Expanding Exergy Analysis to Account for Ecosystem Products and Services

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Exergy analysis is a thermodynamic approach used for analyzing and improving the efficiency of chemical and thermal processes. It has also been extended for life cycle assessment and sustainability evaluation of industrial products and processes. Although these extensions recognize the importance of capital and labor inputs and environmental impact, most of them ignore the crucial role that ecosystems play in sustaining all industrial activity. Decisions based on approaches that take nature for granted continue to cause significant deterioration in the ability of ecosystems to provide goods and services that are essential for every human activity. Accounting for nature's contribution is also important for determining the impact and sustainablility of industrial activity. In contrast, emergy analysis, a thermodynamic method from systems ecology, does account for ecosystems, but has encountered a lot of resistance and criticism, particularly from economists, physicists, and engineers. This paper expands the engineering concept of Cumulative Exergy Consumption (CEC) analysis to include the contribution of ecosystems, which leads to the concept of Ecological Cumulative Exergy Consumption (ECEC). Practical challenges in computing ECEC for industrial processes are identified and a formal algorithm based on network algebra is proposed. ECEC is shown to be closely related to emergy, and both concepts become equivalent if the analysis boundary, allocation method, and approach for combining global energy inputs are identical. This insight permits combination of the best features of emergy and exergy analysis, and shows that most of the controversial aspects of emergy analysis need not hinder its use for including the exergetic contribution of ecosystems. Examples illustrate the approach and highlight the potential benefits of accounting for nature's contribution to industrial activity.

1. Introduction

Ecological goods and services constitute the productive base that is essential for all industrial and economic activity. Examples of ecological goods include water, fertile soil, wood, and coal, and examples of ecological services include rain, pollination, carbon sequestration, and wind. The principle of sustainability implies that the ecological base available for current economic activity should also be available to future generations for their needs. The importance of nature's products and services has been widely recognized in many studies (*1*–*5*). Unfortunately, engineering and economic approaches for industrial decision making tend to ignore or take for granted most ecological inputs, as their contribution is not reflected in market prices. Even most methods for environmentally conscious decision making do not account for the contribution of all the ecological inputs. In fact, Life Cycle Assessment (LCA) focuses mainly on depletion of nonrenewable resources and impact of emissions, whereas Cumulative Exergy Consumption (CEC) analysis considers all natural resources to be equivalent by ignoring ecological goods and services required for the processes being analyzed. Such an attitude of taking nature for granted continues to cause significant deterioration of ecological goods and services that are essential for human sustenance and survival (*4*, *6*, *7*). Consequently, methods to account for the contribution of ecological inputs are essential for ensuring sustainability of our activities.

With increasing recognition of the importance of ecological products and services, some approaches have been suggested to account for their contribution. These approaches are usually based on either economics or physics. Techniques from environmental economics attempt to assign a monetary value to ecological inputs (*8*, *9*). Methods based on physical principles rely on material and energy flow to account for ecological inputs. Material Flow Analysis (MFA) (*10*, *11*) accounts for the flow of materials from the ecosystem to the economy, but ignores the inputs of ecological services. Energy Flow Analysis (*12*) and its variations are promising because of their ability to objectively value all types of material and energy flows without violating physical laws, as methods such as LCA often do. This characteristic makes them ideal for the analysis of industrial and ecological systems.

Exergy or *available energy* is lost or consumed in all processes, making it the ultimate limiting resource for the functioning of all systems. Consequently, exergy analysis has been useful for improving process efficiency (*13*). Cumulative Exergy Consumption (CEC) analysis expands the analysis boundary by considering all industrial processes needed to convert natural resources into the desired industrial products or services. Many recent extensions of exergy analysis have focused on methods for environmentally conscious decision making and LCA (*14*–*18*). The combination of exergy-based methods and LCA is attractive because exergy can provide a common ground for ecological and industrial processes, in which all types of material and energy streams can be fairly assessed, or valued. In addition, exergy may be related to some environmental impacts of emissions (*19*), may quantify the sustainability of processes (*20*), and characterize self-organized systems (*21*). However, all these and related efforts ignore the contribution of ecological products and services, thus limiting their ability to evaluate the "full cost" and sustainability of industrial activities.

Emergy analysis is another thermodynamic approach developed by systems ecologists (*22*), and it has been used for the analysis of ecological and economic systems (*23*). This approach determines the energy used directly and indirectly, in equivalents of solar radiation, required to sustain industrial and ecological systems. It treats all systems as networks of energy flow and organizes them hierarchically according to their energy quality. An important and powerful feature of emergy analysis is that it accounts for all possible inputs, including the contribution of ecological products and services. Unfortunately, emergy analysis has encountered a lot of resistance and criticism, particularly from economists, physicists, and engineers. Typical criticisms refer to controversial claims and sweeping generalizations about its relevance to economics and self-organized systems. Fur-

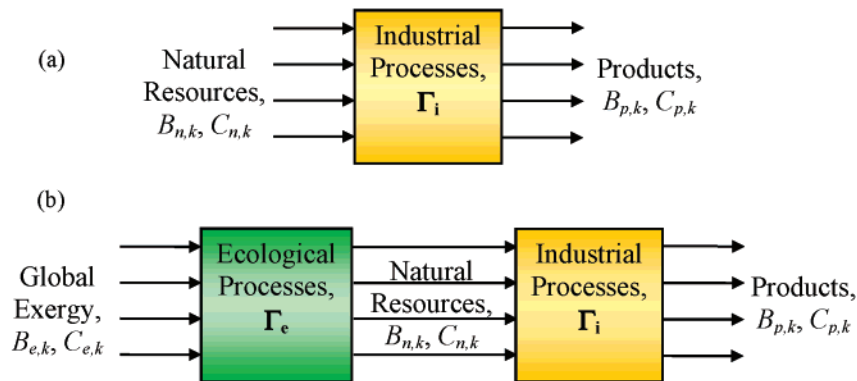* Corresponding author phone: 614-292-4904; fax: +614-292-3769; e-mail: bakshi.2@osu.edu.

FIGURE 1. (a) Industrial Cumulative Exergy Consumption (ICEC) analysis; (b) Ecological Cumulative Exergy Consumption (ECEC) analysis.

thermore, details about the techniques for determining the emergy of various streams and in a network have been difficult to find. Consequently, emergy analysis is often misunderstood and has not been used outside a small group of researchers (see (*24*) and references therein).

Considering the importance of accounting for the contribution of ecosystems and the obstacles hindering broader use of emergy, this paper starts with traditional or industrial CEC analysis, and expands it to include the contribution of ecosystems. Traditional or Industrial Cumulative Exergy Consumption (ICEC) analysis considers only the exergy content of the natural resource inputs needed for a process. The approach proposed in this article determines the Ecological Cumulative Exergy Consumption (ECEC) which also includes the exergy consumed by ecological processes to produce the raw materials, dissipate the emissions, and functioning of industrial processes. A systematic algorithm is presented for ECEC computation. Comparison of ECEC with emergy indicates that the two concepts are closely related. In fact, *ECEC becomes equivalent to emergy if the analysis boundary, allocation approach, and method for combining global energy inputs are identical.* Such explicit identification of the link between exergy and emergy should clear much of the confusion and misunderstanding about both concepts, and enable combination of the best features of both methods. This insight is used in this article to devise practical ways of combining emergy and exergy analyses to include the contribution of ecological inputs to industrial processes, without being handicapped by the controversial aspects of emergy analysis (*24*). The general approach in this paper is illustrated with the examples of the chlor−alkali process and solar and coal-based processes for generating electricity. These examples demonstrate the benefits of accounting for nature's inputs, and the unique insight about sustainability that may result from such accounting.

2. Background

2.1 Cumulative Exergy Consumption Analysis.
Definition 1. Exergy, *B*, is a measure of the maximum amount of useful energy that can be extracted when matter is brought to equilibrium with its surroundings.

Although energy is neither created nor destroyed, it is converted from useful to useless as work is performed. For instance, kinetic energy is converted into dissipated heat through friction as a fluid is transported in a pipeline. In the process, exergy is lost as useful energy is consumed or converted. Therefore, exergy is a better measure of the quality of energy than energy because it represents the real potential of a system to do work. Exergy analysis determines how much exergy is consumed in the process and how efficient the system is in producing work. A more detailed introduction to exergy analysis is provided in the Supporting Information.

Some shortcomings of exergy analysis are that it ignores critical inputs such as capital and labor, and is narrow in scope due to its focus on the process while ignoring the performance of the rest of the production chain. Extensions of exergy analysis such as CEC (*13*), Thermoeconomics (*25*), and Extended Exergy Accounting (*15*) address some of these shortcomings. Figure 1a depicts a traditional or ICEC analysis. A stream is considered to be a natural resource if it is a direct product from ecological processes and a raw material for human activities, for example, coal, iron, and fresh water.

Definition 2. ICEC of a process is the sum of the exergy of all the natural resources consumed in all steps of the process and previous processes in the production chain.

In general, ICEC of the production chain, C_p, is

$$C_p = C_n = \sum_{k=1}^{N_i} C_{n,k} \tag{1}$$

where N_i denotes the number of process units included in the industrial production chain, and $C_{n,k}$ and $C_{p,k}$ are, respectively, the cumulative exergy of the natural resource entering and of the product leaving the *k-th* process unit. To apply the input−output network algebra developed in Section 4, each unit in the network is considered to have only one external input and output. These "final demand" and "value added" streams represent the sum of the exergy of all natural resources entering or final products leaving a single unit. ICEC analysis considers exergy and cumulative exergy of natural resource inputs to be equal, that is,

$$C_{n,k} = B_{n,k} \tag{2}$$

Definition 3. Industrial Cumulative Degree of Perfection (ICDP), η, is the ratio of the exergy of the final product(s) to the cumulative exergy consumed to make the product(s).

$$\eta_p = \frac{\sum_{k=1}^{N_i} B_{p,k}}{\sum_{k=1}^{N_i} C_{n,k}} = \frac{B_p}{C_p}; \quad \eta_{p,k} = \frac{B_{p,k}}{C_{p,k}} \tag{3}$$

where η_p and $\eta_{p,k}$ represent the ICDP of the production chain and the *k-th* product, respectively. Equation 3 may also be written as

$$\mathbf{C_p} = \eta_p^{-1} \cdot \mathbf{B_p} \tag{4}$$

where $\mathbf{B_p}$ is the vector of product exergies, $B_{p,k}$, $\eta_\mathbf{p}$ is the $N_i \times N_i$ diagonal matrix with $\eta_{p,k}$ forming the diagonal terms, and $\mathbf{C_p}$ is the vector of product CEC, $C_{p,k}$. The approach for

computing CEC of each product stream is discussed in detail in Section 4. In general, the relationship between CEC for each product, $C_{p,k}$, and CEC of the inputs, $C_{n,k}$, may be written as

$$\mathbf{C_p} = \mathbf{\Gamma_i} \cdot \mathbf{C_n} \qquad (5)$$

where $\mathbf{C_n}$ is the vector of input CEC, $C_{n,k}$, and $\mathbf{\Gamma_i}$ is the $N_i \times N_i$ allocation matrix. This matrix represents the exergy flow network and the selected allocation method. More details about allocation are provided in Section 4.2.

ICEC analysis shares some features of LCA as both methods consider, to some extent, the life cycle of the product. Unlike LCA, ICEC analysis ignores emissions and their impact. ICEC analysis has been widely used and calculations for many industrial processes are available (*13*).

2.2 Emergy Analysis. Emergy analysis emphasizes the importance of treating all products and services in terms of a common exergetic basis. Between identical quantities of wood and solar exergy, the former is of higher quality because it is more concentrated and easier to harness. Consequently, for a fair comparison of different types of exergy, they should be compared on the same basis, as equivalents of exergy of the same kind per unit of ability to do work. Emergy analysis considers all systems, ecological and economic, as a vast energy network which transform the global energy inputs into other kinds of energy, and ultimately into work and dissipated heat. The work produced sustains the dynamics of the planet. The global energy inputs are solar insolation, deep earth heat, and tidal energy. Because incoming energy from solar insolation is considerably larger than that from the other two sources, equivalents of this energy are selected as the common basis.

Definition 4. Solar Emergy is the available solar energy used up directly and indirectly, through multiple pathways and subsystems, to create a service or product (*22*).

Definition 5. Solar Transformity is the solar emergy required to make one Joule of an available service or product (*22*).

Solar emergy and solar transformity are measured in solar-equivalent joules (sej) and sej/J, respectively. Because solar energy serves as the basis for emergy analysis, its transformity is defined to be unity. Emergy and exergy are related through transformity as

$$M = \tau B \qquad (6)$$

where M is emergy, τ is transformity, and B is exergy. When an energy carrier flows through an ecological or industrial chain, its exergy per unit of emergy decreases due to entropy production along the chain, causing its transformity to increase. Because exergy tends to concentrate as it advances through the chain, transformity has been regarded as a measure of quality, particularly of ecological products which have been subjected to "optimization" due to evolutionary pressure. However, the relation between transformity and quality of energy may be much weaker for industrial systems. Thus, the higher quality of wood versus solar exergy is reflected by the higher transformity of wood. Values of transformity for many ecological and economic goods and services have been calculated (*22, 26*), and details of some typical calculations are shown in the Supporting Information. Odum and co-workers have used emergy analysis for analyzing ecological and economic systems. These methods account for all types of inputs, including labor and services, in terms of emergy.

Emergy analysis is one of the very few methods that accounts for the contribution of ecological products and services to economic activity. However, it has not been used much outside a small circle of researchers due to controversy surrounding extremely broad claims about the relevance of emergy to economic value and self-organization, and misunderstanding due to many years of inadequate access to details about its computation and approach. Additional details about these issues are discussed elsewhere (*24*). The rest of this paper proves the close link between exergy and emergy. This indicates that information about the thermodynamics of ecosystem goods and services compiled by emergy analysts can be readily used to include the contribution of ecosystem goods and services to economic activity. This can be done without succumbing to the main controversial aspects of emergy analysis including the emergy theory of value, the maximum empower principle, and the inclusion of prehistoric energy.

3. Including Ecological Inputs in Exergy Analysis

3.1 Ecological Cumulative Exergy Consumption. Ecological processes convert global exergy inputs into ecological goods and services that are converted into economic goods and services by industrial processes. Including ecological processes requires expansion of the system boundaries of ICEC analysis. Thus, Figure 1a needs to be expanded by including the exergy consumption of ecological processes, as shown in Figure 1b. The exergy and cumulative exergy of inputs that drive ecological processes are represented as $B_{e,k}$ and $C_{e,k}$, respectively.

Eq 2 does not hold anymore for Figure 1b. In fact, exergy and CEC of natural resources, $\mathbf{B_n}$ and $\mathbf{C_n}$ respectively, can be related through an equation similar to eq 4

$$\mathbf{C_n} = \mathbf{\eta_n}^{-1} \cdot \mathbf{B_n} \qquad (7)$$

where $\mathbf{\eta_n}$ is the $(N_i + N_e) \times (N_i + N_e)$ diagonal matrix with $\eta_{n,k}$ forming the diagonal terms. N_e denotes the number of units included in the ecological supply chain. As mentioned in Section 2, the number of inputs and outputs is equal to the total number of units because each unit has one external input and output. Variable $\eta_{n,k}$ represents the efficiency with which ecological processes create the natural resource entering the *k-th* process unit from global exergy inputs. Clearly, as indicated by eq 2, ICEC analysis implicitly assumes that these efficiencies are unity, consequently ignoring ecological processes. On the basis of Figure 1b, the exergy consumed in ecological processes to produce the natural resources and that for converting natural resources to industrial products may be written as

$$\mathbf{C_n} = \mathbf{\Gamma_e} \cdot \mathbf{C_e} \text{ and } \mathbf{C_p} = \mathbf{\Gamma_i} \cdot \mathbf{C_n} \qquad (8)$$

$\mathbf{\Gamma_e}$ and $\mathbf{\Gamma_i}$ are the allocation matrixes for mapping ecological inputs to natural resource outputs and natural resources to industrial products, respectively. The cumulative exergy consumption in ecological and industrial processes (ECEC) to create each product may be written as

$$\mathbf{C_p} = \mathbf{\Gamma} \cdot \mathbf{C_e} \qquad (9)$$

where $\mathbf{\Gamma}$ represents the overall allocation matrix for ecological and industrial processes together. Whether $\mathbf{\Gamma}$ is equal to the product of $\mathbf{\Gamma_e}$ and $\mathbf{\Gamma_i}$ or not depends on the allocation method, as elaborated in Section 4.2. Alternate equations for ECEC may also be written as follows by combining eqs 7 and 8

$$\mathbf{C_p} = \mathbf{\Gamma_i} \cdot \mathbf{\eta_n}^{-1} \cdot \mathbf{B_n} \qquad (10)$$

The total ECEC for the ecological−industrial production chain in Figure 1b may be written as

$$C_p = C_n = C_e = \sum_{k=1}^{N_i + N_e} C_{e,k} \qquad (11)$$

Eqs 9–11 indicate that determining the total ECEC, C_p, requires knowledge of $B_{n,k}$, and $\eta_{n,k}$, whereas determining the ECEC of each product, $C_{p,k}$ requires the allocation matrix, Γ. Similarly, determining the CDP of ecological processes requires the allocation matrix, Γ_e and the ecological inputs, $B_{e,k}$. The allocation matrix, Γ, depends on the network and the selected allocation method, for partitioning cumulative exergy between multiple outputs.

The ecological inputs, $B_{e,k}$, represent global inputs such as solar, tidal, and deep earth exergy. Equations analogous to eqs 4 and 7 may calculate the CEC of global inputs as

$$\mathbf{C_e} = \eta_e^{-1} \cdot \mathbf{B_e} \text{ or } C_{e,k} = \eta_{e,k}^{-1} B_{e,k} \qquad (12)$$

Eq 12 is important for connecting exergy and emergy, as shown in Section 3.2. Here, $\eta_{e,k}$ may equal unity if such inputs are assumed to be directly available without any previous transformation, or if they represent exergy of the same type (quality). This assumption does not ignore any known processes, unlike the assumption of ICEC analysis represented by eq 2. Alternatively, proportionality constants may be assigned to $\eta_{e,k}$ if one global input is to be expressed in equivalents of another, as done in emergy analysis. Equations 9–11 provide alternate ways of estimating the ECEC of products from any production chain.

3.2 Relation Between ECEC and Emergy. Deriving the exact relationship between ECEC and emergy and conditions for their equivalence relies on writing matrix equations for emergy analysis of a network followed by comparing the equations to those derived for ECEC in Section 3.1. Equation 6 relating emergy and exergy may be written in matrix form as

$$\mathbf{M_p} = \mathbf{T_p} \cdot \mathbf{B_p} \qquad (13)$$

where $\mathbf{M_p}$ and $\mathbf{B_p}$ are vectors of emergy and exergy and $\mathbf{T_p}$ is the diagonal matrix of transformities. For a network similar to that considered for ICEC analysis, $\mathbf{M_p}$, may be calculated as

$$\mathbf{M_p} = \Gamma_i' \cdot \mathbf{M_n} \qquad (14)$$

where $\mathbf{M_n}$ is the emergy vector of the natural resources and Γ_i' is the allocation matrix for emergy analysis. As in ECEC analysis, Γ_i' contains information about the allocation rule for emergy, that is, how emergy is assigned among splits, coproducts, and joints. Similarly, the emergy of natural resources, $\mathbf{M_n}$, can be calculated as

$$\mathbf{M_n} = \Gamma_e' \cdot \mathbf{M_e} \qquad (15)$$

Eqs 14 and 15 are analogous to eq 8 for ECEC analysis. As shown in eq 6 and 13, the emergy and exergy of global inputs are related as

$$\mathbf{M_e} = \mathbf{T_e} \cdot \mathbf{B_e} \qquad (16)$$

where, $\mathbf{T_e}$ represents the solar transformities of global inputs. Combining eqs 14, 15, and 16, and using an overall allocation matrix, Γ' analogous to that in eq 9

$$\mathbf{M_p} = \Gamma' \cdot \mathbf{T_e} \cdot \mathbf{B_e} \qquad (17)$$

For ECEC and emergy to be equivalent, eq 18 must be satisfied

$$\mathbf{C_p} = \mathbf{M_p} \qquad (18)$$

Eqs 4, 13, and 18 show that transformity is the reciprocal of the cumulative degree of perfection.

$$\mathbf{T_p} = \eta_p^{-1} \qquad (19)$$

Furthermore, eqs 9, 12, 17, and 18 imply that

$$\Gamma \cdot \eta_e^{-1} = \Gamma' \cdot \mathbf{T_e} \qquad (20)$$

For a fair comparison, it is essential for both ECEC and emergy to have the same analysis boundary that considers the same network of processes. Second, if the allocation rule used by emergy and cumulative exergy analysis is identical, then $\Gamma = \Gamma'$. Under these conditions, eq 20 reduces to

$$\eta_e^{-1} = \mathbf{T_e} \qquad (21)$$

This analysis indicates that ECEC and emergy are identical if cumulative exergy and emergy use the same approach for combining global energy inputs. Alternate approaches include directly adding global energy inputs (using a unit transformity), or representing global energy inputs in solar equivalents using the transformities estimated in emergy analysis. Thus, the condition for equivalence between emergy and ecological cumulative exergy consumption is as follows.

Ecological cumulative exergy consumption and emergy are equivalent if the following are identical: (a) analysis boundary, (b) allocation method, and (c) approach for combining global energy inputs.

This condition shows that ecological cumulative exergy consumption and emergy are very closely related. Moreover, it justifies the use of the reciprocal of transformity to estimate the CDP of natural resources, as in eq 19. The illustrations in Section 5 are based on this insight.

There remain conceptual differences between emergy and ECEC analyses. ECEC analysis does not imply any relationship with economic value. In fact, ECEC analysis can complement economic analysis. Legitimacy of Odum's maximum empower principle is irrelevant for the applicability of ECEC analysis. There are clear links between ECEC and other thermodynamic quantities. Representing global exergy inputs in equivalents of solar energy is not necessary albeit convenient. ECEC faces quantification challenges similar to those of emergy, but these challenges are no different from those faced by any holistic approach including Life Cycle Assessment (*24*).

4. ECEC Computation

The equations for ECEC analysis given in Section 3 do not provide adequate details about how ECEC may be computed in practice. This section addresses practical issues such as allocation and network algebra followed by a formal algorithm for ECEC analysis.

4.1 Network Representation and Algebra. The network algebra of input–output analysis provides a convenient and rigorous way of analyzing flow in any network. For such analysis, it is convenient to set up the original process flowchart such that each unit has only one external input and output that goes outside the network. Dummy units may be created to satisfy this requirement as shown in the Supporting Information. For any network, the vector of CEC of the process units, $\mathbf{C}$, can be calculated via input–output analysis as

$$\mathbf{C} = (\mathbf{I} - \gamma^{\mathbf{T}})^{-1} \cdot \mathbf{C_n} \qquad (22)$$

Here, γ is the matrix of transaction coefficients representing the interaction between units, and $\mathbf{C_n}$ is the vector of CEC of natural resources (see Supporting Information for detailed derivation of these equations). Furthermore, the vector of
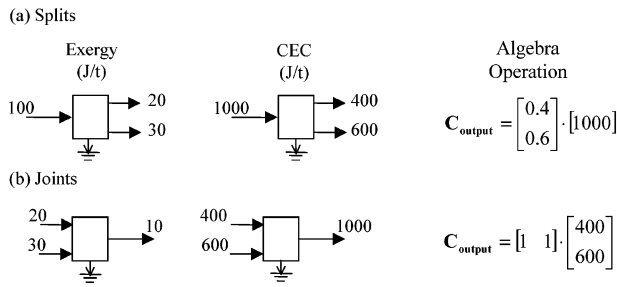
FIGURE 2. Allocation in industrial systems: (a) for splits; (b) for joints.

FIGURE 3. Allocation in partially known systems: (a) for splits; (b) for joints.

CEC of products, $\mathbf{C_p}$, is related to the vector of CEC of natural resources as

$$\mathbf{C_p} = \gamma_\mathbf{p} \cdot (\mathbf{I} - \gamma^\mathbf{T})^{-1} \cdot \mathbf{C_n} \qquad (23)$$

where $\gamma_\mathbf{p}$ is a diagonal matrix with coefficients representing the fraction of a unit's CEC leaving the system forming the elements along the diagonal. Use of this network representation and algebra for computing the CEC and ECEC of any network depends on the allocation approach, as discussed next.

4.2 Allocation. Because most industrial and ecological processes have multiple outputs, it often becomes necessary to allocate or partition the inputs between multiple outputs. Because of its subjective character, a variety of methods have been suggested for allocation. These are based on the market value, mass, energy or exergy content, and energy quality of the outputs. Techniques for avoiding allocation by modifying the system have also been suggested (27) and are recommended in the ISO 14000 standards (28).

Allocation in Fully Defined Networks. Allocation according to the exergy of output streams is popular in ICEC analysis (13, 29). In this approach, the cumulative exergy of an output stream from unit i to unit j, C_{ij}, is

$$C_{ij} = \gamma_{ij} C_i$$

where

$$\gamma_{ij} = \frac{B_{ij}}{\sum\limits_j B_{ij} + B_{p,i}} \qquad (24)$$

where γ_{ij} is the transaction coefficient from unit i to unit j, B_{ij} is the exergy delivered from unit i to unit j, and $B_{p,i}$ is the product stream from unit i. Product streams, $B_{p,i}$, are output streams that leave the system. Figure 2a shows the allocation based on eq 24. As shown in Figure 2b, when the streams allocated according to this scheme are combined, their CEC can be added. Equations 5 and 23 show that the allocation matrix for all industrial processes is

$$\Gamma_\mathbf{i} = \gamma_\mathbf{p} \cdot (\mathbf{I} - \gamma^\mathbf{T})^{-1} \qquad (25)$$

This allocation approach relies on detailed knowledge of the network and outputs for allocation. Its benefits are that cumulative exergy follows laws of conservation, making the algebra quite straightforward, intuitive, and consistent with widely used network algebra.

Allocation in Partially Defined Networks. If knowledge about the network structure and its outputs is not available, it is not possible to use eq 24 for allocating the cumulative exergy consumption to the outputs. For instance, Figure 3a shows a system where only two outputs are fully defined, whether there are more ou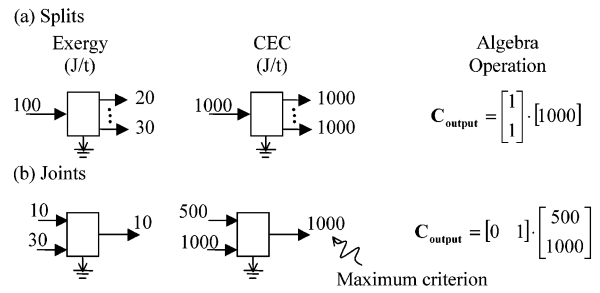tputs or not is unknown, portrayed by the triple dots between the known outputs. Even if the existence of additional outputs was known, it is often not possible to know their exergy content or network. This is usually the case with ecosystems, as complete knowledge about the ecological network and its goods and services is not available. One strategy for such partially defined systems is to avoid allocation entirely, and consider the exergy consumption of the process to be essential for making each product. Figure 3 illustrates this allocation approach. The main advantage of this approach is that the transaction matrix, γ, can be defined by ignoring the unknown streams without losing information. However, because this allocation scheme violates conservation, special care is needed to avoid double counting when outputs from such systems are combined. If the input streams originate from a partially known system like that in Figure 3a, adding their cumulative exergy consumption will result in double counting. If the streams are known to follow the allocation scheme shown in Figure 3a, then the approach shown in Figure 3b, referred as maximum criterion, is used for combining streams. This avoids double counting by considering only the largest cumulative exergy of the set of inputs from a system under allocation scheme described in Figure 3. However, if the combined streams represent cumulative exergy over different temporal horizons, they may be added without double counting.

A similar allocation approach is used in emergy analysis (22) for determining the transformities of many ecological products and services as well as for allocation between "coproducts", even in fully defined networks. Odum's justification for using this allocation approach is that inputs cannot be allocated among coproducts because they cannot be produced independently by using a fraction of the process' exergy consumption. Emergy analysis also selects the allocation approach depending on whether the products are of same or different energy quality, which is reflected in the transformities, and whether they are produced over different time horizons. Thus, in general, "renewable" resources are considered to be nonadditive, whereas "nonrenewable" resources are additive. Although this is a legitimate and appealing approach, it has been the source of much confusion because it can cause the results of emergy analysis to change with the selected analysis boundary, and as more details become available (24). In this paper, the allocation approach depicted in Figure 3 is used only for those ecological goods and services where details about the network and products are unknown. The sensitivity of the results to the allocation method and techniques for avoiding allocation altogether are subjects of ongoing research.

4.3 Algorithm for ECEC Analysis. Given an industrial network consisting of the main process and relevant processes in the supply chain, an exergy flow diagram can be derived by considering the main process units and calculating the exergy of each stream. The algorithm shown in Table 1 is for ECEC of a network of N units, where every unit delivers no more than one stream to another unit and has only one

TABLE 1. General ECEC Analysis Algorithm

```
1    MAINPROGRAM, ECEC_Analysis
2      FOR i = 1 TO N
3        INPUT B_{n,i}
4        INPUT B_{p,i}
5        INPUT η_{n,i}
6        FOR j = 1 TO N
7          INPUT B_{ij}
8        END
9      END
10     FOR i = 1 TO N
11       FOR j = 1 TO N
```

12
$$\gamma_{ij} = \frac{B_{ij}}{\sum_j B_{ij} + B_{p,i}}$$

13   **END**

14
$$\gamma_{p,i} = \frac{B_{p,i}}{\sum_j B_{ij} + B_{p,i}}$$

```
15     END
16     γ = MATRIX (γ_{ij})
17     B_n = VECTOR (B_{n,i})
18     B_p = VECTOR (B_{p,i})
19     η_n = DIAGONAL MATRIX (η_{n,i})
20     γ_p = DIAGONAL MATRIX (γ_{p,i})
```

21     $\mathbf{\Gamma_i} = \mathbf{\gamma_p} \cdot \left(\mathbf{I} - \mathbf{\gamma^T}\right)^{-1}$

22     $\mathbf{C_n} = \mathbf{\eta_n}^{-1} \cdot \mathbf{B_n}$

```
23     PRINT "Can natural resource streams
         be added (system is fully specified)?"
24     INPUT Q
25     IF Q = "no" THEN
26       GO TO MaxSelect
27     END
```

28     $\mathbf{C_p} = \mathbf{\Gamma_i} \cdot \mathbf{C_n}$

```
29     PRINT C_p
30   END
```


FIGURE 4. Illustrative example of ECEC analysis.

TABLE 2. Subprogram for Avoiding Double Counting

```
31   SUBPROGRAM, MaxSelect
32     FOR i = 1 TO N
33       FOR r = 1 TO (N-1)
34         k = r
```
35         $a_{ik} = (\mathbf{\Gamma_i})_{ik} \cdot C_{n,k}$
```
36         FOR j = (r+1) TO N
37           PRINT "Are inputs " k " and " j " additive?"
38           INPUT Q
39           IF Q = "yes" THEN
```
40             $a_{ij} = (\mathbf{\Gamma_i})_{ij} \cdot C_{n,j}$
```
41             IF a_{ij} > a_{ik} DO
```
42               $(\mathbf{\Gamma_i})_{ik} = 0$
```
43               k = j
44             END
```
45   **OTHERWISE** $(\mathbf{\Gamma_i})_{ij} = 0$
```
46           END
47         END
48       END
49     END
50   END
```

input stream and one output stream crossing the system boundaries. The approach also requires values of CDP or transformity of the relevant inputs from the ecosystem.

The ECEC algorithm can use one or both allocation methods illustrated in Figures 2 and 3. When CEC of natural resource streams can be added, the allocation matrix and CEC of products are calculated with eqs 25 and 10, respectively. When natural resource inputs cannot be added, the maximum criterion described in Section 4.2 is applied to decide the CEC of the products. The algorithm is shown in Table 2. The j-th column of the allocation matrix contains the fraction of CEC of the j-th natural resource assigned to each product. The algorithm multiplies each column of the allocation matrix by the ECEC of its corresponding natural resource. Then, all numbers of the set of non-additive inputs in each row, except the maximum, are set to zero. This algorithm is also equivalent to doing separate ECEC analyses for each natural resource input to obtain multiple ECEC values at each network edge corresponding to each ecological input. The ECEC values at each edge are added for additive ecological inputs, or the maximum value is taken for nonadditive natural resources. The allocation methods and formal algorithm presented in this section avoid the confusing algebra that has plagued emergy analysis, without sacrificing the ability of emergy analysis to account for ecological inputs.

4.4 Illustrative Example. The ECEC approach is illustrated via a simple network shown in Figure 4 (see Supporting Information for details about application of the algorithm). The two natural resource inputs are assumed to be from the same ecological processes, and cannot be added. The ECEC for each natural resource is shown in parentheses below each network edge in Figure 4, and is propagated independently through the network. The input ECEC is allocated on
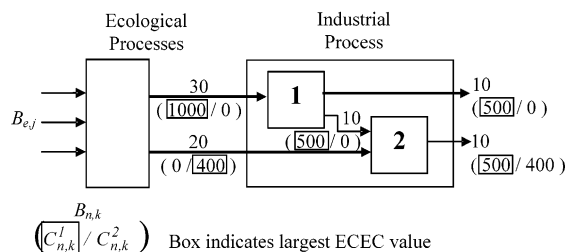
the basis of exergy in unit 1. Because the ECEC values from the two resources cannot be added, the ECEC at each edge is the maximum value that is in the box. However, if the inputs were additive, the result at each edge would be the sum of the ECEC values in the corresponding parentheses.

5. Examples

These examples illustrate the application of ECEC analysis to processes after completing their ICEC analysis. The first example illustrates the large contribution from ecosystems to a typical chemical process that is ignored by ICEC analysis. The second example compares electricity generation by solar thermal versus coal thermal power plants. Both examples consider a narrowly defined boundary, and ignore labor and capital requirements, and the impact of emissions. Consequently, these analyses *cannot* be used for decision or policy making, but simply serve to illustrate the direct extension of ICEC to ECEC via transformities. Furthermore, as standard emergy analysis accounts for labor and capital requirements, equivalence between standard emergy analysis and the ECEC results of this section requires a broader boundary. More holistic analysis of these processes along with metrics for comparing the impact and sustainability of industrial processes are topics of ongoing research.

5.1 Chlor-Alkali Process by Mercury Cell. A simplified flow diagram of selected processes from the extraction of natural resources to three products, sodium hydroxide, hydrogen, and liquid chlorine, and a byproduct, dilute sulfuric acid is shown in Figure 5 (*30*). This process has four inputs: water, salt, coal, and sulfur. The exergy and ECEC are indicated on each stream of Figure 5, with ECEC surrounded by parentheses (see Supporting Information for details about applying ECEC analysis). The exergy, ECDP or reciprocal of transformity, and ECEC calculated via eq 7 are listed in Table
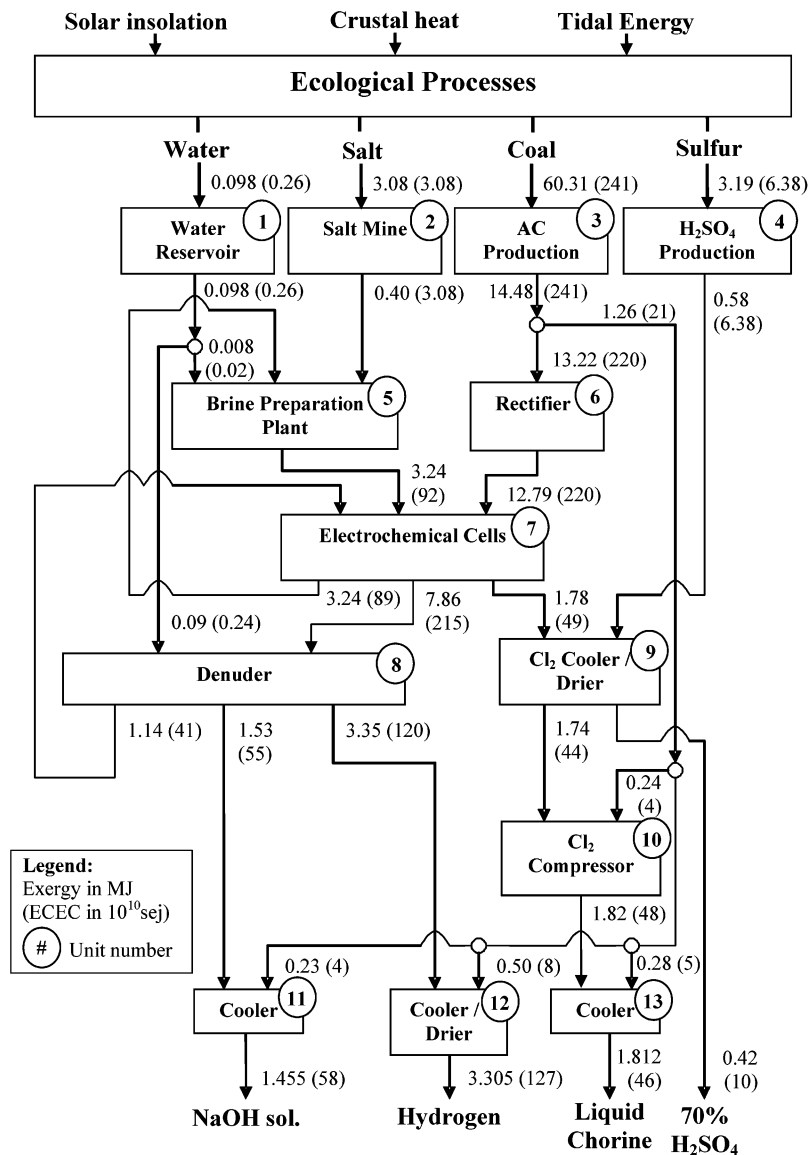
FIGURE 5. Flow diagram of the mercury cell process.

TABLE 3. ECEC of Mercury Cell Process

i	stream material	B_i (MJ)[a]	$\eta_i = 1/\tau_i$ (10^{-5} J/sej)	C_i (10^{10} sej)
$n,1$	water reservoir	0.098	3.717[b]	0.26[c]
$n,2$	salt mine	3.08	10.000[b]	3.08[c]
$n,3$	coal (for electricity)	60.31	2.500[b]	241.24[c]
$n,4$	sulfur (for H$_2$SO$_4$)	3.19	5.000[b]	6.38[c]
n	*overall*	*66.68*		*247.62*
$p,11$	NaOH sol	1.455	0.248[d]	58.60[e]
$p,12$	hydrogen	3.305	0.258[d]	128.25[e]
$p,13$	liquid chlorine	1.812	0.345[d]	52.58[e]
$p,9$	70% H$_2$SO$_4$ (waste)	0.420	0.396[d]	10.60[e]
p	*overall*	*6.992*	*0.282[d]*	*247.62*

[a] Morris (*30*). [b] Odum (*22, 26*). [c] Eq 7. [d] Eq 3. [e] Algorithm in Table 1.

3. All the inputs are derived from the earth main sources, namely solar insolation, crustal heat, and tidal energy. Water, salt, and sulfur are considered to originate from the sedimentary earth and hydrological cycles, calculated on a yearly basis in ref *26*. Because they follow the allocation for partially defined networks described in Section 4.2, their ECEC cannot be added when combined. However, ECEC of coal can be added because it belongs to a different temporal horizon. With different approaches for obtaining the transformities of these natural resources, alternate methods could be used for their combination. For example, all four inputs should be added if they are partitioned as in fully defined networks, as done in ref *22* for geological products, or come from different temporal horizons. Ideally, the sensitivity of the results to these variations should be evaluated. Results of the ECEC analysis are provided in Table 3.

The overall analysis shows that ICEC is 66.68 MJ for the mercury cell process, resulting in a ICDP of 10.5 %. In contrast, the ECEC is 247.62 × 10^{10}sej, and the ECDP is 2.82 × 10^{-6}J/sej. This example shows that accounting for the exergy consumed in ecological processes can change the numbers by as much as 5 orders of magnitude, which confirms the huge contribution of ecosystems due to ecological processes that convert low-quality energy into high-quality raw materials. This indicates that focusing only on the industrial processes from resource extraction onward may be too narrow for life cycle or sustainability assessment.

5.2 Electricity from Coal versus Solar Energy. This example compares electricity generation via solar-based versus coal-based thermal processes. It relies on ICEC analysis data provided by Szargut et al. and Horlock (*13, 31*). Like
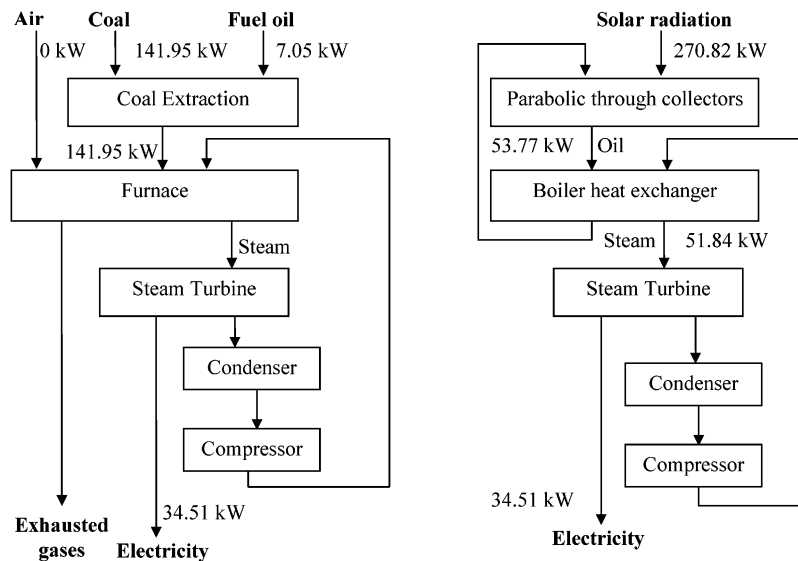
FIGURE 6. (a) Exergy flow diagram for a coal-driven power plant; and (b) exergy flow diagram for a thermal solar power plant.

TABLE 4. ICEC Analysis of Solar and Coal-Based Power Plants

electricity from	C_p (kW)[a]	η_p (%)[b]
coal	149.00	23.2
solar energy	270.82	12.7

[a] Eq 1. [b] Eq 3.

TABLE 5. ECEC Analysis of Solar and Coal-Based Power Plants

electricity from	C_p (10^3 sej/s)[a]	η_p (10^2 J/sej,%)[b]
coal	6,058,624.40	0.0006
solar energy	270.82	12.7

[a] Eq 10. [b] Eq 3.

ICEC analysis, this example also ignores emissions and their impact, capital inputs such as equipment and land, and human resource inputs such as labor. Consequently, this analysis is not holistic enough to permit decisions about either approach. However, it does illustrate the approach developed in this paper.

Figure 6a shows the exergy flow diagram of a coal-driven steam power plant. An additional 7.05 kW of exergy from fuel oil is required to extract 141.95 kW of coal from the ground. Coal is mixed with air in a combustion chamber to heat the steam that moves the turbine that produces the electricity. To complete the Rankine cycle, the partially condensed steam is recycled. Using eqs 1 and 3, the ICEC of the process is 149.00 kW and ICDP of the process is 23.2%.

Figure 6b shows the exergy flow diagram of a photothermal steam power plant. A network of parabolic through-collectors receives exergy of 270.82 kW in the form of solar radiation. The collectors concentrate the solar radiation on the receivers to heat the working fluid, typically oil. The heat content of the oil is transferred to the steam, in the boiler heat exchanger. Data for this process were obtained from ref *32*. From eqs 1 and 3, ICEC of the process is 270.82 kW and ICDP of the process is 12.7%.

Table 4 summarizes the results of the ICEC analysis. Exergy of exhausted gases has been neglected for the case of the coal-driven power plant so exergy of natural resources are all allocated to electricity. The coal-driven power plant is more efficient as evidenced by a higher ICDP, and, from a traditional thermodynamic viewpoint, generating electricity from coal seems to be more efficient, due to its higher ICDP, than solar-based electricity.

For ECEC analysis, the ECDP or reciprocal of transformity values of solar radiation, coal, and fuel oil are 1 J/sej, 2.50 × 10^{-5} J/sej, and 1.85 × 10^{-5} J/sej, respectively. For the coal-based power plant, the ECEC of coal and fuel oil can be added. Table 5 summarizes the results after accounting for ecological goods and services. Because of the unit ECDP or

transformity of sunlight, the ECDP of the solar plant is equal to its ICDP. However, the ECDP of the coal-driven power plant is significantly lower due to the exergy invested by ecological services in coal and oil for converting it into a more concentrated and higher-quality source of energy. ECEC analysis now shows that photothermal electricity may be overwhelmingly thermodynamically superior to coal-based electricity. However, inclusion of the exergy consumption due to economic and capital inputs and the impact of emissions may have a large effect on these numbers, and is necessary before reaching any conclusions about comparing these technologies. Further extensions to include the contribution of indirect activity in the economic network are also essential for improving the accuracy of the results. A variety of existing methods may be useful for meeting these challenges (*15, 22, 33*).

This work is expected to help "bridge the gap between Ayres' industrial ecology and Odum's systems ecology" (*34*) and lead to new methods and insight for evaluating and improving the sustainability of industrial activity. Many opportunities are available for further work. The challenge of combining resources over multiple temporal and spatial scales plagues many holistic techniques, including the ones discussed in this paper. The transparency and utility of existing methods could be improved by developing a tiered system which distinguishes between resources according to their replenishment time. Instead of categorizing resources as renewable or nonrenewable, this system could separate resources according to their renewability over daily, short-cycle, long-cycle, or cosmological time scales. A similar spatial hierarchy could also be defined. Ideally, a systematic multiscale statistical framework is needed that considers differences in the quality (uncertainty) of data at multiple temporal and spatial scales, and combines these data in an "optimal" and transparent manner. Concepts of "opportunity" and "sunk" costs from economics could also be useful for considering opportunities and alternatives that may be lost due to a decision. Research in these and other related

areas is necessary for recognizing the full potential of thermodynamic methods for sustainability.

Acknowledgments

Supporting Information Available

Details of exergy analysis, calculation of transformities of main earth processes, network algebra for cumulative exergy consumption calculations and for the examples. This material is available free of charge via the Internet at http://pubs.acs.org.

Nomenclature

B	Exergy
$\mathbf{B}$	Vector of exergies
C	Cumulative exergy
$\mathbf{C}$	Vector of cumulative exergies
M	Emergy
$\mathbf{M}$	Vectors of emergies

Greek Letters

η	Cumulative degree of perfection
η	Diagonal matrix of CDP's
γ	Allocation coefficient
γ	Matrix of γ_{ij}'s
$\gamma_{\mathbf{p}}$	Diagonal matrix of $\gamma_{p,k}$'s
Γ	Allocation matrix
τ	Transformity
$\mathbf{T}$	Matrix of transformities

Sub-indices

e,k	Global energy input to unit k
$\mathbf{e}$	Global energy inputs or ecological processes
ij	from unit i to unit j
$\mathbf{i}$	Industrial processes
n,k	External input to unit k
$\mathbf{n}$	Natural resource
p,k	External output from unit k
$\mathbf{p}$	Product

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