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RESEARCH PAPER

Exergy Analysis: A Guide to Sustainability?

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Abstract: This paper argues for a continuing exploration of Nature's organizing principles that sustain prolonged homeostasis of the earth's ecosystems punctuated by forceful transitions to new emergent states. Ecosystems develop and maintain a dynamically stable state by transacting energy and materials with the surrounding flows to keep reversing their continual fall to the ground state. Conversely, the elevation of any component of the ecosystem above the ground level may be regarded as a measure of its functional efficiency. This measure, called exergy, can be calculated for an eco-subsystem based on knowledge of the energy and material fluxes that thread it and, most importantly, of where the ground level happens to be. Admittedly, it is not straightforward to quantify these figures, and the departure of assumptions from reality will inevitably translate into errors in the calculated exergy figures. However, the variance may be estimated by analysing the results of an ensemble of calculations with randomly perturbed input values. Even with these limitations, however, a map of exergy losses characterizing different parts of an ecosystem has the potential to reveal relative thermodynamic efficiencies for appropriate ameliorative interventions.

Keywords: Exergy, Ecosystem, Thermodynamic limits

1. INTRODUCTION

Sustainability is not a value-neutral concern, begging the question as to what is it aimed at. But at its heart lies the ambition to prolong the ambient state of the earth's ecosystems, whose future trajectories are inalienably conditioned by the current state. Insightful hints to design a path towards sustainability, irrespective of the focus of its concern, can perhaps be gleaned by looking more incisively at the way ecosystems work.

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Planet earth's ecosystems are unique in the solar system. They evolved from rudimentary forms of self - replicating molecules, feeding off solar radiation or energy from the deep earth, growing slowly at first and then more deliberately by dispersal and structure formation. The first of these is a piece of the universal process that inexorably enlarges the degrees of freedom available to a system's condition, a natural consequence of unbiased treatment of all aspects of a situation. The second process, also seen at work in inanimate systems fed by constant energy (such as atmospheric convection) has been extensively studied through laboratory experiments (for example, the Bénard convection). The results suggest that structure formation in constantly powered systems (like ecosystems) greatly enhances the rate of energy dissipation, perhaps to hasten the descent to equilibrium. The significant fact is that they develop and sustain low-entropy organized entities in the very act of falling along a gradient.

Every habitat on earth, including that of humans, belongs to some ecosystem of the planet (Figure 1). Ecosystems are a society of living and breathing beings much like our own, sustained by throughflows of matter, energy, and information exchanged with the surroundings. They grow, develop and stay alive by abstracting energy from other sources, such as solar radiation and solar-driven cycles of wind and water, to constantly restore the driving gradients of their arterial flows. Their potential energies keep falling inexorably toward the dead state of equilibrium through the very act of flowing. This is the spontaneous process forever at work in the universe — a progressive flattening of all gradients. Highlands erode to peneplains, gurgling mountain streams slow down to staid meanders, concentrated materials disperse into environmental wastes, and energy molecules oxidize to inert ones.

Unless injected constantly with fresh energy, these downhill processes would eventually lay all systems to eternal rest (Figure 2). Even when a source such as the daily inflow of solar radiation exists, and the landscape can sustain thermal, topographic, and material flows (as seen in other planets in the solar system) these do not result in a 'Goldilocks world' where the conditions for life are just right. For that to happen, the solar-driven flows need to be channelled through entities that can transform their energy into useful work; entities that would keep reversing the downhill processes by assembling inert matter into a chain of energy molecules, and transforming wastes to clean the environment and mitigate hazards. This functional machinery developed on earth as its ecosystems, made possible by the planet's special endowments: just the right mass to hold an atmosphere in its gravitational cage and the right distance from the sun to let liquid water exist. In turn, these conditions orchestrated the evolution of a blue planet, dynamically driven within by plate tectonics and on its surface by the hydrological cycle. In time, the latter greened and flowered its land, turning it into one of the most spectacular objects in space.

Figure 1: A Visual Representation of an Ecosystem

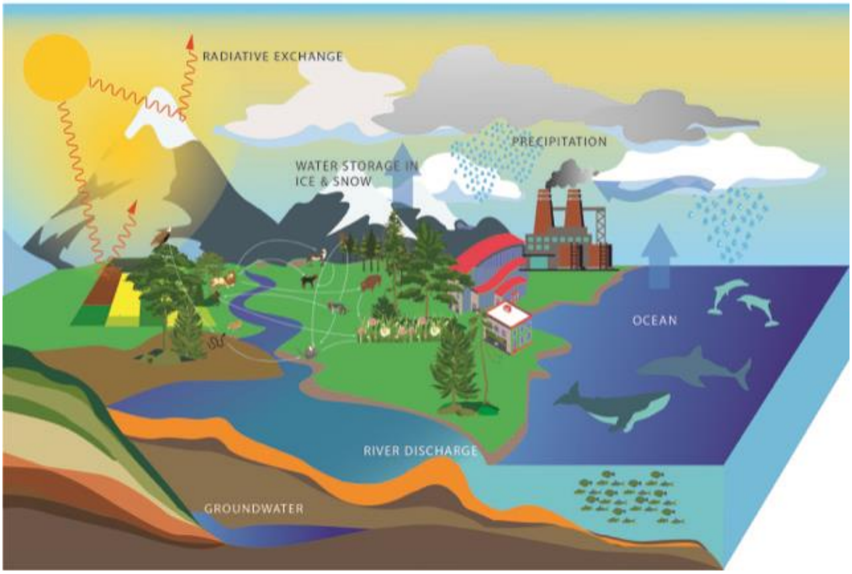

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Figure 1 presents an iconic view of an ecosystem. Its several distinctly recognizable units are, in fact, mutually supported through invisible streams of energy, materials, and information flows. These flows, primarily driven by the thermal and electrochemical gradients created by solar radiation, are, in turn, channelled through a vast network of energy, material, and information transforming devices or 'eco-engines'. The latter use the work potential of their throughflows to maintain their live state and resist the universal tendency towards levelling. In the process, they perform critical ecosystem services, most notably, they help other eco-engines down the line do the same.

2. ECOSYSTEMS AS A HIERARCHICAL NETWORK OF ECO-ENGINES

Since energy can neither be created nor destroyed, but only transformed through flows of heat, work, materials, or information, ecosystems are essentially constituted as energy transforming devices called 'engines'. In the manner of all dynamical systems with continual energy inputs, which are known to maximize the efficiency of energy transformation by developing an orderly structure (for example, Bénard convection cells, as examined in Demirel, 2002), ecosystems too develop an optimal network of energy-transforming flows. They exploit all possible configurations allowable by their landforms and the daily and seasonally renewable stocks of energy and materials, to maximize their flow density pathways, especially of the miracle substance, water. The extraordinary properties of water as a universal solvent and its large thermal inertia, further enhance an ecosystem's opportunity space for differentiation and co-development. The result is a hierarchically ordered web of material and energy flows and their storages that nourish and create the foundational structure of the food chain: soils, forests, lakes, wetlands, groundwater, and biodiversity (Allen & Starr, n.d.; Müller, 1992; O'Neill et al., 1989; Pahl-Wostl, 1993).

The invention of steam engines in the seventeenth century was inspired by the experiential learning of early civilizations about transforming heat to mechanical energy (for example, fire pistons used by Neolithic communities) and creation of several ingenious devices that used steam power to move shafts. In the nineteenth century, an analytical inquiry in the efficiency of energy transformation processes led to an understanding of energy quality as distinct from energy quantity. Analyzing the results of a thought experiment, Sadi Carnot (Kelvin *et al.*, 1924), showed that whilst steam flowing from a high temperature source can be made to perform work by moving a piston to drive a wheel, the amount of work (W) performed by it was only a certain fraction (η) of the input steam energy (Q). As the energy of flowing steam is progressively consumed in the process of performing work, its thermal potential, that is, its temperature, gradually reaches equilibrium with the surroundings. Thereupon, the residual heat, unable to flow and be transformed any further, simply joins the vast and unusable stock of environmental heat. The part of a system's total energy capable of being turned completely into work can thus be measured by the elevation of its ambient state above the equilibrium level. This is called 'exergy', and it is measured in the same unit as energy on a scale defined by the zero potential energy of the equilibrium state or a state of complete stasis.

Equivalently, the exergy of a particular system state is the energy required to create it from the chemically inert, thoroughly dispersed, zero gradient states of its components. For example, the exergy of one mole (a pack of a given number of molecules) of biogas (methane) being ~832 kJ, means that a mole of the gas will produce 832 kJ of energy when allowed to unpack itself. This is in fact, equal to the energy stored in every mole of methane through the work performed by bio-organisms to i) extract carbon dioxide (20 kJ) and water (2.6 kJ) from the environment, ii) bond the extracted carbon and hydrogen molecules into one of methane (818 kJ), and iii) return the residual oxygen (–7.8 kJ) to space. Unlike energy, exergy is not conserved, and is, therefore, a more sensible qualifier of the work potential of material and energy flows.

Figure 2: Flow of Energy within an Ecosystem

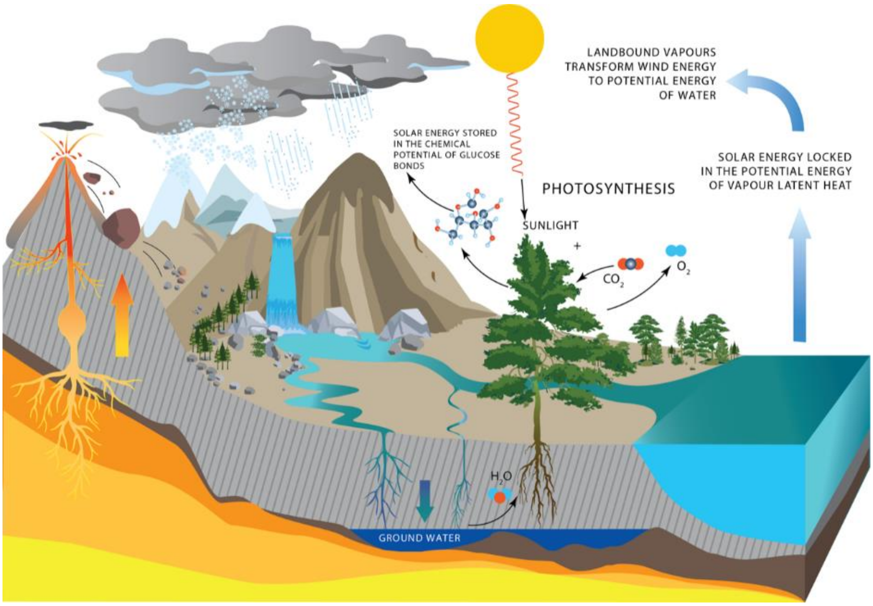

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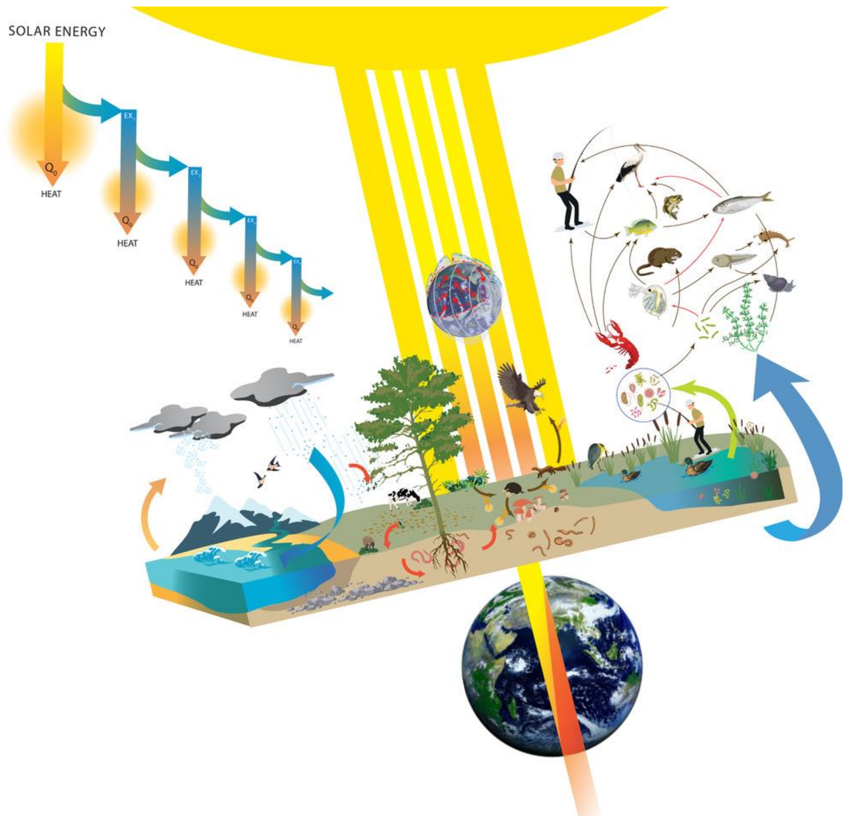
Figure 2 illustrates the ability of systems to perform work through certain processes by virtue of the fact that their elevated states are lifted above the flat equilibrium state: raised highlands erode to renew soil fertility, evaporated sea water is blown by wind to drive the hydrological cycle, inert carbon dioxide molecules hydrogenated through photosynthesis form high-energy glucose molecules, and the osmotic flow of water to plant roots is driven by the concentration gradient. Left to their own devices, systems possessing potential energies tend to move downhill to the zero gradient equilibrium state, consuming the stored exergy that can be utilized to perform useful work if channelled through an engine, such as the production of electricity from falling water or metabolic energy from the oxidation of carbohydrates in the guts of living beings. Ecosystems integrate these processes into a biogeochemical cycle by abstracting the exergy of inflowing solar energy and outflowing heat energy from the earth's depths to build gravitational and chemical potential energies in the form of landscapes and biomass.

Ecosystems maintain their health and build reserves for the future by channelling the surrounding flows of materials, energy, and information into a succession of lower-order streams thereby harvesting the maximum of the available exergy (Silow & Mokry, 2010). Exergy extracted from the daily and seasonally restored natural flow gradients that drive the atmosphere and oceans, and proton flows in plant cells, is consumed to re-build other less consumptive gradients of the ecosystem. Fertile flood plains develop in the wake of diminishing stream power, as do wetlands, where an incredible diversity of bio-organisms reduce environmental wastes to organic carbon, thus preparing the base of the food chain. As some exergy is irretrievably lost along each flow path as dead heat (because of the ubiquitous presence of irreversibilities), the hierarchically organized chain of eco-engines is driven by a progressively diminishing sequence of residual exergies delivered by a preceding one (Figure 3). The entire exergy of solar radiation extracted by ecosystems is, thus, used up by a succession of their eco-engines to sustain the vital environmental flows and store some of it as chemical exergy in the food and fuel molecules for use in the lean season (Silow et al., 2011).

Analogously, one can visualize the same process at work when considering a mountain stream that drives large rock masses down a steep valley and deposits them on the flattening valley floor on entering the plains (Figure 3). This happens because the reduced gradient and approaching closeness to equilibrium reduces the potential for energy exchange, reducing the stream's power even as the quantity of its flow remains the same. This progressive reduction in stream's power continues apace, depositing finer and finer sediments into the biogeochemical marvel of a delta as it levels with the sea. Thus, all of the earth's energy requirements, including those of its biosphere and human civilization, are met from the exergy or quality of solar energy (Figure 3), not its quantity as in case of a hydroelectric plant (which draws from the gravitational exergy of a flowing stream without consuming a single drop of water).

Figure 3 shows how the exergy of solar energy is used by the two principal thermodynamic engines of the earth system: the atmosphere-ocean and the ecosystem, by harnessing the electromagnetic (thermal and electronic) gradients created by the high exergy solar radiation. One is created by the earth's non-uniform heating, and the other by excitation of its otherwise inert molecules (photosynthesis). The first converts solar exergy to move the atmosphere & oceans, which in turn, drive the hydrological cycle and a cascade of progressively smaller engines, notably the nutrient cycle and the longer time-scale rock cycle (not shown). The hydrological & nutrient cycles collaborate with the photosynthesizing engine to grow and develop the living world, which continually reverses the various potential gradients to maintain its low entropy islands against their ineluctable attrition. Like all dynamic systems that evolve into an organized structure, the earth's primary engines too, harness the daily supply of solar radiation to structure the earth's climate and ecosystems. The figure (left middle) shows how the exergy of solar radiation is used up in maintaining and developing the living earth through a progressively diminishing cascade of energy and material transforming Carnot engines, losing some exergy at every stage as heat without using any of the energy received from the sun, which at the end of the day, is radiated back to space with all its exergy reduced to zero.

Figure 3: Uses of the Exergy of Solar Energy



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At the top of the earth's exergy flow pyramid are two major flow–field gradients forged directly by the sun (Figure 3). The first one is the thermal gradient resulting from the non-uniform distribution of temperature on earth because of its asymmetry with respect to the sun – earth axis and the varying reflectivity of its variegated surface features. The inexorable levelling of the thermal gradient mediated, in turn, by convective flows of the earth's fluid spheres keeps the planet at a moderate temperature and creates humidity gradients, thereby driving a hydrological cycle. The latter, interacting with solid earths near surface texture and topographic gradients, creates surface flows of freshwater and its delayed release storages in mountain glaciers, soils and in the ground below.

The second major gradient, collaboratively created with hydrological flows and the entrained nutrients, is the electrochemical gradient created by the absorption of solar photonic energy by electrons in the green molecules of plants and algae (called chlorophyll). The exergy yielded by the flow of protons down this gradient hydrogenates the carbon dioxide (CO2) molecules plucked from the air, packing part of the flow energy in the molecular bonds of the new glucose molecule ($C_6\ H_{12}\ O_6$), which is the basic building block of all life. An economically viable replication of the process may indeed deliver us one day from the conundrum of global warming.

The earth's internal thermodynamic engine too builds topographic and geochemical gradients through episodic upheavals, subsidence, and volcanic effusions, but this involves much longer time scales than the diurnal and seasonal flows of energy powered by the sun and the solar energy–driven hydrological cycle. However, the former is responsible for sculpting the longer-lasting surface features of the earth into smaller biogeophysical units in which the annual and seasonal scale solar-powered environmental processes operate.

Ecosystems flourish by flowing their share of fresh water and materials along their landscape gradients (principally the gravitational and the climatic) and generating a cascade of new ones using the exergy extracted from the former. The latter gradients, which are primarily biogeochemical, tend to organize themselves into a network of productive subsystems to maximize the extraction of all available free energy for conversion into biomass and ecological services, which is required by dependent communities. The efficiency with which the seasonally replenished natural resources of an ecosystem can be harnessed to sustain its well-being and productivity is largely determined by the efficiency with which available free energy in its various flow systems is harvested. Haphazard anthropogenic interventions across the globe have disrupted many ecosystems with self-organized flows. However, these may yet be rewired to maximize the productivity of their eco-engines using creative engineering designs informed by thermodynamic limits. What are these limits?

3. THERMODYNAMIC LIMITS

As explained previously, living systems (Figure A1) survive by being open, that is, by exchanging materials and energy with the environment, and by using up the latter's exergies to maintain their well-being, and, thereby the functioning of their subsystems. Healthy ecosystems unceasingly deliver vital eco-services in the form of energy and material storages for use in regular and lean seasons and ensure the availability of clean water and a clean environment by transforming wastes. These processes, however, proceed in strict accordance with the laws of thermodynamics. The first of these laws states that energy is always conserved in any process. This is a corollary of the fundamental principle of symmetry established by Emmy Noether in 1915, a principle which helps explain the evolving universe. Since energy transformation can only be mediated through the exchange of heat, matter, information, or work, and the total energy must be conserved, we can represent this fact symbolically as:

$$Q_{net} + E_{net}\,(\text{matter}) + E_{net}\,(\text{Info.}) - W_{net} = (\Delta E_{internal})_{syst.} \qquad (1)$$

The RHS of (1) denotes net additions to a system's energy stock accrued from transformations of flowing streams of heat (Q), materials, and information minus the work (W) delivered by the system. Work (W), in particular, denotes the energy associated with the displacement of materials mediated by force or pressure (such as moving a shaft). The statement asserts that the net sum can only appear as a change in the system's molecular structure and its kinetic energy, collectively understood as its internal energy ($\Delta E_{internal}$).

However, this statement gives no indication of the quality or potential of the resulting exergy in terms of performing work. For example, the heat energy of a stable atmosphere, which is known to be very large, cannot be made to perform any work unless it is made to flow along a temperature gradient, which is done by artificially creating a colder reservoir.

Quantifying energy *quality* is a concept that is explored in the second law of thermodynamics, which was distilled from the analysis of a deeply insightful thought experiment by Sadi Carnot in 1824. Assuming the flow to be unhurried to allow reversing the process at any instant without any losses (such as pushing a bicycle pump infinitely slowly), he proved that the maximum useful work (W) extractable from a heat flux (Q_H) flowing from a hot reservoir at temperature T_H to a colder one at temperature T_0 (to drive a motor, for example), is only a certain fraction (η) of the total inflow (Q_H). The unhurried, reversible condition specified in his thought experiment was used to ensure that no part of the input energy leaked out as waste heat (as would otherwise happen, for example, when a bicycle pump is pushed energetically). The efficiency (η) with which heat energy can be transformed to work is equal to $\{1 - (T_0 / T_H)\}$, which is always less than 100%, even in a slowly transforming reversible process, because, when flowing down a thermal gradient with concomitant cooling, a part of it ($= Q_0$) cannot produce any work when it reaches equilibrium with the surrounding air at T_0. He further proved that this limitation was universally true irrespective of the nature of the material flowing through the engine, thereby making the result applicable to a wide range and variety of energy transformation processes. Of equal significance is the fact that he proved that there was no way by which this theoretical limit of efficiency could be breached, and further, that in a reversible process of energy transformation from state A to state B, the quantity, $S_B = (Q/T)_B$, remained constant irrespective of the path of transformation. Claussius (1824) recognized this quantity as a characteristic of the state of a system and called it 'entropy'—a Greek word related to transformation. As explained previously, entropy is inevitably generated in any process that transforms heat to work when a part of the input energy is reduced to impotence upon reaching equilibrium with its surroundings. Indeed, entropy is generated in the transformation of even those energies that possess 100% exergy, such as electric energy or mechanical work, because of the various dissipative losses involved in all physical operations. The ubiquitous presence of irreversibility in the real world, such as friction-generated heat, thus makes the entropy of a subsequent state of any physical system (S_B) greater than the entropy of the preceding state (S_A). Biological systems and refrigerators transform energy to create lower entropy islands locally at the expense of a larger quantum being added to the environment. This one-way street, where a system constantly evolves into a state of higher entropy, is thus an unexceptional rule of energy transformation in the universe.

Or, $dS_{A\rightarrow B} = (S_B - S_A) = (Q_B / T_B - Q_A / T_A) = \int_{A\rightarrow B} d(Q/T) = \int_{A\rightarrow B} dS \geq 0$ (2)

The equality holds strictly true for a reversible process where $Q = TS$, which, however, provides a reference for how far removed the efficiency of a non-reversible physical system is from the ideal, and how imaginative interventions may enable minimizing the gap. Given the thermodynamic arbitrage imposed by the second law, we can restate the conservation law for reversible processes as:

$$TS + E_{net}\,(\text{matter}) + E_{net}\,(\text{Info.}) - W_{net} = (\Delta E_{internal})_{syst.} \quad (3)$$

Drawing logical corollaries from the above equation, we can show (vide Appendix) that under reversible, ideal conditions, the rate of performing useful work, or the power delivery of an open system exchanging heat, matter, and information, is provided by (4) below.

$$\dot{W}_{cv} = -\, d/dt(E_{cv} - T_0 S_{cv}) + \Sigma_{i=1\rightarrow n}\, \dot{Q}_i\,(1 - T_0\,/T_i) + \Sigma\dot{m}\,(h + h^* - T_0 s) \qquad (4)$$

Here, W_{cv} is the work potential of the system, or its exergy, expressed as the net sum of various inflowing exergies (of its internal energy, heat, mass, and information).

However, irreversibilities in real-world systems invariably destroy some of the available exergy depending on the degree of their imperfections, reducing the actual delivery to less than what was computed from equation (3). The quantum of exergy destruction by an open system distilled from (3) is given by (5):

$$(\text{Exergy destruction rate})_{cv} = T_0\{d/dt(S_{gen})\} \qquad (5)$$

The exergy destruction figures of an ecosystem or of its subsystems (which can be calculated by applying (5) to the observed data) are an illuminating indicator of their respective health. By mapping the exergy destruction figures of sub-systems across an ecosystem, we can identify the ones whose performance is short of the theoretical limit for reversible processes, and thus warrant design interventions.

4. EXERGY FLOW THROUGH THE EARTH SYSTEM

The earth system receives a daily supply of highly concentrated radiation energy, $Q_s \approx 1.4 \times 10^{22}$ joules, or 1.74×10^{17} watts (Kleidon 2012), shone by a 6000* K hot sun. Since this radiation is non-uniformly distributed on earth, a thermal gradient develops between the equator and the poles, driving atmospheric and oceanic flows that keep the earth at an average temperature of ~300 ± 27* K. Despite this prodigious supply of daily radiation, the earth system, on average, is not heating or cooling significantly during the day, as it radiates back virtually the entire Q_s, after abstracting its exergy $\approx \eta Q_s = (1 - 300/6000)\ Q_s = 0.95 \times 1.74 \times 10^{17} = 1.65 \times 10^{17}$ Watts, to fuel its works and the living world.

Additionally, the moderate thermal state of the earth, mediated by its circulating fluid spheres and constantly hydrated by the wind-driven hydrological cycle, promotes photosynthesis. The latter process can produce biomass exergy equal to 7.0×10^{20} joules per day at 5% theoretical efficiency (Zhu *et al.* 2008), if every ray of sunlight were to be captured by a green plant. Actual biomass production on earth is, however, limited by non-ideal conditions to ~70 giga-tonnes/yr. (Popp *et al.* 2014), providing a daily budget of ~3.5 x 10^{18} joules of chemical potential energy that fuels all life forms on earth and most of their eco-service requirements.

The significant point to note here is that in any energy transformation process, which is only possible through the exchange of heat, matter, information, or work, mediated by a system (or engine), while energy itself is conserved, the part available for performing work, that is, its exergy, even under ideal conditions, is always less than the original: exergy $\leq \eta$ energy.

Thus, while the exergies of various forms of energy have some maximum theoretical limits denoted by η, the values actually realised are less than η because of the ubiquitous presence of irreversible processes in far from ideal, real-world systems. The latter are determined by the texture of specific systems, such as friction-generated heat losses in an electric motor despite the 100% theoretical exergy of electrical energy or pollutants-induced biogeochemical debilitation in the performance of ecosystem services. The deficit of an actual state, compared with the maximum attainable energy (represented by η) of various system components, may thus be regarded as a measure of exergy loss that could be minimized by better design.

The numerical values of the available or designed exergies of eco-subsystems, can, therefore, prove quite useful, not only in ranking their relative contributions to an ecosystem's well-being, but also in targeting potentially ameliorative ones. Furthermore, exergy, being a system's work potential, is a dynamic quantity that increases when energy is stored in it and decreases as the system moves downhill in the course of performing some work. Its value at any given stage thus measures both its economic worth and health. Also, as work potential, it acts as a universal metric (in joules) for quantifying the state of any component of a system, whether physical, chemical, or biological.

5. EXERGY OF ECOSYSTEMS

The exergy of ecosystems is primarily driven by their biomass, which includes all life forms. It can be explicitly calculated by unpacking the second term, E_{net} (matter), in (3) above. This can be shown (vide A6f of Appendix) to be equal to the sum of the fractional concentration densities x_q of the endemic chemical and biological species present in a given ecosystem, multiplied by their respective weighting factors, β_q, that is:

$$Ex_{eco} = \Sigma_{k=0\rightarrow n} (\beta_k \, x_k) \qquad (6)$$

The β values for a fair number of commonly occurring species have been calculated based on data from various ecosystems, which, in turn, determines the efficiency of their exergy use. These values have been updated accordingly in newer models (Jørgensen 2002; Jørgensen *et al.* 2005). Some interesting applications in the study of the exergy of ecosystems can be found in Silow *et al.* (2011).

The wide range of ecological services that sustain us are rarely acknowledged. What receives even lesser recognition, however, is the role played by the immense diversity of life forms in sustaining the perennial wheeling of energy and material cycles, which are essentially mediated by the biochemical functions ordained by their embodied genetic information. As explained above, the growth space available to ecosystems for maximizing the harvestable exergy of solar radiation is dependent on the number and variety of their eco-engines, that is, their biodiversity. The latter also reinforces the resilience of ecosystems when it comes to withstanding newly emerging stressors. Eco-engines do this by increasing their bio-geographical spreads by creating new niches that suit a proportionately larger pool of differentiated genetic traits. Indeed, some studies on exergy analysis of ecosystems (Silow et al., 2011) confirm that the movement away from thermodynamic equilibrium during ecosystem growth and development coincides with higher levels of organization, system configurations, and maximization of exergy use and storage of both its chemical and information potential.

In essence, the pursuit of rational inquiry looks for an organizing principle underlying masses of data. The intriguing work of living organisms in relentlessly reversing downhill universal processes to maintain a dynamically stable state has long engendered the conjecture that life processes are governed by some overarching principles. Based on acute observations of how the living world sustains itself, Lotka (1921–22), in his papers, proposed that in the event of there being higher available exergy than utilized, "an opportunity is furnished for suitably constituted organisms to enlarge the total energy flux through the system". This prescient conjecture implies a self-directed orientation towards a higher range and level of organization and complexity (information potential) in ecosystems that would maximize the harvesting of available exergy, given the existence of a suitably constituted genetic order. An interesting experiment designed by Horowitz and England (2017) showed that a special configuration of atoms (Lotka's suitably constituted genetic order), will start tapping into those energy sources, aligning and rearranging to better absorb energy and dissipate it as heat. Prigogine and Stengers (1984) state that the growth of organized structures, which characterize the growth of all living systems, can only be maintained by exporting a proportionately higher entropy energy, produced by higher dissipation. This could, therefore, be a directive principle leading the evolutionary trajectory of all dynamical systems. Further, the implied principle, in order to be specific, must in some way be unique, such as an extremal principle (Kelidon and Lorenz, 2005). Indeed, several other indicators of ecosystem health have been proposed, notably *emergy* (Odum 1991), *total system throughflow* (Patten 1995), and *ascendency* (Robert E Ulanowicz 2000). However, as Fath *et al.* (2001) argue, they are either implied by each other or are complementary. Thus, persuasive as these ideas are, they remain to be tested, even though a substantial amount of data may now be available in traditional archives of ecological research.

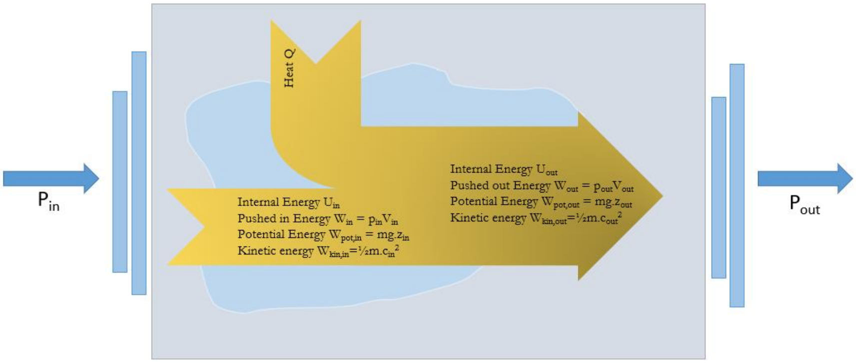
Exergy analysis of eco-subsystems (by providing a direct measure of their efficiency) lights a path to maximize exergy storage for a given set of inputs, thereby also maximize the total system throughflow (considered by some as an independent goal function). In our view, therefore, exergy analysis by itself or, wherever possible, complementarily with other indicators, offers obvious advantages in designing ecosystems and subsystems at various scales to serve urgent contemporary objectives such as meeting the decadal goals of ecosystem rehabilitation. It also holds high promise of leading to a robust theory of ecosystems, further enriching the methodology and approach to ecosystem design that would streamline its human dimension.

APPENDIX

Exergy Analysis of Ecosystems

Ecosystems constitute a web of energy-transforming sub-systems (Figure 3) that constantly exchange energy, materials, and information with their surroundings to maintain their evolving dynamic states above the thermodynamically dead state of equilibrium. Their ability to keep producing ecosystem goods and services is accordingly measured by their dynamically maintained distance (potential) from the downhill flat equilibrium state. This equals the total useful work or exergy that a system will yield if it were allowed to drift towards the equilibrium state of zero exergy when it ceases to exchange any energy or materials with its surroundings (Figure 2). Similarly, this potential is equal to the energy required to create this system out of the zero gradients everywhere of all physical and chemical potentials.

Figure A1: A Schematic of an Open System



Source: Authors

Figure A1 provides a schematic of an open system—an energy and material-transforming engine— lying in the field of flowing streams of heat, information, and work from which it abstracts exergies depending on its specific structure. The application of the principles of thermodynamics to the ambient dynamical parameters of the open system enables us to calculate the gap between their actual functioning and a possible one, thereby providing a diagnostic tool to identify their state of viability and design engineering interventions to improve their condition.

To calculate the exergy produced by such a system, we visualize a representative element of it, called the control volume (Figure A1), with flowing streams of heat, materials, information, and work. Let Q_{in} (t), m_{in} (t), I_{in} (t), and W_{in} (t) denote the heat, mass, information, and work, respectively, contained in an imaginary wafer of thickness dx, ready to be pushed in such a control volume at the time instant t, by pressure p_{in}. A similar wafer containing the respective quantities of Q_{out}, m_{out}, I_{out}, and W_{out} leaves the control volume, Δt, seconds later at the time $(t + \Delta t)$, pushed out by pressure p_{out}. Unlike the heat and work streams, however, the material stream carries at least five forms of energy: i) internal energy, ii) the work performed by the difference of pressures moving the wafers through the system, iii) kinetic energy, iv) gravitational potential, v) and chemical potential released by chemical reactions such as the digestion of food. Material streams also contain much of the information flowing through the system in the form of biodiversity (gene codes) and learned knowledge that guides the various organisms to seek food and mates and protect themselves from predators. Thus, the second and third terms in (1) can be written as:

E_{net} (matter) + E_{net} (Info.) = $[\Sigma_j\, m_{in}\{(u + pv_{sp.}) + (c_{in}^2/2 + gz + \Sigma\mu_{q0j} + I)\}_{in} - \Sigma_k\, m_{out}\{(u + pv_{sp.}) + (c_{out}^2/2 + gz + \Sigma\mu_{q0k} + I)\}_{out}] = \Sigma_{1\to j}\, m(h + h^*)_{in} - \Sigma_{1\to k}\, m(h + h^*)_{out}$, (A1a)

Here, the summation over j and k denotes the number of inlet and outlet portals an open system may have, c is the velocity term in kinetic energy, h is the specific enthalpy per unit mass of internal energy u, pv_{sp} is the work performed by the inlet and outlet pressures, and h* denotes the sum of the kinetic and potential energies of gravitation, information, and chemical bonds of the q^{th} chemical species.

Accordingly, it is instructive to rewrite the conservation equation (1) more explicitly by including all forms of energy:

Q_{net} + E_{net} (material) + E_{net} (Info.) $- W_{net} = (\Delta E_{internal})_{cv.} = [\Sigma_{1\to n}\, Q_{net} + \Sigma_{1\to j}\, m(h+h^*)_{in} - \Sigma_{1\to k}\, m(h+h^*)_{out}] - Q_0 - W_{cv}$, (A1a)

Or, $W_{cv} = -\Delta E_{cv} + \Sigma_{1\to n}\, Q_{net} + \Sigma_{1\to j}\, m(h+h^*)_{in} - \Sigma_{1\to k}\, m(h+h^*)_{out} - Q_0$ (A1b)

Here, W_{cv} is the output work of the system and Q_0 is the heat dumped in the surroundings, adding entropy equal to $\Delta S_{rev.} = Q_0/T_0$ at its equilibrium temperature, T_0. T_0 remains largely unaffected by the various exchanges with the system because of its substantially larger thermal reservoir. We use this fact to temper the conservation law, otherwise devoid of any sense of energy quality, with the limits imposed by the second law.

According to the second law, the change in entropy ΔS_{cv} within the control volume over a time interval Δt is equal to the net sum of entropies associated with the inflowing and outflowing streams of heat and materials $[\Sigma\{(S_Q)_{in} - \Sigma(S_Q)_{out} + \Sigma\,(ms)_{in} - \Sigma(ms)_{out}]$, regarded as ideal reversible processes, in addition to the entropy S_{gen} generated within the system due to all departures from the assumed reversibility. Accordingly,

$\Delta S_{cv} = [\{S_{gen} - (Q_0/T_0)\} + \{\Sigma_{1\to n}\{(Q_i/T_i) + \Sigma_{1\to j}\,(ms)_{in} - \Sigma_{1\to k}\,(ms)_{out}\}]$ (A2a),

where capital S refers to the residual entropies of the system as well as those generated within, and its lower case to specific entropy (per unit mass).

Or, $Q_0 = T_0[-\Delta S_{cv} + \Delta S_{gen} + [\Sigma_{1\to n}\,\{(Q_i/T_i) + \Sigma\,(ms)_{in} - \Sigma(ms)_{out}]$ (A2b)

Substituting the above value of Q_0 into (A1), one obtains the work output of the system as:

$W_{cv} = -(\Delta E_{cv} - T_0\Delta S_{cv} + T_0 S_{gen}) + \Sigma_{1\to n} Q_{net} (1 - T_0 / T_i) + \Sigma_{1\to j} m (h + h^* - T_0 s) - \Sigma_{1\to k} m (h + h^* - T_0 s)$ (A3a)

The first term on the RHS is the sum of i) exergy lost from the internal energy of the system due to various irreversibilities of energy transformation over the time interval Δt, while the second and third terms are the exergies gained by the system from the streams of heat and materials through a reversible transformation. Dividing the various difference terms in (A3a) by Δt, the time interval over which the change in the flow regime through the system is defined by the entry of an infinitesimally thin wafer of their contents and the exit of another, one can express the work output of the system by an equivalent power output as:

$\dot{W}_{cv} = - d/dt(E_{cv} - T_0 S_{cv} + T_0 S_{gen}) + \Sigma \dot{Q}_i (1 - T_0 / T_i) + \Sigma \dot{m} (h + h^* - T_0 s)$ (A3b)

Since exergy is the work potential of a system assuming reversibility of transformations, it is obtained by deleting the $T_0 S_{gen}$ term from (A3b), being the only one caused by irreversibilities. Thus:

$(\text{Exergy Power})_{cv} = -d/dt(E_{cv} - T_0 S_{cv}) + \Sigma \dot{Q}_i (1 - T_0 / T_i) + \Sigma \dot{m} (h + h^* - T_0 s)$ (A3c)

The difference between (A3b) and (A3c) yields the amount $(Ex)_{Dest}$ of exergy lost or destroyed by a given transformer.

$(Ex)_{Dest\ rate} = d/dt(T_0 S_{gen})$ (A4)

Since $(Ex)_{Dest}$ should ideally be zero for a perfect system or only marginally positive for a healthy one, its value above zero indicates the health of an ecosystem. Mapping the numerical values of the exergy destruction of eco-subsystems, which can be calculated using (A4), provides a powerful tool for auditing the functioning of extant ecosystems as well as for testing the efficacy of those ecosystems designed for engineering interventions.

As an example, consider the case of a flowing stream in a steady state, that is, $d/dt(E_{cv}) = 0$, and all heat exchanges taking place at the environmental temperature T_0. With these conditions the exergy/mass of a steadily flowing stream is given by:

$(\text{Specific Exergy})_{\text{steady flowing stream}} = (h + h^* - T_0 s)_{in} - (h + h^* - T_0 s)_{out}$ (A5)

Exergy of Ecosystems

The work potential of biomass resides in i) energy stored in the chemical bonds that hold the molecules of a substance together, ii) information contained in the genetic code of bio-organisms that ordain their functioning, and iii) the network of biological society that catalyses their collective synergy. Thermodynamic processes involving material transformations either perform work to raise the exergy of lower exergy inert molecules or extract the energy stored in their chemical bonds by breaking them. In either case, the energy transaction alters the chemical potential of the molecular assemblage, which is accordingly defined as the energy required to add or remove an atom or molecule from a given mass. The chemical potential μ_q of a particular species q in a mixture is accordingly defined as the partial derivative of the energy of the substance with respect to the number of that species, all other species remaining constant $\mu_q = \partial E/\partial n_q$. The chemical exergy of an ecosystem is hidden in the last term of (A3c).

Therefore, when rewriting this expression in a differential form for a unit molar mass and dropping the suffixes, we get:

$$dE = d(TS - PV) + \Sigma_{q=1\to n} d\mu_q \qquad \text{(A6a)}$$

Or, $(dE - TdS - SdT - Pdv + VdP) = \Sigma\, d\mu_q$,
which, for isothermal and constant volume processes largely true for ecological systems, may be reduced to:

$$VdP = \Sigma d\mu_q = (RT/P)dP \qquad \text{(A6b)}$$

Integrating (A6b), one obtains:

$$\Sigma\mu_q = RT\Sigma[\log(P_q/P_{q0}) - \mu_{q0}] = RT\,\Sigma_{q=0\to n}\, x_q\,[\log(x_q/x_{q0}) - \mu_{q0}] \qquad \text{(A6c)}$$

where P_q is the partial pressure associated with the flow of the q^{th} chemical species $= x_qP_0$, x_q being the molar fractional concentration of the q^{th} species such that $\Sigma x_q = 1$, and x_{q0}, its value in the zero gradient equilibrium state. The summation includes species of inorganic ($q = 0$) and organic molecules ($q = 1$) and bio-organisms ($q \geq 2$). The latter, viewed as information exergy engines, are driven by both coded information in the genes of different communities and network information.

The biochemical exergy of an ecosystem, which is defined as the work potential above the equilibrium state $x_q\,\mu_{q0}$, is therefore given by:

$$Ex_{ecosystem} = RT\,\Sigma_{q=0\to n}\; x_q \log(x_q/x_{q0}) \qquad \text{(A6d)}$$

Values of x_q for the inorganic as well as organic molecules in the ecosystem can be determined by measuring their fractional values in the laboratory. To obtain these with respect to bio-organisms, we must interpret them from the perspective of the probability of their occurrence in the environment: $x_q = p_q X$, where

$$X = \Sigma_{q=1\to n}\; x_q, \text{ and } X_0 = \Sigma_{q=1\to n}\; x_{q0} \qquad \text{(A6e)}$$

where X_0 is the total organic matter per mole, at the equilibrium state, which, for an evolving ecosystem, represents a previous state. Assuming, however, that there is no substantial transfer of matter during the period, we see:

$$Ex_{ecosystem} = XRT \Sigma_{q=0\rightarrow n} p_q \log(p_q / p_{q0}) = \Sigma_{q=0\rightarrow n} \beta_q x_q, \quad \text{(A6f)}$$

Jørgensen (2002) indicates how the quantity RT $\log(p_q / p_{q0}) = \beta_q$, may be calculated by measuring the concentration density of the respective species in the environment. This calculation is based on available knowledge of the genetic structure of endemic communities, and the model assumed for transforming information into eco-products. New research on the structure of information-controlling genes, for example, was used by Jørgensen *et al.* (2005) to revise Jorgensen's earlier determinations of β_q values (Jørgensen 2002). Researchers continue to update these values for better evaluation of ecosystem exergy as new understanding is gained about the microstructure of the living world.

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