at irrigated cropland and grassland sites rarely falls below a value of 25% (25th percentile) with the exception of years 2011 and 2012 for rainfed cropland and grassland sites. As outlined above, whenever β is below 1, LE is greater than H which means that the energy partitioning at the surface is favoring dissipation of heat through LE . The opposite is true when β values are above 1. Similarly, values of NEE above 0 indicate a carbon source, while values below 0 indicate a carbon sink.

Compared to irrigated cropland sites, rainfed cropland sites ARM and

Figure 3: Monthly average daytime (9am-4pm) values of σ ($\text{WK}^{-1}\text{m}^{-2}$), SWC (%), β , and NEE ($\mu\text{mol C m}^{-2}\text{s}^{-1}$) for 2008-2012 at rainfed cropland sites (a) ARM and (b) NE3, irrigated cropland sites (c) NE1 and (d) NE2, and grassland sites (e) KFS and (f) KON.

NE3 have lower σ , higher β values, and larger NEE values making them smaller carbon sinks. The ARM site is the most arid with the lowest SWC and β values that rise throughout most months of the 2012 drought. At NE3, the NEE values vary according to the maize-soybean rotation from year to year. Across rainfed cropland and grassland sites, the drought of 2012 is seen in lower SWC values. The irrigated cropland sites maintain SWC values around 25% in 2012, but the σ values for NE1 and NE2 are especially elevated during this time.

To determine the role of the 2012 drought on σ at each site, Table 2 outlines the variation in mean and maximum annual values, mean growing season values, and the number of times σ is elevated above $1.5 \text{ WK}^{-1}\text{m}^{-2}$ as shown in Figure 3. While the Nebraska sites experience an increase in mean and maximum annual σ , mean growing season σ , and the number of times σ is above $1.5 \text{ WK}^{-1}\text{m}^{-2}$ for 2012, the ARM and grassland sites exhibit little variation from previous years. Of the Nebraska sites, the rainfed NE3 site still has lower σ values than irrigated sites NE1 and NE2 in 2012.

The regression trees in Figure 4 attempt to clarify the role of SWC , β , and NEE in thermodynamic entropy production and identify important thresholds for these variables. Mean squared error (MSE) values for all nodes in all three trees are shown in Table 3, indicating that the root node for all trees have similarly low error allowing them to be compared. The relationship between NEE and σ is evident in Figure 4 and further supported by a pairwise, Pearson correlation matrix shown in the Supplemental Material. Given values of SWC , β , and NEE , the correlation matrix indicates that values of σ across sites are most correlated with values of NEE , with corre-

Table 2: Based on time series shown in Figure 3, this table exhibits the mean and max annual values of σ ($\text{WK}^{-1}\text{m}^{-2}$), the number of times throughout a year that σ is above $1.5 \text{ WK}^{-1}\text{m}^{-2}$, and the mean growing season (GS) values of σ for April through September. Mean GS values for the ARM site are not shown due to the difference in growing season.

	ARM	KFS	KON	NE1	NE2	NE3
2008						
Mean Ann σ	1.132	1.069	1.077	1.195	1.102	1.104
Max Ann σ	2.211	1.712	1.798	1.936	1.726	1.772
$\sigma > 1.5$	21	9	12	29	18	18
Mean GS σ		1.270	1.276	1.442	1.349	1.354
2009						
Mean Ann σ	1.072	1.119	1.125	1.184	1.135	1.130
Max Ann σ	1.799	1.859	1.936	1.958	1.877	1.813
$\sigma > 1.5$	15	21	21	29	24	23
Mean GS σ		1.449	1.363	1.455	1.421	1.395
2010						
Mean Ann σ	1.092	1.102	1.187	1.195	1.102	1.086
Max Ann σ	1.833	1.983	1.915	1.978	1.987	1.901
$\sigma > 1.5$	21	22	26	28	18	13
Mean GS σ		1.394	1.367	1.465	1.401	1.375
2011						
Mean Ann σ	1.078	1.088	1.169	1.232	1.204	1.120
Max Ann σ	1.730	1.862	1.897	1.912	1.897	1.782
$\sigma > 1.5$	15	18	18	29	30	17
Mean GS σ		1.340	1.340	1.502	1.471	1.378
2012						
Mean Ann σ	1.163	1.111	1.131	1.312	1.277	1.177
Max Ann σ	2.153	1.811	1.923	2.123	2.066	1.904
$\sigma > 1.5$	21	21	20	37	30	27
Mean GS σ		1.361	1.423	1.651	1.580	1.469

lations between -0.46 and -0.51 at all sites except ARM where the correlation is -0.11.

In rainfed cropland sites (Figure 4a), higher σ values of $1.2 \text{ WK}^{-1}\text{m}^{-2}$ and greater (50% of data) occur when a site is a net source above $0.9 \text{ } \mu\text{mol C m}^{-2}$ or a net sink below $-4.5 \text{ } \mu\text{mol C m}^{-2}$. Values of σ around $1 \text{ WK}^{-1}\text{m}^{-2}$ occur with NEE between -1.5 and $0.9 \text{ } \mu\text{mol C m}^{-2}\text{s}^{-1}$ and β values greater than $1.4 \text{ WK}^{-1}\text{m}^{-2}$, while lower σ values around $0.81 \text{ WK}^{-1}\text{m}^{-2}$ occur when β values are less than $1.4 \text{ WK}^{-1}\text{m}^{-2}$. SWC is not shown to be a primary variable in distinguishing between levels of σ for rainfed cropland sites.

For irrigated cropland sites (Figure 4b), the highest σ values of $1.7 \text{ WK}^{-1}\text{m}^{-2}$ occur when NEE is below $-34 \text{ } \mu\text{mol C m}^{-2}\text{s}^{-1}$ corresponding to a large uptake of carbon. As long as NEE indicates a net sink between -34 and $-7.9 \text{ } \mu\text{mol C m}^{-2}\text{s}^{-1}$, σ remains high around $1.4 \text{ WK}^{-1}\text{m}^{-2}$. Lower σ values between 0.81 and $1.2 \text{ WK}^{-1}\text{m}^{-2}$ (62 % of data) occur as NEE transitions from a net sink of $-7.9 \text{ } \mu\text{mol C m}^{-2}\text{s}^{-1}$ to a net source of $1.3 \text{ } \mu\text{mol C m}^{-2}\text{s}^{-1}$ and above. Similar to rainfed cropland sites, higher values of σ around $1.1 \text{ WK}^{-1}\text{m}^{-2}$ occur when β is larger than $1.4 \text{ WK}^{-1}\text{m}^{-2}$, while lower σ values around $0.81 \text{ WK}^{-1}\text{m}^{-2}$ tend to happen when β is less than $1.4 \text{ WK}^{-1}\text{m}^{-2}$. SWC is also not a primary variable in distinguishing between levels of σ for irrigated cropland sites.

When σ of grasslands is examined as a function of SWC , β , and NEE , σ values on the order of $1.4 \text{ WK}^{-1}\text{m}^{-2}$ (34% of data) can be explained by NEE that is less than $-4.4 \text{ } \mu\text{mol C m}^{-2}\text{s}^{-1}$ (Figure 4c). Lower σ values of $1.1 \text{ WK}^{-1}\text{m}^{-2}$ and less are explained when NEE is between -4.4 and $1.3 \text{ } \mu\text{mol C m}^{-2}\text{s}^{-1}$. In addition, some of the lowest σ values of $0.85 \text{ WK}^{-1}\text{m}^{-2}$

Figure 4: Regression trees for σ from SWC , β , and NEE values at (a) rainfed cropland sites ARM and NE3, (b) irrigated cropland sites NE1 and NE2, (c) and grassland sites KFS and KON.

Table 3: Mean standard error (MSE) values at each node (number in brackets) for Figure 4a-c.

Node	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
(a)	0.154	0.148	0.049	0.131	0.135	0.135	0.143	0.116	0.117	0.093	0.085				
(b)	0.171	0.146	0.053	0.126	0.124	0.111	0.102	0.091	0.121	0.101	0.075	0.073	0.026		
(c)	0.164	0.134	0.122	0.114	0.068	0.088	0.076	0.092	0.031	0.099	0.099	0.084	0.032	0.110	0.094

occur when NEE is between -1.5 and $1.3 \mu\text{mol C m}^{-2}\text{s}^{-1}$, SWC is equal to or greater than 19%, and β is less than 3.7. If SWC dips below 19%, greater σ of $1.3 \text{ WK}^{-1}\text{m}^{-2}$ may occur.

4. Discussion

Selecting meaningful indicators and metrics for agroecosystem sustainability begins with trials regarding their ability to identify pertinent stressors and underlying processes within certain spatial and temporal boundaries. In this case study, variability of σ across AmeriFlux cropland and grassland sites is indicative of differences in land cover, land management, and the climatic impact of drought. For example, despite sufficient levels of SWC in irrigated cropland sites, Nebraska croplands exhibited higher thermodynamic entropy production during the extreme drought year of 2012 compared to non-drought years and to other sites examined. Yet, no conclusions related to increased or decreased sustainability among sites can be drawn due to the lack of statistical significance testing for differences between sites and the lack of first-principle hypothesis testing to establish entropy production as a biophysical metric of agroecosystem sustainability.

Still, by comparing σ with SWC , the Bowen ratio, and NEE of carbon, we attempt to identify processes associated with higher or lower σ that may

someday render the metric more useful for evaluating agroecosystem sustainability. If the key to achieving greater agroecosystem sustainability is to minimize σ given energy inputs (Steinborn and Svirezhev, 2000; Svirezhev, 2000; Patzek, 2008), such as those related to irrigation and fertilizer, our results can help explore when this might occur.

Average σ is the highest at irrigated cropland sites NE1 and NE2 that both grow maize requiring large inputs of fertilizer. This result reminds us of the findings of Patzek (2008) that maize monocultures are not sustainable regardless of tillage practice. Compared to other cropland sites, NE1 and NE2 also have an average SWC that is higher, an average β that is lower, and an average NEE that is the most negative corresponding to the greatest sinks of carbon (Table 1). However, NE2 has average values that are slightly lower for σ , higher for SWC and β , and less negative for NEE. These differences between the NE1 and NE2 sites are most likely related to the maize-soybean rotation occurring until 2009 at NE2, where years in soybean production are associated with lower fertilizer applications and lower vegetation fraction (Verma et al., 2005). While we are only examining daytime values for NEE, our finding that NE1 is a greater carbon sink than NE2 is corroborated by Verma et al. (2005).

Rainfed cropland site NE3, which also has a maize-soybean crop rotation, exhibits the lowest average σ , lowest average SWC, highest average β , and least negative average NEE of the Nebraska sites (Table 1). Considering the lower inputs of fertilizer associated with maize-soybean rotation similar to NE2 (Verma et al., 2005) and the lack of irrigation, it is not surprising to see that it has the lowest σ compared to both NE1 and NE2. However,

the lower σ accompanies a NEE that is indicative of the smallest sink of carbon of all Nebraska sites across daytime hours of all years. From 2001-2004, Verma et al. (2005) found the site to be carbon neutral, and grain yield was smaller mostly because of differences in plant densities which are lower on rainfed plots (Verma et al., 2005). Without the data to quantify the crop yield and biomass exported off-site during 2002-2012 across all sites, the relationship between σ and NEE in our study remains relative to on-site, daytime production. Excluding the nighttime values of NEE from our analysis also disregards the role of respiration.

The ARM rainfed cropland site in Oklahoma exhibits the lowest average σ , the lowest average SWC, the highest average σ , and the least negative average NEE of all cropland sites (Table 1). The primary crop grown at this site is winter wheat, which requires less fertilizer inputs than maize but more than soybeans (USDA, 2013) and has a growing season from approximately October to May. Similar to site NE3, the ARM site is rainfed so there are no anthropogenic inputs of energy related to irrigation. The influence of the lack of water on SWC, σ , and NEE is especially pronounced during the Southern Plains drought in 2011 when Oklahoma experienced extremely dry conditions (Karl et al., 2012). During this time, the ARM site does not exhibit a rise in mean or maximum annual σ , though it does exhibit a slight elevation in 2012 (Table 2). This is likely due to the timing of both the 2011 and 2012 drought in relation to the growing season for winter wheat.

Kansas grassland sites KFS and KON have an average σ higher than the ARM site, which may again be due to winter wheat production and the vegetative fraction during certain times of the year Brunsell et al. (2011).

The Kansas sites also exhibit the greatest average SWC and β , and NEE values that are higher than the ARM site but lower than the Nebraska sites. Comparing the grassland sites, the KON site has unexpectedly higher σ than KFS. Increased σ due to the annual burns in April and associated green-up may indicate that annual burns at KON are less sustainable than five-year burns at KFS. Maintaining a native prairie by burning every year at KON might actually be putting more stress on the system by forcing it to remain as a tallgrass system and not allowing it to evolve toward a site with woody encroachment, which is happening on neighboring Konza Prairie plots with different burn regimes Cochran et al. (2013). In addition, missing data in months with lower σ may be skewing the KON average to be higher than both KFS and the rainfed cropland site of NE3.

According to Figure 4c, when σ values are low in grasslands a set of conditions occur where NEE is between -1.5 and $1.3 \mu\text{mol C m}^{-2}\text{s}^{-1}$, SWC is greater than or equal to 19%, and β is less than 3.7. In other words, at times when grasslands are basically carbon neutral, SWC can be low, and H can be high or low, Kansas grasslands exhibit low σ values. This time may correspond to periods when the grassland is not experiencing rapid changes in water or carbon cycling and is closer to thermodynamic equilibrium. So, given the low values of σ for grasslands during the 2012 drought (Table 2), we can imagine that even if a grassland is water or heat stressed, as long as it remains carbon neutral, it will remain more sustainable.

While σ was elevated at all cropland sites during 2012, an extreme drought year for the Central US (Karl et al., 2012), it was especially elevated during the growing season at irrigated sites NE1 and NE2 (Table 2). Above normal

maximum and minimum temperatures in Spring and Summer of 2012 broke previous records from 1934 (Karl et al., 2012). July 2012 was the hottest month in the instrumental record and by August 2012, the US Drought Monitor categorized the drought in Kansas, Nebraska, and Oklahoma as extreme to exceptional. During this time, NE1 and NE2 exhibited higher mean growing season σ values compared to previous years and compared to other sites in 2012. One explanation for the elevated σ is that extra inputs of irrigation needed to maintain maize production during the 2012 drought resulted in increased gradients of temperatures and fluxes of heat influencing σ . If we relate this to the negative feedback loop in the evolutionary framework described in the Introduction, we can see this as an example of increased σ associated with work done in “deviation-counteracting” processes for maintaining similar levels of NEE to non-drought years.

Above normal temperatures are often associated with periods of water stress, which can also lead to reduced evapotranspiration and LE corresponding to increased β . Regression trees for cropland sites shown in Figures 4a and 4b identify a potential threshold for σ of $1.4 \text{ WK}^{-1}\text{m}^{-2}$. Above this threshold where energy partitioning favors H, σ values remain higher around $1.0 \text{ WK}^{-1}\text{m}^{-2}$ and greater. Below the threshold where energy partitioning favors LE, σ values remain low around $0.8 \text{ WK}^{-1}\text{m}^{-2}$ and lower. The lowest values of σ around $0.5 \text{ WK}^{-1}\text{m}^{-2}$ occur when β is below 0.53 for rainfed croplands and below 0.42 for irrigated croplands.

Therefore, our findings suggest that at times when σ is low in cropland sites, increased LE corresponds with a greater dissipation of heat, a reduction of temperature gradients, and a greater transfer of entropy from the system.

Conversely, at times when σ is higher, a greater H corresponds with temperature gradients between the surface and the atmosphere that are steeper resulting in higher σ and entropy that is being transferred at a much slower rate (Peixoto et al., 1991). Thus, from a biophysical perspective, these results hint that an open agricultural system closer to, but not at, thermodynamic equilibrium may be more sustainable.

Since the values of σ across sites are most correlated with the values of NEE (see Supplemental Material), we infer that energy inputs that drive NEE and associated processes of photosynthesis, respiration, and evapotranspiration may also move croplands farther away from thermodynamic equilibrium. Therefore, like grasslands, croplands may experience a tradeoff between carbon uptake and sustainability. Moreover, given the FAO definition of climate-smart agriculture (Lipper et al., 2010), it is unclear whether rainfed cropland sites ARM and NE3 would fulfill the criteria for GHG mitigation. In drought conditions like 2012 when a rainfed cropland site might be less of a carbon sink, irrigation inputs to maintain a certain level of NEE in cropland sites like NE1 and NE2 may result in an overproduction of entropy as discussed by Svirezhev (2000). In this context, a more sustainable agroecosystem may be one that is not maximizing carbon uptake, like we might be inclined to do for food security and climate change mitigation purposes. If we are to maintain a carbon sink, even in drought conditions, the goal should be to do so without increasing entropy production. Quantifying the entropy production of drought-tolerant crops, such as sorghum, would be an interesting comparison to the crops included in this study and an obvious next step. Overall, the difference between rainfed and irrigated croplands in

Figures 4a and 4b indicates that mitigation of carbon in agroecosystems may become less sustainable when we hit a σ threshold above $1.4 \text{ WK}^{-1}\text{m}^{-2}$.

As we examine our results and consider improvements for continued analyses, we recognize that the availability of AmeriFlux data may contribute to the reliability of results. For example, differences in percent available data between sites and between site years will influence the mean monthly diurnal cycle and introduce error between months to years for any given site. Future studies utilizing additional AmeriFlux or FLUXNET site years could increase the reliability of σ as a sustainability metric. The availability of reanalysis data, such as the ECMWF ERA-Interim product, could also allow for a broader application of this biophysical indicator on a global scale. In addition, detailed land-use histories for AmeriFlux sites are needed to better evaluate influences of anthropogenic energy inputs, like fertilizer, and to account for environmental impacts from pesticides. We need to more thoroughly explore how σ relates to crop and biomass yield, while accounting for carbon exports related to harvest, fire, and mowing. Such information will also help to incorporate social and economic dimensions of sustainability, which may further differentiate between sites.

5. Conclusions

This case study is a first attempt to unify theories of complex ecosystem dynamics with thermodynamic laws to explore agroecosystem sustainability. In line with the mechanisms of Wallace’s evolutionary theory at the ecosystem scale, we present methodology to quantify a move away from or toward thermodynamic equilibrium using an entropy production (σ) metric.

By comparing σ with SWC, the Bowen ratio, and NEE of carbon, we attempt to identify processes associated with higher or lower σ that may render the metric more useful.

Except for the ARM site in Oklahoma, σ is most correlated with NEE, which highlights the role of vegetation on the equilibrium conditions of the land surface (Brunsell et al., 2011). Elevated σ occurs in irrigated and rain-fed agroecosystems that are stressed by drought conditions in 2011 and 2012. Though irrigation may allow agroecosystems to maintain non-drought levels of NEE, as exemplified by site NE1 with irrigated maize, the associated energy inputs result in higher σ above a threshold of $1.4 \text{ WK}^{-1}\text{m}^{-2}$. In other words, more work is required to overcome gradients created by an irrigated system in drought conditions, and we suggest that the system remains “forced” in a negative feedback loop where it is not experiencing changes that can result in adaptation at the ecosystem scale. A decrease in adaptive potential has implications for agricultural production, food security, and climate-smart agriculture, especially in areas that depend on irrigation and fertilizer use.

Additional studies testing first-principle hypotheses using longer-term data over a larger number of sites are needed to establish entropy production as a biophysical metric of agroecosystem sustainability. Further calculations of the overall entropy budget could confirm whether entropy production consistently captures the impact of land cover and land management on thermodynamic equilibrium. Testing a hypothesis that relates a move away from thermodynamic equilibrium to a move away from agroecosystem sustainability would require examination of agroecosystems that, based on other

metrics or indicators, have proven to be more or less sustainable. Perhaps such agroecosystems would include small-scale, indigenous plots that have been productive for centuries in contrast with areas of repeated crop failures. Obtaining necessary, long-term data from such sites, especially within similar climate zones, may be quite difficult, and efforts to initiate data collection should not delay. Researchers should also continue to explore available data from eddy-covariance towers, satellite remote sensing instruments, and re-analysis output to empirically study interactions and processes associated with biophysical indicators and thermodynamic metrics that may lead to an improved understanding of agroecosystem sustainability.

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References

- Altieri, M. A., 1987. Agroecology. The scientific basis of alternative agriculture. Westview Pr.
- Baldocchi, D., Falge, E., Wilson, K., Feb. 2001. A spectral analysis of biosphere–atmosphere trace gas flux densities and meteorological variables across hour to multi-year time scales. *Agricultural and Forest Meteorology* 107, 1–27.
- Breiman, L., Friedman, J., Stone, C. J., Olshen, R. A., 1984. Classification and regression trees. CRC press.
- Brunsell, N. A., Schymanski, S. J., Kleidon, A., 2011. Quantifying the Thermodynamic Entropy Budget of the Land Surface: Is This Useful? *Earth System Dynamics* 2 (1), 87–103.
- Brutsaert, W., 1975. On a Derivable Formula for Long-Wave Radiation From Clear Skies. *Water Resources Research* 11, 742–744.
- Cochran, F., Brunsell, N., Mechem, D., Feb. 2013. Comparing Surface and Mid-Tropospheric CO₂ Concentrations from Central U.S. Grasslands. *Entropy* 15 (2), 606–623.
- Conway, G. R., 1985. Agroecosystem analysis. *Agricultural Administration* 20 (1), 31 – 55.
- Fischer, J., Manning, A. D., Steffen, W., Rose, D. B., Daniell, K., Felton, A., Garnett, S., Gilna, B., Heinsohn, R., Lindenmayer, D. B., MacDonald, B., Mills, F., Newell, B., Reid, J., Robin, L., Sherren, K., Wade, A., 2007a.

- Mind the sustainability gap. *Trends in Ecology & Evolution* 22 (12), 621–624.
- Fischer, M. L., Billesbach, D. P., Berry, J. A., Riley, W. J., Torn, M. S., Sep. 2007b. Spatiotemporal Variations in Growing Season Exchanges of CO₂, H₂O, and Sensible Heat in Agricultural Fields of the Southern Great Plains. *Earth Interactions* 11 (17), 1–21.
- Foken, T., 2006. 50 Years of the Monin–Obukhov Similarity Theory. *Boundary-Layer Meteorology* 119 (3), 431–447.
- Gnaiger, E., Jun. 1994. Negative Entropy for Living Systems: Controversy Between Nobel Laureates Schrodinger, Pauling and Perutz. *Modern Trends in BioThermoKinetics* 3, 1–9.
- Goody, R., Abdou, W., 1996. Reversible and irreversible sources of radiation entropy. *Quarterly Journal of the Royal Meteorological Society* 122 (530), 483–494.
- Gutowski, T. G., Sekulic, D. P., Bakshi, B. R., Apr. 2009. Preliminary thoughts on the application of thermodynamics to the development of sustainability criteria. In: 2009 IEEE International Symposium on Sustainable Systems and Technology (ISSST). IEEE, pp. 1–6.
- Hermanowicz, S. W., Feb. 2007. Entropy and Energy: Toward a Definition of Physical Sustainability. *Water Resources Center Archives*, 1–15.
- Holdaway, R. J., Sparrow, A. D., Coomes, D. A., 2010. Trends in entropy production during ecosystem development in the Amazon Basin. *Philosophical*

- Transactions of the Royal Society B: Biological Sciences 365 (1545), 1437–1447.
- Karl, T. R., Gleason, B. E., Menne, M. J., McMahon, J. R., Heim, Jr, R. R., Brewer, M. J., Kunkel, K. E., Arndt, D. S., Privette, J. L., Bates, J. J., Groisman, P. Y., Easterling, D. R., Nov. 2012. U.S. Temperature and Drought: Recent Anomalies and Trends. *Eos, Transactions, American Geophysical Union* 93 (47), 473–496.
- Kleidon, A., 2009. Non-equilibrium thermodynamics, maximum entropy production and Earth-system evolution. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 368 (1910), 181–196.
- Kostitzin, V., 1934. Symbiose, parasitisme et evolution. *Bull. Amer. Math. Soc.* 40 (1934), 788 DOI: <http://dx.doi.org/10.1090/S0002-9904-1934-05983-4> PII, 0002–9904.
- Krotscheck, C., Oct. 1997. Measuring Eco-Sustainability: Comparison of Mass and/or Energy Flow Based Highly Aggregated Indicators. *ENVIRONMENTAL METRICS* 8, 661–681.
- Liao, W., Heijungs, R., Huppes, G., Mar. 2012. Thermodynamic analysis of human–environment systems: A review focused on industrial ecology. *Ecological modelling* 228, 76–88.
- Lipper, L., Mann, W., Meybeck, A., Sessa, R., 2010. The Hague Conference on Agriculture, Food Security and Climate Change. Tech. rep.

- Liu, Y., San Liang, X., Weisberg, R. H., 2007. Rectification of the bias in the wavelet power spectrum. *Journal of Atmospheric and Oceanic Technology* 24, 2093–2102.
- Mayer, A. L., 2008. Strengths and weaknesses of common sustainability indices for multidimensional systems. *Environment International* 34 (2), 277–291.
- McMahon, G. F., Mrozek, J. R., Aug. 1997. Economics, entropy and sustainability. *Hydrological Sciences Journal* 42 (4), 501–512.
- Mori, K., Christodoulou, A., Jan. 2012. Review of sustainability indices and indicators: Towards a new City Sustainability Index (CSI). *Environmental Impact Assessment Review* 32 (1), 94–106.
- Patzek, T., 2008. Thermodynamics of agricultural sustainability: The case of US maize agriculture. *Critical Reviews in Plant Sciences*.
- Peixoto, J. P., Oort, A. H., De Almeida, M., Tomé, A., 1991. Entropy budget of the atmosphere. *Journal of Geophysical Research: Atmospheres* (1984–2012) 96 (D6), 10981–10988.
- Perry, G. L. W., Sep. 2002. Landscapes, space and equilibrium: shifting viewpoints. *Progress in Physical Geography* 26 (3), 339–359.
- Phillips, J. D., Sep. 1999. Divergence, Convergence, and Self-Organization of Landscapes. *Annals of the Association of American Geographers* 89 (3), 466–488.

- Phillips, J. D., Feb. 2008. Goal functions in ecosystem and biosphere evolution. *Progress in Physical Geography* 32 (1), 51–64.
- Scherr, S. J., Shames, S., Friedman, R., 2012. From climate-smart agriculture to climate-smart landscapes. *Agriculture & Food Security* 1 (1), 1–1.
- Schneider, E., Kay, J., 1994. Life as a Manifestation of the Second Law of Thermodynamics. *Mathematical and Computer Modeling* 19 (6-8), 25–48.
- Smith, C. H., 1986. A contribution to the geographical interpretation of biological change. *Acta biotheoretica* 35 (4), 229–278.
- Smith, C. H., Oct. 1989. Historical biogeography: Geography as evolution, evolution as geography. *New Zealand Journal of Zoology* 16 (4), 773–785.
- Smith, C. H., Aug. 2005. Alfred Russel Wallace, past and future. *Journal of Biogeography* 32 (9), 1509–1515.
- Steinborn, W., Svirezhev, Y., 2000. Entropy as an indicator of sustainability in agro-ecosystems: North Germany case study. *Ecological modelling* 133 (3), 247–257.
- Stewart, J., Kustas, W., Humes, K., 1994. Sensible heat flux-radiometric surface temperature relationship for eight semiarid areas. *Journal of Applied Meteorology*.
- Svirezhev, Y., 2000. Thermodynamics and ecology. *Ecological modelling* 132, 11–22.
- Therneau, T. M., Atkinson, B., Ripley, B., 2010. rpart: Recursive partitioning. R package version 3.8 Edition.

USDA, 2013. Usda economic research service.

URL <http://www.ers.usda.gov/data-products/fertilizer-use-and-price>

Verma, S. B., Dobermann, A., Cassman, K. G., Walters, D. T., Knops, J. M., Arkebauer, T. J., Suyker, A. E., Burba, G. G., Amos, B., Yang, H., Ginting, D., Hubbard, K. G., Gitelson, A. A., Walter-Shea, E. A., Jul. 2005. Annual carbon dioxide exchange in irrigated and rainfed maize-based agroecosystems. *Agricultural and Forest Meteorology* 131 (1-2), 77–96.

Walker, B., Salt, D., 2012. Resilience thinking: sustaining ecosystems and people in a changing world. Island Press.

Wezel, A., Bellon, S., Doré, T., Francis, C., Vallod, D., David, C., 2009. Agroecology as a science, a movement and a practice. A review. *Agronomy for Sustainable Development* 29 (4), 503–515.

Wilson, K., Goldstein, A., Falge, E., Aubinet, M., Baldocchi, D., Berbigier, P., Bernhofer, C., Ceulemans, R., Dolman, H., Field, C., Grelle, A., Ibrom, A., Law, B., Kowalski, A., Meyers, T., Moncrieff, J., MONSON, R., Oechel, W., Tenhunen, J., Valentini, R., Verma, S., 2002. Energy balance closure at FLUXNET sites. In: *Agricultural and Forest Meteorology*. Univ Calif Berkeley, ESPM, Berkeley, CA 94720 USA, Univ Calif Berkeley, ESPM, Berkeley, CA 94720 USA, pp. 223–243.

Wu, W., 2010. Radiation entropy flux and entropy production of the Earth system. *Reviews of Geophysics* 48, RG2003.