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Assessing the Capacity of Local Ecosystems to Meet Industrial Demand for Ecosystem Services

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Abstract

Despite the importance of ecosystems, engineering activities continue to ignore or greatly undervalue their role. Consequently, engineered systems often overshoot nature's capacity to support them, causing ecological degradation. Such systems tend to be inherently unsustainable, and they often fail to benefit from nature's ability to provide essential goods and services. This work explores the idea of including ecosystems in chemical processes, and assesses whether such a techno-ecological synergistic system can operate within ecological constraints. The demand for ecosystem services is quantified by emissions and resources used, while the supply is provided by ecosystems

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on the manufacturing site. Application to a biodiesel manufacturing site demonstrates that ecosystems can be economically and environmentally superior to conventional technologies for making progress toward zero emissions and net positive impact manufacturing. These results highlight the need for shifting the paradigm of engineering from that of dominating nature to embracing nature and respecting its limits.

Introduction

Like most disciplines, engineering has also developed with the implicit assumption that ecological systems have nearly endless capacity to provide resources and absorb wastes. Not only has engineering greatly undervalued the role of nature, its goal had been stated more than a century ago to be "the control of nature by man" and to "replenish the earth and subdue it".[1] This attitude has served humanity quite well as evidenced by many advances and conveniences that have enhanced human well-being by controlling and manipulating nature. Examples include straightening rivers to make them navigable; draining wetlands and clearing forests for farmland; agricultural technologies such as artificial fertilizers, pesticides, and genetic engineering for enhancing food production; and synthesizing new molecules that did not exist in nature but have beneficial properties such as refrigerants, pharmaceuticals, plastics, solvents, etc. However, large-scale use of many such products and technologies has also resulted in unintended harm due to unexpected side-effects. Examples include the ozone hole due to chlorofluorocarbon compounds; ecological toxicity of pesticides, pharmaceutical compounds and other synthetic molecules; aquatic deadzones due to fertilizer runoff; large floating islands of plastic trash in the world's oceans; and rising concentration of greenhouse gases in the atmosphere.

With increasing ability of engineering to control nature, combined with growth in population and consumption, today's world is quite different from the world when basic principles of science and engineering were developed. At that time, taking nature for granted may have been more justifiable since the impact of human activities on the biosphere was relatively small. However, the world of today is very different, and is so dominated by human activities that geologists are suggesting this to be a new epoch called the anthropocene.[2] Consequently, the engineering paradigm that was developed under the old worldview needs to adapt to the new reality of the anthropocene. Nature cannot be taken for granted and kept outside the engineering boundary any more. It must be included in engineering decisions to enable a new sustainable engineering that respects ecological constraints.[3]

Increasing environmental impact of chemical processes has been acknowledged over the last several decades, and much research has focused on new technologies and methods for reducing this impact.[4] Initial efforts for improving the environmental performance of process industries resulted in techniques like pinch analysis,[5] Mass Exchange Networks Synthesis,[6] waste minimization approaches[7] and the use of end-of-pipe solutions for reducing resource use and emissions from a manufacturing process. Other approaches such as the Waste Reduction (WAR) algorithm[8,9] focused on reducing toxic waste emissions, while more recent approaches aim to enhance eco-efficiency by reducing environmental impact per unit of production.[10,11] While these approaches have helped in reducing pollution at the unit operation level, incremental reductions at this scale do not always result in lower emissions at larger scales.[12] Furthermore, these efforts treated environmental protection as a constraint, and not an objective. Cano and McRae[13] extended this idea to designing chemical processes and emphasized the need to start accounting for environmental issues as a part of the objective itself, rather than as a constraint and this resulted in the use of multiobjective optimization approaches to solve large scale problems related to the design of chemical processes.

More recent efforts consider environmental impact not just due to the process but from its entire life cycle. These efforts rely on advances in methods such as Life Cycle Assessment (LCA)[14,15] and footprint analysis.[16,17] These methods have been used for process design with the help of multi objective optimization methods to incorporate life cycle environmental impacts along with monetary objectives.[18] Inclusion of life cycle environmental impact and conventional economic aspects in process design[19] is necessary to prevent the shifting of problems outside the analysis boundary, thus overcoming the common reason why engineering solutions meant to reduce environmental impact may often fail to do so. Life cycle thinking is also being incorporated in many areas of process synthesis[20,21] and process optimization.[22] More recently, advances in Sustainable Process Design (SPD) methods have been applied to a variety of process and supply chain problems including bioethanol and biorefinery design.[23–25] Geographical factors, location of farms, effect of using land for fuel versus food as well as market demands have also been incorporated in the design problems.

These studies rely mainly on information from process based LCA[26] for analyzing the life cycle impacts of a system and inventory obtained from process LCA account only for a small aspect of the entire life cycle of a process, neglecting flows and impacts from larger scales. The process under study is also treated as a black box without any consideration of interactions between processes at different scales. Thus in the design problems, effect of decisions made at the unit operation level on the life cycle scale and vice-versa are not usually accounted for.[27] Development of the Process-to-Planet framework[28,29] as an integrated multi-scale modeling technique overcomes these shortcomings by considering interactions between multiple scales in the life cycle of a system.

Another innovation to address the need for sustainable development of industries that has been gaining popularity is that of Industrial Symbiosis.[30,31] The underlying idea is that analogous to natural ecosystems, industries also need to move from a linear throughput of materials and energy to a closed-loop system with most materials getting recycled, thus reducing environmental damage. Networks of industrial processes are developed to optimize resource and energy usage among a cluster of industries. This has also led to the development of eco-industrial parks to facilitate exchange of by-products, resources and energy flows between industries located in the park.[32–34]

All these and other conventional design and assessment approaches are primarily concerned with reducing the impacts of processes within a large selected boundary. None of these methods consider the capacity of ecosystems to provide resources or absorb wastes.

Current design approaches based on life cycle and footprint methods focus on continuous improvement by reducing life cycle impacts per unit of product or doing "less bad",[11] which encourages technological status quo instead of breakthrough innovation that moves us away from inherently unsustainable activities.

The ability of ecosystems to satisfy human needs has been known for centuries and is being rediscovered by areas such as ecological engineering.[35] The resulting eco-technology[36,37] applications are most widely used in the restoration of lakes and rivers, development of sustainable agro-ecosystems, biomanipulation of species, and treatment of waste water. These systems are based on the self-designing capabilities of ecosystems with minimal technological interventions. Green infrastructure applications like relying on oyster reefs to enhance coastal resilience, green roofs and green buildings to reduce energy consumption in buildings are some other efforts that rely on ecological systems to meet human needs with smaller environmental impact.

In the chemical industry, wetlands have been used for treating wastewater.[38,39] However, such ecological engineering solutions are set up for end-of-the-pipe treatment. These applications rely on a limited range of services from nature, and lack systematic methods and tools for benefiting from synergies between technological and ecological systems.

With recent work on the goods and services provided by nature, their role in sustaining human well-being, and recognition of their dire state across the world,[40] some efforts are being directed toward accounting for the interactions between technological and ecological systems[41] by the application to residential systems[42] and bioenergy production systems[43] but until now no such work exists in the area of manufacturing . A framework for assessing and encouraging synergies between technological and ecological systems has been developed to consider systems at multiple spatial scales ranging from local to global.[44] This theoretical framework for Techno-Ecological Synergy (TES) aims to encourage synergies for small systems such as a house and its yard, a manufacturing process and its site, as well as larger scale systems that extend to consider the entire life cycle. This paper relies on the idea of

TES and develops ways of enhancing synergies between a local scale manufacturing process and the land around it. It explores the ability of local ecosystems on the site around a manufacturing process to supply goods and services demanded by the manufacturing activity. Thus the novelty of this work is in including ecosystems in process flowsheets and treating them in a manner analogous to unit operations. The resulting flowsheet is then analyzed to determine the economic and environmental feasibility of this techno-ecological synergistic system. This is the *first* effort, to the best of our knowledge, that includes ecosystems in a manufacturing process. Results of this study demonstrate the vast potential of developing this idea further as a step toward closed loop, circular, or self-contained manufacturing systems that can be "islands of sustainability" for at least some ecosystem services. This work is also a step toward shifting the engineering paradigm of previous centuries from that of dominating nature to a *twenty-first century paradigm* of learning from and working with nature.

The next section provides some background on ecosystem services and their role in supporting industrial activities. A general approach for assessing synergies between technological and ecological systems is then presented followed by a detailed case study that evaluates the practical feasibility of including ecosystems as unit operations in a manufacturing process.

Background

Ecosystem Services

Ecosystem goods and services, collectively called as ecosystems services, are benefits to humanity from nature including goods like food, fuel, fiber, and services like carbon sequestration, biogeochemical cycles, and disease regulation. The Millennium Ecosystem Assessment (MEA)[40] has classified ecosystem services into four categories shown in Figure 1: provisioning services like food and water; regulating services like air quality and flood regulation; cultural services like aesthetic and spiritual benefits; and supporting services like nutrient cycling and soil formation. Natural capital refers to the stock of natural ecosystems that can provide ecosystem goods and services depending on the ecosystems functioning. Thus, forest ecosystems and tree canopies are stocks of natural capital that can provide ecosystem services like climate and air quality regulation.

Human well-being is strongly linked to the flow of ecosystem services, making these goods and services critical for our sustainability. Some examples include pollination services for supporting food production, biogeochemical cycles for supporting carbon and nitrogen flows, and fisheries for supporting food and nutrition requirements. Industrial activities also interact with ecosystems and changes in ecosystems can directly and indirectly have an impact on its operation. Availability of mineral, fossil and freshwater resources is crucial for manufacturing and production, and at the same time, emissions and industrial waste can also impact the functioning of natural ecosystems.

Several tools have been developed over the years, for quantifying and valuing ecosystem services. Some of the popular tools include the EnviroAtlas[45] developed by the US EPA, ARIES (ARtificial Intelligence for Ecosystem Services)[46] and InVEST (Integrated Valuation of Ecosystem Services and Trade offs).[47] ARIES and InvEST are open source decision support tools for mapping and valuing goods and services provided by nature from the local to national level, and for identifying hot-spots or locations where investments in natural capital can enhance human development.

Currently the average value of world's natural capital is estimated to be close to $145 Trillion per year[48] for 17 different types of ecosystem services. Economists measure the value of these services by approaches such as the willingness of people to pay money to enhance or preserve ecosystems. In this regard, the concept of Payment for Ecosystem Services (PES) refers to schemes set up to offer incentives to those who manage and protect ecosystems that generate these services. However, while some ecosystem services like timber and fisheries that are sold in markets have a market value associated with it, most of the other services like regulating, supporting and cultural services lack a formal market and these services are severely undervalued. Most of these services are also affected by externalities and the value associated with ecosystems currently does not reflect it, posing a bigger challenge to ecosystems management decisions.

Over the last several decades, anthropogenic activities have resulted in the degradation of about two-thirds of the world's ecological systems. For instance, conversion of agricultural lands for industrial development, over-exploitation of freshwater resources by agriculture, industry and households, and disturbance of native ecosystem functions are some of the major consequences that exist today. Scientists also claim that three out of the nine biophysical planetary boundaries have already exceeded the 'safe operating zone for humanity', as a result of anthropogenic activities. This includes disruption of carbon and nitrogen cycles and loss of biodiversity, resulting in long term harm to society.[49] Studies such as the Millennium Ecosystem Assessment[40] highlight the importance of ecosystem services and emphasize on the urgent actions needed to enhance the conservation and sustainable use of ecosystems.

Ecosystem Services and Industrial Activities

Industrial systems depend directly and indirectly on the availability of ecosystem services for their functioning. They rely on inputs of natural resources like fossil fuels, minerals, timber, biomass and water for producing products and by-products while also generating emissions and wastewater. These emissions rely on services of air and water quality regulation for dissipation in the environment. Land, being a non-renewable provisioning service is also extensively used for setting up these manufacturing facilities and related activities like offices, buildings and warehouses.

Furthermore, industrial systems are also one of the major drivers of global environmental changes due to their impact on ecological systems that affects the generation of many ecosystem services. Emissions and wastes generated by these systems have had some detrimental impacts including pollution of waterways, air, and land causing human health problems.

Given the high inter-dependencies between ecological and industrial systems, it becomes crucial to understand the reliance of industrial systems on ecosystems for their operation while also minimizing impacts on ecological systems. Figure 2 shows some direct interactions between manufacturing and ecological systems around industrial sites. The red arrows represents flows of emissions and resource use by industries and the green arrows represent goods and service flows from ecological processes like air pollutant removal by trees, water quality remediation by wetlands, provisioning of minerals and fossils by the soil ecosystem and freshwater resource by watersheds.

Tree canopies have the capacity to regulate air quality by directly taking up pollutants from the atmosphere like CO_2, PM_{10}, $PM_{2.5}$, NO_X, SO_X, Ozone etc. These ecosystems also sustain the water cycle by preventing excessive water run-off from impervious surfaces and help in increasing the ground water table. Wetland ecosystems have the ability to treat water pollutants such as aromatics, endocrine disruptors, solvents, pesticides, sewage and nutrients such as nitrogen and phosphorus.[50,51] In addition, wetlands also provide co-benefits to society by preventing soil erosion, providing flood regulation and recreational benefits. Soil ecosystems also play a crucial role in maintaining fertility and biogeochemical cycles. Soil has the highest capacity to sequester and store CO_2 present on land, three times more than what can be stored in living plants and animals. These ecosystems also act as sinks for air pollutants including carbon monoxide, nitrogen dioxides, nitrogen oxides and sulfur dioxide.

The degree to which industrial activities rely on ecosystem services depends on the type of industrial system and the type of ecological system present. Chemical industries including fertilizer manufacturing processes have a strong and direct dependence on the availability of all provisioning services and some regulating services to maintain air and water quality standards and they also indirectly rely on other supporting services like soil formation, nutrient cycling, and pollination.[52,53] With the realization that decline of natural capital can have a direct impact on business performance, many corporations are interested in accounting for the contribution of natural capital to their business bottomline and for decision making.[54]

Method and Models

In this work, the approach for assessing the role of nature in manufacturing processes is based on quantifying the demand and supply of ecosystem services and determining the difference between the two quantities to gain insight into the current extent of ecological overshoot and for identifying designs that could be closer to satisfying ecological constraints. One of the requirements to ensure the sustainability of processes is the balance between the demand and supply of ecosystem services, at the largest spatial scale or serviceshed applicable.[44] Servicesheds refer to the spatial extent of areas that contain stocks of natural capital that can support ecosystem service demand. The serviceshed for ecosystem services such as carbon sequestration is global in scope due to the presence of global carbon pools and fluxes, and because this molecule maybe taken up anywhere on the earth's surface. In contrast, the serviceshed for air quality regulation is regional since criteria air pollutants like particulate matter and sulfur dioxide tend to have a regional effect and can be mitigated at this scale. The serviceshed of water provisioning is the watershed, while that of pollination is a small local region based on how far pollinators travel.

Engineering within ecological constraints[3] can be accomplished by designs that reduce the demand for ecosystem services or those that restore or protect ecosystems to increase the supply of services. Given the local focus of this work, we consider a condition for a local "island of sustainability" which is that the demand should not exceed the supply at the local scale. As mentioned earlier, many companies and organizations are striving to achieve such local sustainability by goals of net carbon, zero waste or water. Thus in this direction of work, we strive toward technological and ecological systems that operate in a mutually beneficial manner, and consider both systems simultaneously in engineering design and operation. Engineering activities should consider the dependence and impact of technological systems on ecosystems, and the capacity of relevant ecosystems to supply the demanded goods and services while ecosystems should be protected, restored and developed to be capable of supplying the needed ecosystem services. The rest of this section provides details on a general methodology for assessing TES systems at the scale of the manufacturing site, followed by an overview of the relevant models.

Method

The ecosystem services approach towards assessment and design proceeds in three main steps, beginning with boundary definition of all components in the system. Boundaries for the technological component not only include the unit operation level boundaries, but also physical boundaries in terms of plant location, equipment layout, and planning. Ecological components included in the decision boundary are based on the nature of ecosystem service that is of relevance to the technological system at each scale and by the type of ecological system present in the geographical region. The following section provides details about each step involved in the assessment approach.

Step 1: Quantifying the demand for ecosystem services.

Consider a situation where a production flowsheet for an existing or new process is already available. Emissions, wastewater streams, consumption of natural and fossil fuel resources like coal and minerals for operation collectively create a demand for ecosystem services in a particular region, over a period of time. A preliminary assessment of these environmental interventions must be carried out to obtain information about the different types of demands on nature created by manufacturing facilities, and the kind of ecosystems that can supply these services to satisfy the demand. Detailed information about ecosystem services demanded from processes can be obtained through process simulation that includes emissions and waste generation. Where detailed information on the demand cannot be obtained, environmental interventions data from process LCA databases[55,56] for the same process or average processes can also be used. Finally, national level inventories[57–59] representing highly aggregated processes[60,61] can also be used to determine the demand for ecosystem services, when detailed information is unavailable.

In general, the demand for ecosystem service can change over time and space depending on the operating conditions of the plant, and to a moderate extent this demand is also driven by the supply of ecosystem services. For instance, demand for provisioning services like grains and seeds for biofuel production are influenced by the availability of such materials from sources in close proximity to the plant itself. Emissions of air pollutants, aerosols and hazardous air pollutants create a demand for the air quality regulation ecosystem service within a local or regional scale depending on the pollutant molecule, and these demands can be measured based on the concentration of pollutants in the air or based on the critical emissions load in mass units. Methane, CO_2 and N_2O emissions create a local and a global demand for climate regulation service, while wastewater emissions and freshwater consumption create a demand for water quality regulation and water provisioning services, respectively.

Chemical industries also depend directly or indirectly on other supporting services like soil formation and nutrient cycling, and regulating services like pollination. Tools such as Ecologically-Based LCA[62,63] can provide information on the demand for many such services.

Step 2: Estimating the supply of ecosystem services.

Quantifying the supply of ecosystem services requires knowledge about the relevant ecological systems that can provide the services and their spatial presence in the vicinity of production sites. Table 1 provides details about the different types of demands created by manufacturing facilities and the kind of ecosystem that can potentially supply these services locally to balance the demand. The supply of ecosystem services is very closely linked to natural conditions like land cover around industrial sites, soil conditions, presence of vegetation, climate, slope etc. Many manufacturing sites have large areas of land, either close to their manufacturing sites or at other locations.

The supply of ecosystem services provided by current or future ecosystems at such sites can be estimated using ecological models described in the next section. Land cover information available from remote sensing data, Geographical Information System (GIS) and other field survey information can also be used to determine the existing ecological systems and assess the feasibility of restoring new ecosystems for providing these services, including land-use change effects. Most of these models and data are spatially specific and can provide good estimates of available ecosystem services based on local information. Ecological models typically do take dynamics into account, but this work takes a static snapshot of technological and ecological systems at multiple time periods. The use of dynamics models is beyond the scope of this work, since this is the first effort that assesses the demand and supply of ecosystem services for a manufacturing facility.

Step 3: Assess synergies between technological and ecological systems.

Once the demand for an ecosystem service and the relevant ecological systems that can supply this service are known, the following index of sustainability from the Techno-Ecological Synergy framework may be used to guide system development.

$$V_k = \frac{S_k - D_k}{D_k} \tag{1}$$

Here, D_k represents the demand and S_k represents the supply of the k^{th} ecosystem service. Use of this ecosystem service may be considered to be sustainable at the selected scale if the demand is less than the supply, that is, if

$$V_k \geq 0 \tag{2}$$

A positive sustainability index would indicate that services demanded by manufacturing sites are within the capacity of local ecosystems to supply them. This corresponds to a situation where emissions from a manufacturing site are less than what can be taken up by local ecosystems, leading to a situation of net zero or even net negative emissions for selected ecosystem service at the manufacturing site. The ecosystem may have the potential to provide additional services beneficial to other systems in the surrounding environment, and if markets exist, they may even be sold to others.

An important characteristic and benefit of using the proposed sustainability metric is that it can encourage both, enhancing system efficiency to reduce impact by reducing demand, and enhancing ecosystem supply by increasing their capacity. This is an important benefit as compared to conventional methods that only focus on the former objective of reducing demand. Use of this metric encourages synergy based on doing "less bad" by reducing emissions and "more good" by restoring and protecting nature. For instance, CO_2 emissions from an industrial site create a demand for the carbon sequestration service. The sustainability index for this service may be increased by reducing emissions by activities that enhance manufacturing efficiency or replace fossil fuels, or by increasing ecosystem capacity to sequester CO_2 by ecosystem conservation and restoration efforts. Similarly, emissions like NO_2 and PM_{10} create a demand for the air quality regulation service that can be offset by investing in forest conservation and revegetation efforts. In some cases, specific hot-spots that are sources of ecosystem services can be identified and protected for ecosystem service supply and these areas can vary from a small local coppice, agricultural fields and water bodies, to larger forests, open-spaces, and watersheds.

Figure 3 summarizes the three steps involved in the ecosystem assessment approach. Information about the technological systems T_1 include unit operation level constraints, process operating conditions and spatial information about the plant layout that can be used to determine the demand for ecosystem services (D_k) as marked by the red dashed arrows. The supply of ecosystem services (S_k) by an ecological system E_1, as marked by the green dashed arrows depends on the type of ecological systems, its associated parameters and local meteorological and spatial conditions. The black dashed arrows represents the connection between the ecosystem service demand from the technological systems and the type of services supplied by the ecological systems.

Models

Ecological modeling has been an active area of research for many decades. The resulting models capture highly complex behavior with fine details, based on a theoretical understanding of relevant ecological processes. Over the last few years, these models are being used for developing various decision-support tools based on systematic assessment of ecosystem services. Most of these tools rely on spatially specific field survey data, remote-sensing information, or by transfer of information from similar studies.

Remote sensing information collected by agencies like the United States Geological Survey (USGS)[64] and Natural Resources Conservation Service (NRCS) can provide near to real-time information on the land cover, vegetation cover, land use and land cover trends. These can be a good starting point for estimating the benefits of ecological systems to society. Several other decision-support tools for the valuation of ecosystem services are available, and Bagstad et.al[65] provides a detailed review of how these tools can be used according to the preference and goals of the modeler. However, these tools are best for estimating the supply of ecosystem services at large scales, but are not accurate enough to estimate supply for services like air quality regulation, provisioning of freshwater, and carbon sequestration that are specific to a selected industrial site.

The National Land Cover Database[66] is a land-classification scheme that provides information about land cover up to a spatial resolution of about 30 meters, including changes and trends in land cover pattern. This database can be used to quantify the type of land cover in a particular region and inferences can be made about the type of ecosystem service present in that geographical region that would be of most relevance to the system under study.

Forest ecosystems

Vegetation (trees, shrubs, grasses) has the ability to regulate local air quality by taking up molecules from the atmosphere through the diffusion of particles onto the plant surface. These molecules either dissolve into the exterior surface if the surface of the plant is wet and if the particle is water soluble, or diffuse into the stomata if the leaf surface is dry or if the particles have low water solubility. The rate of pollutant transfer from the atmosphere to the interior surface of the leaf is regulated by a series of resistances through the atmosphere, the stomata surface and the mesophyllic resistance.[67]

Vegetation can also catch and deflect rain and snow. Some of the water returns back to the atmosphere through evapotranspiration while most of the water seeps into the soil and local streams, thus reducing water-runoff. Water that reaches the ground seeps deeper, collecting in underground aquifers and maintaining the ground water table. The USDA Forest Service has developed the iTree tool for quantifying the ecosystem services provided by woody vegetation (trees and shrubs), and this tool is most widely used in urban forest management activities and in forest conservation efforts. The entire iTree suite has several models including the iTree Eco,[68] iTree Canopy,[69] iTree Vue[70] etc.

The iTree Eco tool uses field survey information along with local meteorological data to quantify the environmental benefits of urban forests and shrubs, and its value to communities. The tool includes two components of the Urban Forest Effects (UFORE) model: the UFORE-D (Dry Deposition) and UFORE-C (Carbon sequestration) models. The air quality regulation services and the monetary benefits provided by trees by the uptake of pollutants are analyzed using the UFORE-D model.[71] The pollutant flux, F (g/m^2/s) is calculated as a function of the deposition velocity, V_d (m/s) and the atmospheric pollutant concentration, C_{air} (g/m^3),

$$F = V_d C_{air} \tag{3}$$

The deposition velocity V_d is calculated as a function of the aerodynamic resistance, quasi-laminar boundary layer and canopy resistance, calculated as an inverse sum.

$$V_d = (R_a + R_b + R_c)^{-1} \tag{4}$$

$$R_a = u(z)u_*^{-2} \tag{5}$$

$$R_b = 2(Sc)^{(2/3)}(Pr)^{(2/3)}(\kappa u_*)^{-1} \tag{6}$$

$$\frac{1}{R_c} = \frac{1}{(r_s + r_m)} + \frac{1}{r_t} + \frac{1}{r_{soil}} \tag{7}$$

where, R_a represents the aerodynamic resistance in s/m calculated as a function of the wind velocity $u(z)$ at height z and frictional velocity u_*. R_b represents resistance in the quasi laminar boundary layer in s/m calculated as a function of the Prandtl's number (Pr) and Schmidt's number (Sc) for each pollutant, and the von Karmann's constant (κ) and frictional velocity. R_c represents the canopy resistance in s/m, which depends on resistances of the leaf stomata r_s, mesophyll resistance r_m, culticle resistance r_t, and soil resistance r_{soil}.

The pollutant concentration term C_{air} represents the overall atmospheric concentration at a particular location. The UFORE model uses hourly meteorological data obtained from the National Climatic Data Center (NCDC) database, based on the weather station closest to the area of study and location specific pollutant concentration data. Figure 4 shows the model components to run the iTree simulations.

Stand structure attributes of trees can be predicted based on field-survey information or semi empirical data based on regression studies. Four critical functional parameters necessary to predict the ecosystem services provided by woody vegetation include, the diameter at breast height for the tree stump, the total tree height measured from the ground, the crown width which represents the spread of the crown around the stump and the height to crown base ratio which predicts the bole ratio of the tree.

Carbon sequestration by trees is estimated using the UFORE-C model.[72] This quantity is based on the total above ground and below ground biomass of trees estimated using allometric equations.[73] The gross carbon sequestered (Ω_{seq}) is calculated based on the growth rate of tree species as,

$$\Omega_{seq} = k\Delta W_{bm} \tag{8}$$

$$\Delta W_{bm} = (W_{bm})_{x+1} - (W_{bm})_x \tag{9}$$

where k is a genus specific conversion factors, ΔW_{bm} is the fresh weight tree biomass, $(W_{bm})_{x+1}$ is the tree biomass at time period $x + 1$ and $(W_{bm})_x$ is the tree biomass at time period x.

Wetland Ecosystem

Constructed wetlands are, broadly classified as surface flow and subsurface flow wetlands depending on the water flow regime. Surface flow wetlands have the same hydrological flow regime as natural wetlands, flowing from an inlet point to an outlet point over the soil surface. In subsurface flow wetlands, water flows through a bed of plants eliminating direct exposure of the water to the outside environment. These wetlands are further classified as horizontal or vertical flow wetlands according to the direction of water flow. Horizontal Subsurface Flow Wetlands (HSSF) are the most widely used wetland treatment systems for tasks such as treating water from municipal, industrial and urban run-off sources. HSSF wetlands consists of a layer of gravel with a selected wetland plant species, and water treatment takes place through sedimentation, sorption, plant uptake and microbial decomposition.[74] A popular plant species in such wetlands is Phragmites.

Figure 5 depicts the model components required for designing a HSSF wetland. First order rate equations developed by Kadlec et. al[75] assume ideal plug flow behavior between the inlet and the outlet stream, are used for designing the wetland system. The steady-state first-order rate equation for a HSSF wetland is as follows,

$$\frac{(C_{out} - C^{*})}{(C_{in} - C^{*})} = \exp(-K_V \tau_{wetland}) \tag{10}$$

where C_{in} represents the influent pollutant concentration in mg/l, C^{*} represents the background concentration in mg/l, C_{Out} represents the concentration of the effluent stream in mg/l, K_V is the volumetric rate constant measured in day^{-1} and $\tau_{wetland}$ represents the hydraulic residence time in days.

Surface water temperature effects can be captured using the Arrhenius equation as,

$$K_V = K_{V,20}\theta^{(T-20)} \tag{11}$$

where T is the temperature of the water surface in °C, $K_{V,20}$ is the rate constant at 20 °C and θ is the temperature factor.

Typically, wetland designs are based on the improvement in water quality of one or more of the major pollutants present in the wastewater stream and the size of the wetland is critical for maximizing pollutant removal. Thus, selection of the wetland area is determined depending on a specific pollutant that requires the largest size for maximizing its removal.

Some model enhancements have been proposed by Kadlec et.al[76] to incorporate the effect of precipitation and evapotranspiration on the performance of wetlands, yielding a power-law profile between the inlet and the outlet concentration,

$$\frac{C_{out} - C'}{C_{in} - C'} = [1 + \frac{\alpha}{q}]^{-[1+\frac{K_V \epsilon h}{\alpha}]} \tag{12}$$

where,

$$C' = C^* \frac{K_V \epsilon h}{K_V \epsilon h + \alpha} \tag{13}$$

$$\alpha = P - E \tag{14}$$

where, ϵ represents the bed porosity, h represents the bed height in m, q represents the hydraulic loading rate , P represents the precipitation rate, and E represents the evapotranspiration rate, all in m/day.

The wetland area is calculated based on the influent stream flowrate and the hydraulic loading rate of the pollutant as,

$$A_{wetland} = \frac{Q_{water}}{q} \tag{15}$$

where, $A_{wetland}$ is the wetland area in m^2 and Q_{water} is the wastewater flowrate in m^3/day.

Case Study: Biodiesel Facility

To demonstrate the environmental and economic feasibility of techno-ecological synergies of manufacturing processes, we apply our approach to a biodiesel manufacturing process located at a site near Cincinnati, Ohio, as shown in Figure 6. The objective of this case study is to demonstrate use of the proposed analysis method to develop an integrated techno-ecological biodiesel production process by investing in natural capital in the vicinity of the manufacturing site. The economic and environmental aspects of such a system are also assessed.

We consider a situation where a corporation aims toward a target of zero emissions from their sites. Common strategies for making progress toward such a goal include optimizing the process for greater efficiency, adopting cleaner production strategies by switching to renewable fuels, and investing in end-of-the-pipe control technologies for eliminating emissions. We compare such 'techno-centric' approaches with the proposed 'techno-ecological' approach'. We consider cases where ecosystems already exist, or are developed at the time of plant start-up and grow to provide services over the years. The conventional or techno-centric and techno-ecological cases are compared based on their environmental and economic characteristics.

The biodiesel manufacturing plant, marked by the red boundary in Figure 6, has an annual capacity of 5 million gallons per year. Biodiesel (Fatty Acid Methyl Ester) is produced by the alkali-catalyzed transesterification of soybean oil. This oil, produced from the hexane extraction process, is reacted with methanol in the presence of potassium hydroxide as a catalyst to form biodiesel and by-product glycerol. Design of the extraction and transesterification processes was based on models from the literature[77,78] as described in Section S1 in the supporting information. Emissions from the production system include hexane as fugitive and vent gas emissions, PM_{10} emissions from the bean crushing operation and CO_2 emissions from methanol processing. These create a demand for the air quality regulation and carbon sequestration ecosystem services. The process also produces wastewater that is mostly a mixture of methanol with small quantities of oil and grease, and a negligible amount of hexane. Table 2 includes information about the amount of water and energy consumed by the biodiesel plant.

An on-site 0.8 MW coal Combined Heat and Power (CHP) plant using a combustion turbine satisfying the utility demand for the host facility is also included in the analysis boundary[79] as described in Section S1 in the SI. The manufacturing process along with the coal CHP occupies an area of 23 acres. The CHP uses bituminous coal as the primary fuel[80] and this process is the main source of air emissions, which include CO_2, SO_2, NO_2 and PM_{10}.[81] To comply with the New Source Performance Standards (NSPS), the coal CHP includes post combustion control equipments like flue gas desulfurization unit to treat the SO_2 stack emissions, a bag-house filter for PM_{10} particles, a post combustion selective catalytic reduction system for NO_2 and a Monoethanolamine (MEA) based CO_2 absorption system. The CHP uses an evaporative cooling tower system with closed-loop water circulation. Water required in the cooling tower is initially withdrawn from the river located next to the production facility as indicated in Figure 6. The total water withdrawn and consumed by the coal CHP is calculated based on the water and heat flow across the plant.[82] Air pollutants including ozone emissions due to excess of NO_2 in the summer months and greenhouse gas emissions from the coal CHP also create a demand for ecosystem services.

Conventional Process

The process flowsheet for the conventional or *techno-centric* process is marked by the red boundary in Figure 7. It includes biodiesel manufacturing and coal CHP processes. The demand for ecosystem services created at the manufacturing site is calculated based on the design of the base case process flowsheet, and is represented by the red bars in Figure 8. Most of this demand is created by the emissions from the coal CHP facility as indicated by the darker shade of red while the lighter shade represents emissions from the biodiesel manufacturing process.

For reducing these emissions, we consider a scenario of reaching zero emissions 15 years after the start of the plant, by investing in add-on control equipments. The additional control equipments installed at year 15 to reach zero emissions include a selective catalytic reduction

(SCR) unit for treating NO_2, a baghouse filter for PM_{10} emissions, a fluegas desulfurization (FGD) unit for SO_2, and a monoethanol amine (MEA) absorption system for CO_2, as shown in Column 4 of Table 1. Currently, the facility also includes a coagulation-flocculation pre-treatment unit followed by an Anaerobic Baffled Reactor (ABR) for treating waste-water. Section S1 in the SI contains information on the basic design equations for each of these components. This techno-centric approach completely ignores the role of ecosystems, as is the current practice.

The rationale behind considering a 15 year time horizon for reaching net zero emissions was because 15 year old trees have the capacity to meet the demand for ecosystem services, for at least one of the criteria air pollutants except ozone. However, this is under the assumption that the land around the industrial site is currently completely barren and ecosystems have to be established and preserved, for producing these services. In most cases, land around industrial sites may already have vegetation cover like small trees, shrubs and grasslands that already provide some ecosystem services. In such situations, the time period to reach zero emissions by protecting and restoring existing vegetation may be much shorter, and investing further in preservation activities may be more beneficial. Thus, the scenario considered in this study represents a worst case.

Techno-Ecological Synergistic Process

We now consider synergies between the biodiesel process and surrounding ecosystems. We consider establishment of forest and wetland ecosystems on the available land next to the manufacturing site at the time of plant commissioning. The region considered for this TES process is marked by the green boundary in Figure 6, and the flowsheet with the forest and wetland as unit operations is shown in Figure 7 marked by the green solid line. This flowsheet includes the role that trees can play in mitigating air emissions, and a wetland for treating wastewater, instead of the conventional ABR.

The wetland considered in this manufacturing process is a floating bed, horizontal subsurface flow reed bed treatment wetland which is designed to treat the wastewater stream from the biodiesel system and the blow-down water from the CHP. This water has a Chemical Oxygen Demand (COD) concentration of approximately 50,000 mg/l, and oil and grease content of approximately 1000 mg/l, with limited quantities of micro-elements.[83–85]

The raw wastewater from the biodiesel system first undergoes a pre-treatment in a coagulation and flocculation unit for removing most of the oil and grease. This unit uses powdered aluminum sulfate as the coagulant, and is effective in removing about 99% of all the oil and grease, and about 53 % of COD.[86]

The wetland considered here is designed to achieve desired levels of COD removal, while the oil and grease removal capacity is calculated based on the removal efficiency of the wetland, after sizing it. Table 4 describes the different parameters considered during the design including the average concentration of the influent stream to the wetlands and approximate effluent standards.

First order rate equations are used to design the wetland system with a removal efficiency $\geq$ 99% COD removal. Thus, based on the influent waste-water characteristics and the desired outlet concentration of the water stream, the area of the wetland necessary to reach the appropriate effluent standards is determined to be 1.10 acres. Pilot scale experiments of horizontal subsurface flow wetland[87] have indicated that the removal efficiency of wetlands does not necessarily reduce with decreasing ambient temperatures. Besides, the mechanism underlying removal or organic matter mostly involves microbial activity of the aerobic and anaerobic bacteria that can take place even at temperatures as low as $5°C$. Since the wetland is a subsurface flow wetland, the water surface is not directly exposed to the atmosphere due to the presence of the plants and the water surface temperature is always 2-3 $°C$ above the average atmospheric temperature.

Process water requirement for operating the biodiesel and coal CHP processes creates a local demand for the freshwater provisioning service, and this is marked by the red bar in the water category in Figure 8. Freshwater supply to meet this demand comes from water provisioning services like rainwater collected from the roof of buildings within that facility, ground water infiltration from precipitation due to the presence of trees and avoided water that would be considered as run-off water in the absence of tree cover. The wastewater treated by the wetlands can also be used as a source of cooling water in the coal CHP plant, provided it meets the regulation specified by the US-EPA within that region.[88]

The remaining 25.88 acres of underdeveloped land around the industrial site was restored with three native species, American Elm (Ulmus Americana), White Oak (Quercus Alba) and Eastern Hemlock (Tsuga canadensis). The capacity of the trees to provide ecosystem services was determined using the UFORE-C and D components in iTree.

To model the benefits of restoration, the entire study area was divided into plots of size 0.04 ha (0.1 acres) and a simple random sampling procedure was used to generate a total of 258 plots using the plot generator tool in i-Tree. Distribution of tree species in each plot was based on a random generation of each of the three species to have an accurate representation of the forest ecosystem. An overall distribution of 36.12 % of American Elms, 33.46 % of White Oaks and 30.42 % of Eastern Hemlock tree species was specified in the sampled plots.

To account for the growth dynamics and the variation in provisioning of ecosystem services by trees with age, the analysis was carried out over multiple periods. Four different time periods of forest growth were considered. Table 3 contains more details on the functional parameters for the stand structures over these four time periods. Two key assumptions in this analysis are,

1. *Plot homogeneity.* Each plot is assumed to have similar characteristics.
2. *Linear scaling.* The effect of one tree in each plot is linearly scaled to the total number of trees in the plot.

Input parameters like weather and environmental conditions and concentration of pollutants are also assumed to be homogeneous over the entire study area. Thus, although the model adopts a lumped parameter approach where the spatial distribution of trees is not taken into account, UFORE-D is the most comprehensive model to estimate ecosystem services provided by trees. The iTree Eco manual available online[89] provides a detailed description of the modeling procedure and assumptions to be made while quantifying ecosystem service benefits.

Conventional vs. TES Systems

The green bars in Figure 8 depict the supply of ecosystem services. These results are based on the assumption that by the time the emissions are captured by the trees, they have reached the ambient concentration of the local atmosphere. Thus, dynamics of emission transportation and mixing are not considered. These results indicate that over a period of 20 years, the restored forest ecosystem can supply enough services to mitigate all the SO_2, NO_2, PM_{10} and O_3 emissions from the biodiesel and coal CHP processes. Coniferous trees like Eastern Hemlock are known to have higher particle removal efficiency than deciduous tree species, due to their needle-shaped leaf structure. Besides, smaller leaves usually have a higher capacity to act as particle collectors than larger leaves as indicated by higher sequestration capacity of the forest ecosystem to take up air pollutants over the first 10 years of its growth.[67] Pollutant uptake capacity of leaves also depends on the type of molecule being absorbed, and the pollutant uptake rate increases with the increase in solubility of the molecule in water. Sulfur dioxide, nitrogen dioxide and ozone, which are highly soluble in water, are more readily absorbed on the leaf surface. However, since the deposition velocity on the leaves is also a linear function of the pollutant concentration in the atmosphere, the low sequestration rates for SO_2 compared to NO_2 and O_3 sequestration can be explained by the lower concentration of this gas in the surrounding air.

The supply of freshwater resources is indicated by the green bars in the water category in Figure 8. The water collected from the rainwater harvesting systems is assumed to be constant over time, while the water supply from ground water increases with tree growth. Local water availability is less than what is demanded by the manufacturing process, indicating that the process overshoots the local ecological capacity with respect to the water provisioning service. But the presence of trees around the manufacturing site intercepts most of the water run-off during precipitation and this avoided run-off water seeps into the ground to reach deeper aquifers. Implementing a rainwater harvesting system, for the TES process, also increases freshwater availability within the boundary of the manufacturing site. The established forest ecosystem also does not have enough capacity to supply carbon sequestration service to meet all the CO_2 demand. One of the underlying reasons for this is because of the rate of CO_2 emission from energy generation systems compared to the limited capacity of forests and soils to take up these emissions. These results also indicate that closing the loop for material cycles with respect to carbon may be difficult at the local scale.

The analysis so far conveys the environmental benefits of including relevant ecosystems in engineering design. We also performed an economic evaluation of the two approaches. Profitability analysis for the conventional case with technological components and control equipments installed in year fifteen is represented in Column 2 of Table 5. For this case, the add-on control equipments are designed to reach zero emissions (100 % efficiency) with the same stack flow rate as the coal CHP. The capital cost required to install the control equipments in the 15^{th} year is set aside as an investment during the time of plant start-up, and this investment is assumed to earn an annual interest of 7%.[90] This was done to allow a fair comparison between investing in natural capital versus investing in control equipments to reach the goal of zero emissions. Column 3 in Table 5 contains the profitability analysis for the technological components along with the established ecological systems. Land costs for establishing the ecosystems,[91] site preparation, establishment and management cost for the forest ecosystem[92,93] and the setup and maintenance cost for the wetlands[94] were also included in the cost analysis. Table S.1 in the supporting information contains a list of parameters and assumptions made while estimating the monetary benefits. The profitability analysis calculations incorporate factors like depreciation of equipments using a straight line depreciation method, interest, taxes and contingency costs. A summary of the economic criteria for the conventional and TES systems, along with the equations for estimating the economic parameters can be found in Section S.2 in the supporting information.

Results of the profitability analysis of the two systems indicate that restoration of ecosystems to supply services to balance the demand is economically superior in terms of having a higher return on investment compared to the conventional techno-centric system. Besides, these results are based on conventional cost analysis and represent the worst case scenario for the techno-ecological case since ecosystems provides additional benefits, beyond what is demanded by the manufacturing process. This is evident from Figure 8 where the forest ecosystems have excess capacity to sequester additional NO_2, SO_2, PM_{10} and O_3 particles, more than what is emitted. This additional service would be available to the locality around the manufacturing site. Including such positive externalities from ecosystems in the profitability analysis would only strengthen the case for the TES design.

We also compare the annualized costs of the ecological systems and conventional methods for pollution control. The add-on control technologies for treating NO_2, SO_2 and PM_{10} emissions were compared with the established forest ecosystem while the anaerobic baffled reactor was compared with the wetland for treating wastewater. Annualized costs were calculated at year 15 and year 20, assuming a 20 year life time for each of the control methods based on the model in Section S2.2 The results as shown in Figure 9 indicate that the cost of the conventional control methods increases over the years as a result of the high maintenance cost, while the cost of ecosystems does not change as a result of the low or zero maintenance cost. As in the return on investment calculations, these results also do not capture the positive externalities that ecosystems provide, beyond the time period when the ecosystem service demand and supply are equal. Thus, this comparison does not capture the fact that ecological systems tend to *appreciate* over time, while technological systems *deprectiate* over time.

Discussion and Future Work

This work introduces and evaluates the idea of including ecosystems as unit operations in a manufacturing process to establish mutually beneficial networks of technological and ecological systems. Such a network is a step toward seeking harmony between chemical manufacturing systems and the ecosystems that they depend on and impact. Until now, most disciplines have neglected the role played by nature in supporting human activities. By continuing to leave ecosystems outside the analysis and design boundary, it is quite unlikely that any effort toward designing sustainable systems will succeed. The idea of developing synergies between manufacturing processes and local ecosystems and its application to a biodiesel manufacturing site demonstrates the promise of this approach for developing integrated systems that could even have net zero emissions and resource use. While the benefits of restoration and preservation of the forest ecosystems for the industrial site are demonstrated in this work, such measures can also help in other ways such as preserving biological diversity and improving well-being of local communities due to improved air quality and access to green spaces. Wetlands also provide valuable benefits to local communities by reducing erosion, moderating water flow around lakes and rivers, recharging aquifers, and supporting biodiversity.

Being among the first efforts to explore the idea of including ecosystems in chemical manufacturing, this work has focused on exploring the environmental and economic feasibility of this idea. The promising results motivate further research on many theoretical and practical aspects of TES systems. Currently, the case study demonstrates the benefits of a TES system for a worst-case scenario. In reality, most industries may have large amounts of land around manufacturing sites or at different locations in proximity to these sites, and accounting for ecosystem services provided by ecological systems will help to offset emissions, to go beyond net zero emissions and toward net positive impact of manufacturing.

An important challenge in operating processes with technological and ecological systems stems from the inherently different dynamic behavior of these systems. Ecological systems self-design and tend to be self-sustaining due to primary reliance on air, water and sunlight. They tend to be resilient to perturbations and unexpected calamities, but are difficult to predict and control. Their performance can be intermittent and vary with seasons and time of day. In contrast, technological systems tend to follow an imposed design, are capable of performing a set of specific tasks with a high degree of predictability and control, but these systems are usually rigid and lack resilience to external disturbances and fluctuations. They are also resource intensive and have a high environmental impact. Appropriate combinations of technological and ecological systems that are designed according to the nature of the demanded ecosystem services, ecological and geographical considerations can provide unique and innovative designs that are superior to those that can be developed by conventional techno-centric methods.

Another important aspect that also needs to be considered is uncertainty associated with the model structure and components as well as the inputs and parameters to define a system. In addition to this, some other sources that contribute to uncertainty may stem from the dynamic behavior of ecological systems and variation in ambient concentration. To minimize these effects, one of the assumptions in this work is the lack of spatial variation in pollution concentration in the vicinity of the site. In other words, the emissions from the stack are assumed to be well-mixed with the ambient air concentration near the tree canopy. In addition, accounting for the annual supply of ecosystem services and keeping aside the dynamic behavior of ecological systems with time and season, may result in the system behavior being within reasonable bounds of the estimated values.

Future work includes developing a framework for integrated design of technological and ecological systems. This framework will also include fate and transport models for the pollutants and account for the temporal and spatial variation of ecological systems, along with uncertainty estimates. Further, for addressing issues related to sustainability, this framework should also consider multiple spatial scales and include all the relevant processes in the life cycle. Wide industrial adoption of the proposed TES systems may require changes in environmental policies and inclusion of the value of nature in prices by means of the free market system. Current policies across the world do not give companies or other landowners credit for most ecosystem services available from their site. Like conventional engineering, traditional or neoclassical economics also takes nature for granted. This means that despite their essential role, goods and services from nature are still considered to be free. Novel schemes involving payment for ecosystem services may be one way of internalizing these economic externalities into the market system. However, commodification of nature's services by reductionist thinking about individual services runs the risk of unintended harm. Systems thinking is essential for avoiding such harm.

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References

[1] Raymond R. W. The New Age.. *Industrial & Engineering Chemistry.* 1913;5:249–251.

[2] Crutzen P. J. *The "anthropocene".* Berlin Heidelberg Springer, 2006.

[3] Schulze P. *Engineering within ecological constraints.* National Academies Press, 1996.

[4] Grossmann I. E, Westerberg A. W. Research challenges in process systems engineering. *AIChE Journal.* 2000;46:1700–1703.

[5] Linnhoff B, Flower J. R. Synthesis of heat exchanger networks: I. Systematic generation of energy optimal networks. *AIChE Journal.* 1978;24:633–642.

[6] El-Halwagi M. M, Manousiouthakis V. Synthesis of mass exchange networks. *AIChE Journal.* 1989;35:1233–1244.

[7] Flower J, Bikos S, Johnson S. A modular approach to synthesis of cleaner processes. *Computers & chemical engineering.* 1995;19:45–50.

[8] Young D. M, Cabezas H. Designing sustainable processes with simulation: the waste reduction (WAR) algorithm. *Computers & Chemical Engineering.* 1999;23:1477–1491.

[9] Hilaly A. K, Sikdar S. K. Pollution balance: a new methodology for minimizing waste production in manufacturing processes. *Air & waste.* 1994;44:1303–1308.

[10] Bjørn A, Hauschild M. Z. Absolute versus relative environmental sustainability. *Journal of Industrial Ecology.* 2013;17:321–332.

[11] Braungart M, McDonough W, Bollinger A. Cradle-to-cradle design: creating healthy emissions–a strategy for eco-effective product and system design. *Journal of cleaner production.* 2007;15:1337–1348.

[12] Smith R, Delaby O. Targeting flue gas emissions. *Chemical engineering research & design.* 1991;69:492–505.

[13] Cano-Ruiz J, McRae G. Environmentally conscious chemical process design. *Annual Review of Energy and the Environment.* 1998;23:499–536.

[14] Guinée J, De Haes H. U, Huppes G. Quantitative life cycle assessment of products: 1: Goal definition and inventory. *Journal of Cleaner Production.* 1993;1:3–13.

[15] Guinée J. B, Heijungs R, Haes H. A. U, Huppes G. Quantitative life cycle assessment of products: 2. Classification, valuation and improvement analysis. *Journal of Cleaner Production.* 1993;1:81–91.

[16] Weidema B. P, Thrane M, Christensen P, Schmidt J, Løkke S. Carbon footprint. *Journal of Industrial Ecology.* 2008;12:3–6.

[17] Wackernagel M, Rees W. *Our ecological footprint: reducing human impact on the earth vol. 9.* New Society Publishers, 1998.

[18] E Grossmann I, Drabbant R, Jain R. K. Incorporating toxicology in the synthesis of industrial chemical complexes. *Chemical Engineering Communications.* 1982;17:151–170.

[19] Bakshi B. R, Fiksel J. The quest for sustainability: Challenges for process systems engineering. *AIChE Journal.* 2003;49:1350–1358.

[20] Stefanis S, Livingston A, Pistikopoulos E. Minimizing the environmental impact of process plants: a process systems methodology. *Computers & Chemical Engineering.* 1995;19:39–44.

[21] Kniel G, Delmarco K, Petrie J. Life cycle assessment applied to process design: environmental and economic analysis and optimization of a nitric acid plant. *Environmental Progress.* 1996;15:221–228.

[22] Azapagic A, Clift R. The application of life cycle assessment to process optimisation. *Computers & Chemical Engineering.* 1999;23:1509–1526.

[23] You F, Tao L, Graziano D. J, Snyder S. W. Optimal design of sustainable cellulosic biofuel supply chains: Multiobjective optimization coupled with life cycle assessment and input-output analysis. *AIChE Journal.* 2012;58:1157–1180.

[24] Kim J, Realff M. J, Lee J. H. Optimal design and global sensitivity analysis of biomass supply chain networks for biofuels under uncertainty. *Computers & Chemical Engineering.* 2011;35:1738–1751.

[25] Hugo A, Pistikopoulos E. Environmentally conscious long-range planning and design of supply chain networks. *Journal of Cleaner Production.* 2005;13:1471–1491.

[26] Suh S, Huppes G. Methods for life cycle inventory of a product. *Journal of Cleaner Production.* 2005;13:687–697.

[27] Jacquemin L, Pontalier P.-Y, Sablayrolles C. Life cycle assessment (LCA) applied to the process industry: a review. *The International Journal of Life Cycle Assessment.* 2012;17:1028–1041.

[28] Hanes R. J, Bakshi B. R. Process to planet: A multiscale modeling framework toward sustainable engineering. *AIChE Journal.* 2015;61:3332–3352.

[29] Hanes R. J, Bakshi B. R. Sustainable process design by the process to planet framework. *AIChE Journal.* 2015;61:3320–3331.

[30] Allenby B. R, Graedel T. *Industrial ecology.* Prentice-Hall, Englewood Cliffs, NJ, 1993.

[31] Chertow M. R. Industrial symbiosis: literature and taxonomy. *Annual review of energy and the environment.* 2000;25:313–337.

[32] Grann H. The industrial symbiosis at Kalundborg, Denmark. *The industrial green game. Implications for environmental design and management.* 1997:117–123.

[33] Cimren E, Fiksel J, Posner M. E, Sikdar K. Material Flow Optimization in By-product Synergy Networks. *Journal of Industrial Ecology.* 2011;15:315–332.

[34] López-Díaz D. C, Lira-Barragán L. F, Rubio-Castro E, Ponce-Ortega J. M, El-Halwagi M. M. Synthesis of eco-industrial parks interacting with a surrounding watershed. *ACS Sustainable Chemistry & Engineering.* 2015;3:1564–1578.

[35] Mitsch W. J. Ecological engineering: a new paradigm for engineers and ecologists. *Engineering within Ecological Constraints. National Academy Press, Washington, DC.* 1996:111–128.

[36] Straskraba M, Gnauck A. *Freshwater ecosystems.* Elsevier Science Pub. Co., Inc., New York, NY, 1985.

[37] Straškraba M. Ecotechnology as a new means for environmental management. *Ecological Engineering.* 1993;2:311–331.

[38] Sheridan C, Hildebrand D, Glasser D. Turning wine (waste) into water: Toward technological advances in the use of constructed wetlands for winery effluent treatment. *AIChE Journal.* 2014;60:420–431.

[39] DiMuro J. L, Guertin F. M, Helling R. K, Perkins J. L, Romer S. A financial and environmental analysis of constructed wetlands for industrial wastewater treatment. *Journal of Industrial Ecology.* 2014;18:631–640.

[40] *Millennium Ecosystem Assessment: Ecosystems and human well-being.* Island Press Washington, DC, 2005.

[41] Urban R. A, Bakshi B. R, Grubb G. F, Baral A, Mitsch W. J. Towards sustainability of engineered processes: Designing self-reliant networks of technological–ecological systems. *Computers & chemical engineering.* 2010;34:1413–1420.

[42] Urban R. A, Bakshi B. R. Techno-ecological synergy as a path toward sustainability of a North American residential system. *Environmental science & technology.* 2013;47:1985–1993.

[43] Martinez-Hernandez E, Leach M, Yang A. Impact of Bioenergy Production on Ecosystem Dynamics and Services: A Case Study on UK Heathlands. *Environmental science & technology.* 2015;49:5805–5812.

[44] Bakshi B. R, Ziv G, Lepech M. D. Techno-Ecological Synergy: A Framework for Sustainable Engineering. *Environmental science & technology.* 2015;49:1752–1760.

[45] Neale A, Pickard B, Megan M, Baynes J. EnviroAtlas: A Spatially Explicit Tool Combining Climate Change Scenarios with Ecosystem Services Indicators. in *AGU Fall Meeting Abstracts*;1:03 2014.

[46] Villa F, Ceroni M, Bagstad K, Johnson G, Krivov S. ARIES (Artificial Intelligence for Ecosystem Services): A new tool for ecosystem services assessment, planning, and valuation. in *11Th annual BIOECON conference on economic instruments to enhance the conservation and sustainable use of biodiversity, conference proceedings. Venice, italy* 2009.

[47] Tallis H, Ricketts T, Guerry A, et al. InVEST 2.1 beta User's Guide. The Natural Capital Project. 2011.

[48] Costanza R, Groot R, Sutton P, et al. Changes in the global value of ecosystem services. *Global Environmental Change.* 2014;26:152–158.

[49] Steffen W, Richardson K, Rockstrom J, et al. Planetary boundaries: Guiding human development on a changing planet. *Science.* 2015;347:1259855.

[50] Brix H, Arias C. A. The use of vertical flow constructed wetlands for on-site treatment of domestic wastewater: New Danish guidelines. *Ecological engineering.* 2005;25:491–500.

[51] Chen T, Kao C, Yeh T, Chien H, Chao A. Application of a constructed wetland for industrial wastewater treatment: a pilot-scale study. *Chemosphere.* 2006;64:497–502.

[52] Singh S, Bakshi B. R. Accounting for the biogeochemical cycle of nitrogen in input-output life cycle assessment. *Environmental science & technology.* 2013;47:9388–9396.

[53] Chopra S. S, Bakshi B. R, Khanna V. Economic Dependence of US Industrial Sectors on Animal-Mediated Pollination Service. *Environmental science & technology.* 2015;49:14441–14451.

[54] Business for Social Responsibility. *The Untapped Opportunity: Solving Business Problems with Natural Systems.* 2016. In Review.

[55] US Environmental Protection Agency. *Lifecycle Inventory Database* 2008. Accessed March 2013. http://www.nrel.gov/lci/.

[56] Frischknecht R, Jungbluth N, Althaus H.-J, et al. The ecoinvent database: Overview and methodological framework (7 pp). *The international journal of life cycle assessment.* 2005;10:3–9.

[57] US Environmental Protection Agency. *Toxic Release Inventory (TRI) Program* 2013. Accessed March 2013. http://www.epa.gov/toxics-release-inventory-tri-program.

[58] US Environmental Protection Agency. *Factilities Level Information on Greenhouse gases Tool* 2014. Accessed June 2014. http://ghgdata.epa.gov/ghgp/main.do.

[59] US Environmental Protection Agency. *The 2011 National Emissions Inventory* 2011. Accessed June 2014. http://www3.epa.gov/ttnchie1/net/2011inventory.html.

[60] Green Design Institute. *Economic Input-Output Life Cycle Assessment.* Accessed June 2014. http://www.eiolca.net/.

[61] Center for Resilience. *Ecologically Based Life Cycle Assessment.* Accessed June 2014. http://resilience.eng.ohio-state.edu/ecolca-cv/.

[62] Zhang Y, Singh S, Bakshi B. R. Accounting for ecosystem services in life cycle assessment, Part I: a critical review. *Environmental science & technology.* 2010;44:2232–2242.

[63] Zhang Y, Baral A, Bakshi B. R. Accounting for ecosystem services in life cycle assessment, part II: toward an ecologically based LCA. *Environmental science & technology.* 2010;44:2624–2631.

[64] Earth Explorer USGS.*Land processes distributed active archive center.* 2012. Accessed March 2015. http://earthexplorer.usgs.gov/.

[65] Bagstad K. J, Semmens D. J, Waage S, Winthrop R. A comparative assessment of decision-support tools for ecosystem services quantification and valuation. *Ecosystem Services.* 2013;5:27–39.

[66] Homer C, Dewitz J, Yang L, et al. Completion of the 2011 National Land Cover Database for the conterminous United States-Representing a decade of land cover change information. *Photogrammetric Engineering and Remote Sensing.* 2015;81:345-354.

[67] Smith W. H. *Air pollution and forests: interactions between air contaminants and forest ecosystems.* Springer Science & Business Media, 2012.

[68] United States Department of Agriculture - Forest Service.*iTree Eco Suite* 2016. Accessed September 2014. http://www.itreetools.org/.

[69] United States Department of Agriculture - Forest Service.*iTree Canopy* 2016. Accessed September 2014. http://www.itreetools.org/.

[70] United States Department of Agriculture - Forest Service.*iTree Vue* 2016. Accessed September 2014. http://www.itreetools.org/.

[71] Hirabayashi S, Kroll C. N, Nowak D. J. Development of a distributed air pollutant dry deposition modeling framework.. *Environmental pollution (Barking, Essex : 1987).* 2012;171:9–17.

[72] Nowak D. J, Crane D. E. Carbon storage and sequestration by urban trees in the USA. *Environmental pollution.* 2002;116:381–389.

[73] McPherson G. E, Nowak D. J, Rowntree R. A. Chicago's urban forest ecosystem: results of the Chicago Urban Forest Climate Project. 1994.

[74] Wetzel R. Fundamental processes within natural and constructed wetland ecosystems: short-term versus long-term objectives. *Water Science & Technology.* 2001;44:11–12.

[75] Kadlec R, Wallance S. *Treatment Wetlands.* CRC Press, 2008.

[76] Kadlec R. Deterministic and stochastic aspects of constructed wetland performance and design. *Water Science and Technology.* 1997;35:149–156.

[77] Baker E. C, Sullivan D. A, Regional N. Development of a Pilot-Plant Process for the Extraction of Soy Flakes with Aqueous Isopropyl Alcohol. 1983;60:1271–1277.

[78] Martín M, Grossmann I. E. Simultaneous optimization and heat integration for biodiesel production from cooking oil and algae. *Industrial & Engineering Chemistry Research.* 2012;51:7998–8014.

[79] US Environmental Protection Agency.*Accounting for CHP in Output-Based Regulations.* 2013. http://www.epa.gov/sites/production/files/2015-07/documents/accounting-for-chp-in-output-based-regulations.pdf.

[80] National Energy Technology Laboratory.*Quality guidelines for energy systems studies. Detailed Coal Specification.* 2012. http://www.netl.doe.gov/File%20Library/research/energy%20analysis/publications/QGESS_DetailCoalSpecs_Rev4_20130510.pdf.

[81] US Environmental Protection Agency.*CHP Emissions Calculator.* 2013. \http://www.epa.gov/chp/chp-emissions-calculator.

[82] Delgado A, Herzog H. J. Simple Model to Help Understand Water Use at Power Plants. *Massachusetts Institute of Technology, Cambridge, MA.* 2012.

[83] Yu H.-Q, Hu Z.-H, Hong T.-Q, Gu G.-W. Performance of an anaerobic filter treating soybean processing wastewater with and without effluent recycle. *Process Biochemistry.* 2002;38:507 - 513.

[84] Wang J, Li X, Fu W, Wu S, Li C. Treatment of artificial soybean wastewater anaerobic effluent in a continuous aerobic-anaerobic coupled (CAAC) process with excess sludge reduction.. *Bioresource technology.* 2012;126:142–7.

[85] Veljković V. B, Stamenković O. S, Tasić M. B. The wastewater treatment in the biodiesel production with alkali-catalyzed transesterification. *Renewable and Sustainable Energy Reviews.* 2014;32:40–60.

[86] Daud Z, Awang H, Nasir N, Ridzuan M. B, Ahmad Z. Suspended Solid, Color, COD and Oil and Grease Removal from Biodiesel Wastewater by Coagulation and Flocculation Processes. *Procedia-Social and Behavioral Sciences.* 2015;195:2407–2411.

[87] Akratos C. S, Tsihrintzis V. A. Effect of temperature, HRT, vegetation and porous media on removal efficiency of pilot-scale horizontal subsurface flow constructed wetlands. *Ecological engineering.* 2007;29:173–191.

[88] US Environmental Protection Agency.*Guidelines for Water Reuse* 2012. Accessed March 2014. `http://nepis.epa.gov/Adobe/PDF/P100FS7K.pdf`.

[89] United States Department of Agriculture - Forest Service.*iTree Eco User's Manual* 2016. Accessed September 2014. `http://www.itreetools.org/resources/manuals/i-TreeEcoUsersManual.pdf`.

[90] Daniel M. *Air Pollution Control Cost Manual.* United States Environmental Protection Agency Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina 27711. 2002.

[91] Nickerson C. J, Morehart M, Kuethe T, Beckman J, Ifft J, Williams R. *Trends in US farmland values and ownership.* US Department of Agriculture, Economic Research Service 2012.

[92] Texas A&M Forest Service.*Cost estimate sheet for forestry practices* 2011. `http://texasforestservice.tamu.edu/`.

[93] Bair L. S, Alig R. J. Regional Cost Information for Private Timberland: Convertion and Managment. 2007.

[94] US Environmental Protection Agency.*Constructed Wetlands Treatment of Municipal Wastewaters.* 2000. Accessed September 2013. `http://www.epa.gov/ORD/NRMRL.`

[95] Larsen D. R, Scott I. R. Developments to the Sylvan Stand Structure Model to Describe Wood-Quality Changes in Southern Bottom-land Hardwood Forests Because of Forest Management. *Forest Growth and Timber Quality: Crown Models and Simulation Methods for Sustainable Forest Management.* 2009:125.

[96] Martin N. A, Chappelka A. H, Loewenstein E. F, Keever G. J, Somers G. Predictive open-grown crown width equations for three oak species planted in a southern urban locale. *Arboriculture and Urban Forestry.* 2012;38:58.

[97] Ritchie M. W, Hann D. W. Equations for predicting height to crown base for fourteen tree species in southwest Oregon. tech. rep.Corvallis, OR: Forest Research Laboratory, College of Forestry, Oregon State University 1987.

[98] Ishikawa Y, Ito K. DBH, height, and crown radius growth of some component species of Nopporo National Forest, central Hokkaido, Japan.. *Environmental science, Hokkaido University: journal of the Graduate School of Environmental Science, Hokkaido University, Sapporo.* 1989;12:117–138.

[99] Hann D. W. Equations for predicting the largest crown width of stand-grown trees in western Oregon. tech. rep.Corvallis, OR: Forest Research Laboratory, College of Forestry, Oregon State University 1997.

[100] Reed S. C. Subsurface flow constructed wetlands for wastewater treatment: a technology assessment. 1993.

[101] Akratos C. S, Papaspyros J. N, Tsihrintzis V. A. An artificial neural network model and design equations for BOD and COD removal prediction in horizontal subsurface flow constructed wetlands. *Chemical Engineering Journal.* 2008;143:96–110.

[102] Oceanic N, Administration A. National Climate Data Center. 2012. https://www.ncdc.noaa.gov/data-access/quick-links.

List of Tables

Table 1: Demand and supply of ecosystem services

Ecosystem service	Demand for ecosystem service (D_k)	Ecological components for meeting demand	Technologies for meeting demand
Carbon sequestration	CO_2 emissions	Vegetation, cropland, soil, water bodies	Pre-combustion capture, Post-combustion solvent capture
Air quality regulation	NO_2 emissions	Trees, Vegetation, soil	Selective catalytic reduction
	SO_2 emissions		Wet and dry scrubbers
	PM emissions		Baghouses, electrostatic precipitators
	Ozone		Control strategies to minimize NO_X and VOCs
Climate regulation	Methane emissions	Soil compartments under tree canopies, undisturbed soils	Methane gas capture technologies, preventing fugitive emissions
Pollination	Crops and flowers needing pollination	Pollinator population in local habitat	Hand pollination, transported bees, genetic engineering
Water quality regulation	Waste-water	Forests, wetlands, estuaries, inland marshes, green urban areas	Anaerobic baffled reactor, sludge treatment
Water provisioning service	Fresh-water	Hydrological cycle precipitation, wetlands, forests, estuaries, inland marshes	Desalination, cloud seeding

Table 2: Energy and water requirements for the biodiesel facility

Input	Amount	Unit
Electricity	1186	kJ/kg Biodiesel
Steam	3560	kJ/kg Biodiesel
Process water	0.0126	kg/kg Biodiesel

Table 3: Functional attributes of tree canopies

Forest structure parameters	Phase 1 - 10 years	Phase 2 - 15 years	Phase 3 - 20 years	Phase 4 - 50 years
White Oak				
Average tree height (m)[95]	4.04	5.88	7.61	15.95
Average Dbh (m)[95]	0.0354	0.0872	0.146	0.521
Average crown width (m)[96]	0.90	3.19	5.41	9.96
Average height to crown base (m)[97]	1.66	2.42	3.14	6.57
American Elm				
Average tree height (m)[95]	3.15	4.62	5.99	12.12
Average Dbh (m)[95]	0.0228	0.0521	0.0873	0.3062
Average crown width (m)[98]	1.47	1.80	2.01	3.28
Average height to crown base (m)[97]	1.68	2.82	3.91	8.83
Eastern Hemlock				
Average tree height (m)[95]	3.41	5.80	8.19	21.28
Average Dbh (m)[95]	0.0189	0.0769	0.1778	1.469
Average crown width (m)[99]	1.71	2.70	4.41	26.33
Average height to crown base (m)[97]	1.40	2.33	3.29	8.55

Table 4: Parameters for wetland design

Parameter	Value
Flow rate in m^3/day (Q_{water})	4.15
Type of media	Fine-to-medium gravel
Average porosity of media (ϵ)[100]	0.42
Max. bed depth in m (h)	0.6
Background COD concentration in mg/l (C')[75]	30
Average surface water temperature in summer in $°C$ (T)	25
Volumetric rate constant at 20 $°C$ in $/day$ ($K_{V,20}$)[101]	0.031
Average annual precipitation in Cincinnati in $m/year$ (α)[102]	1.065
Temperature factor (θ)	1.06
COD concentration in influent stream $mgCOD/l$	26777
Oil & Grease concentration in influent stream mg/l	13.92
COD concentration in effluent stream $mgCOD/l$	100
Oil & Grease concentration in effluent stream mg/l	0.2785

Table 5: Summary of profitability analysis for different scenarios

Parameters	Techno-Centric Approach	Techno-Ecological Approach
Net present value at year 20	$42,176,225	$44,210,862
Discounted payback period (Years)	10.39	9.54
Annual rate of return (%)	19.34	21.80
Return on investment	2.19	2.46

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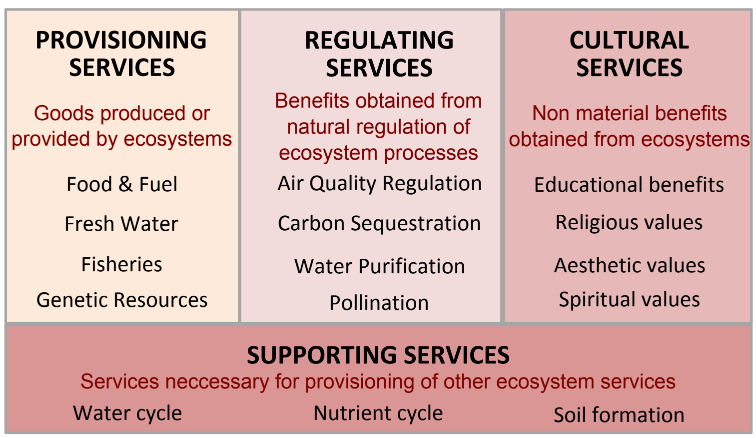


Figure 1: Categories of ecosystem goods and services[40]

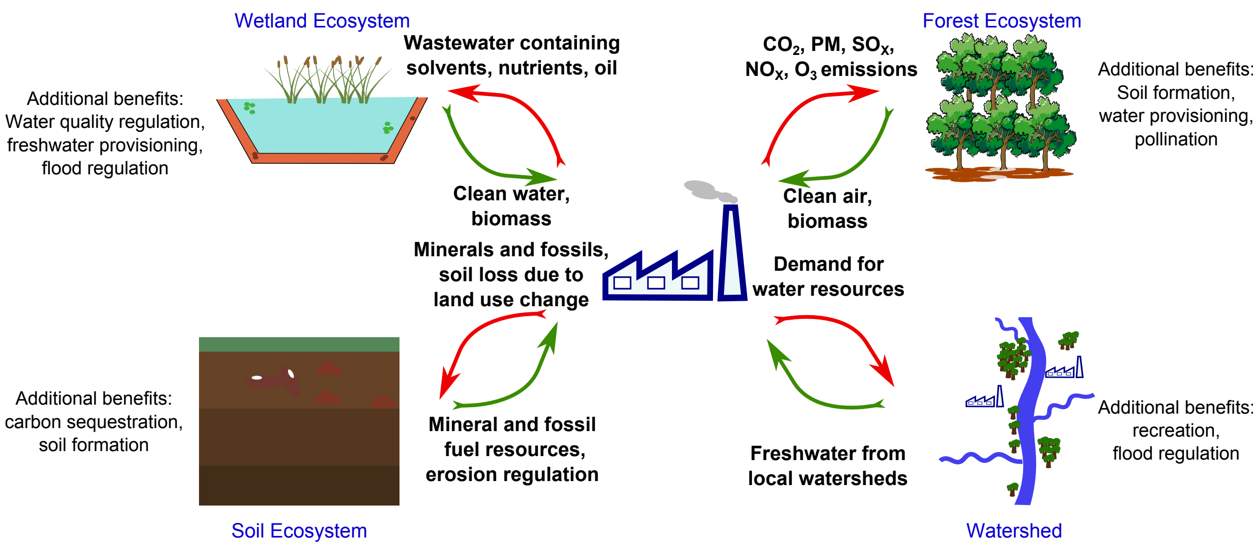


Figure 2: Dependence of manufacturing facilities on ecosystem goods and services

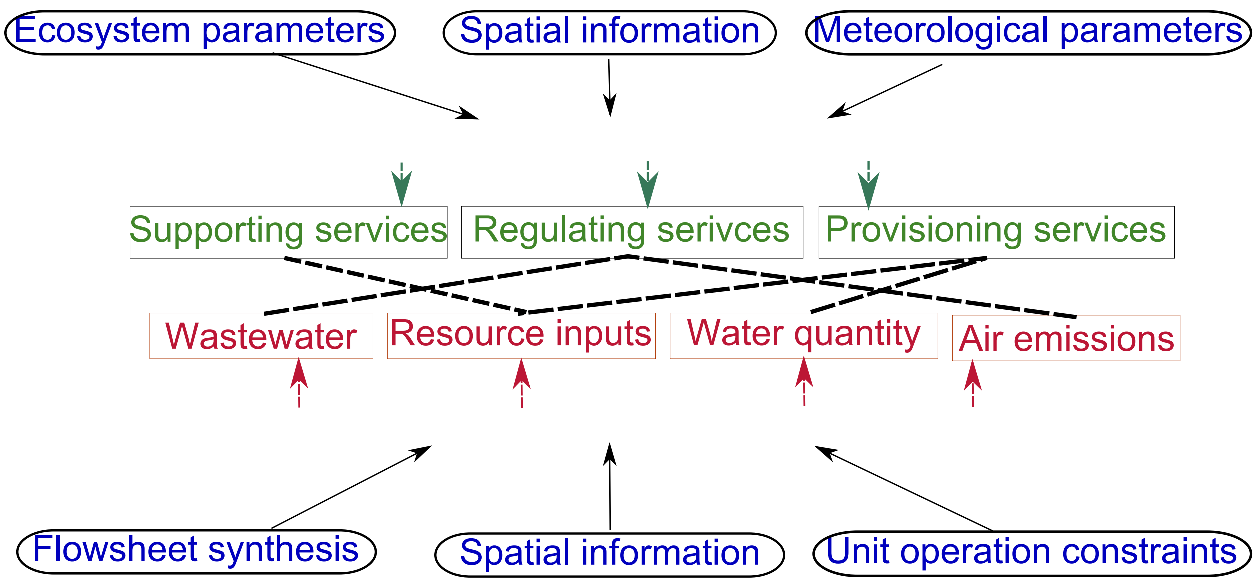


Figure 3: Conceptual figure illustrating the three steps in the TES approach

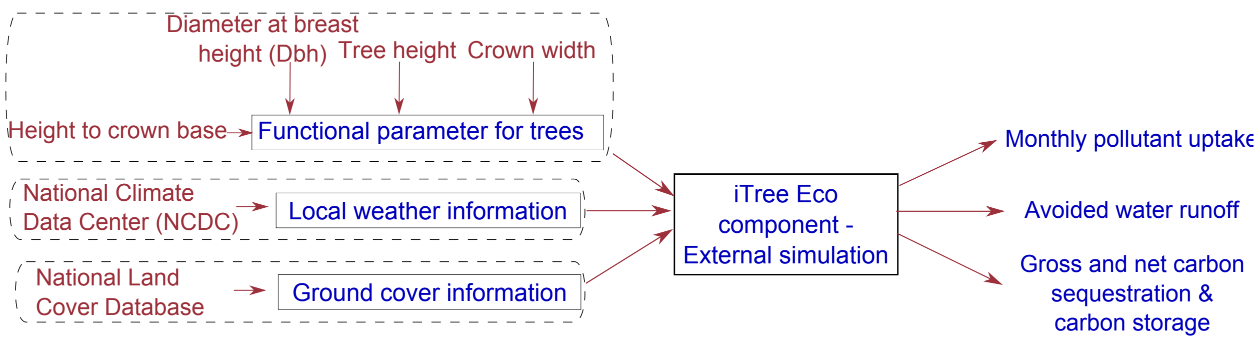


Figure 4: Model components for iTree Eco simulations

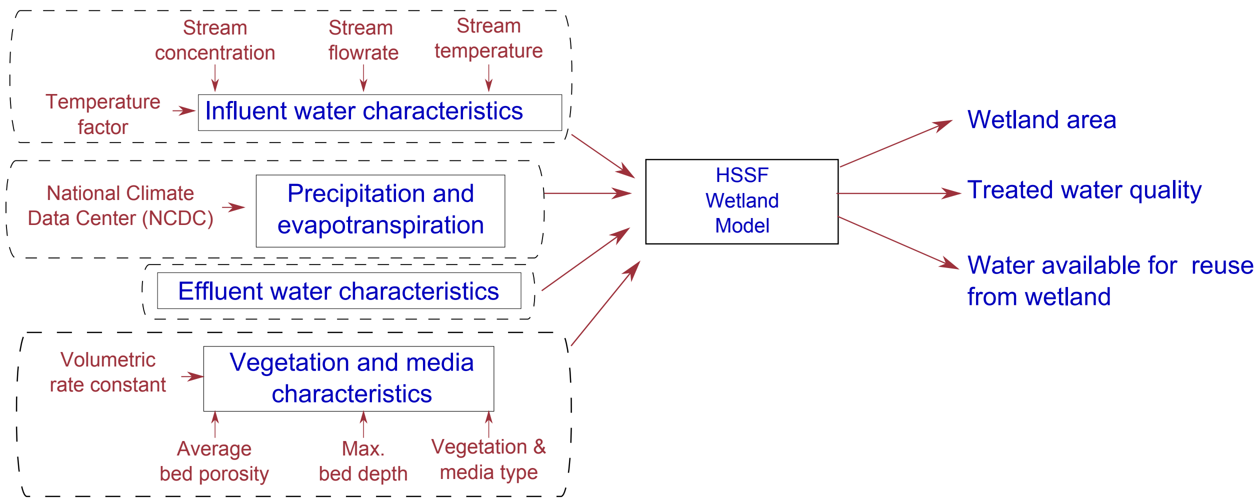


Figure 5: Model components for a designing a horizontal subsurface flow wetland

Figure 6: Biodiesel production site in Cincinnati, Ohio

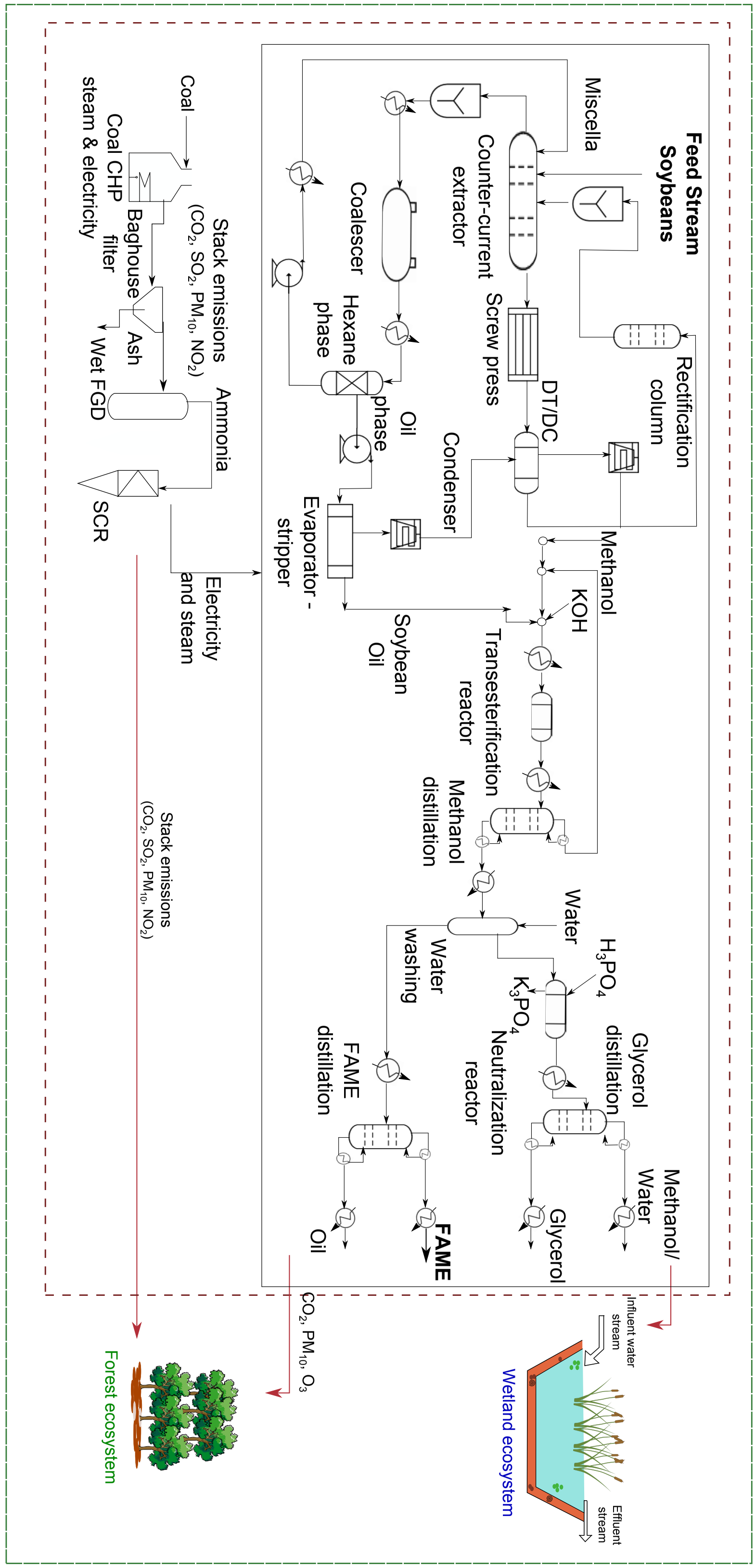


Figure 7: Flowsheet for biodiesel production process with forest and wetland ecosystems

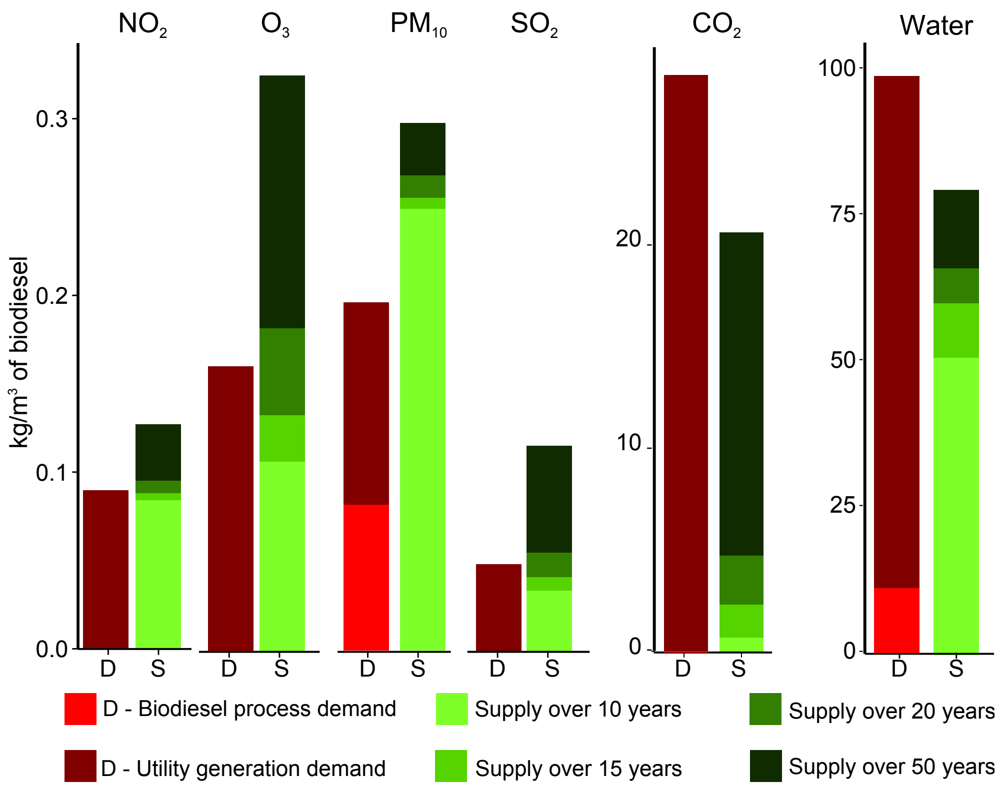
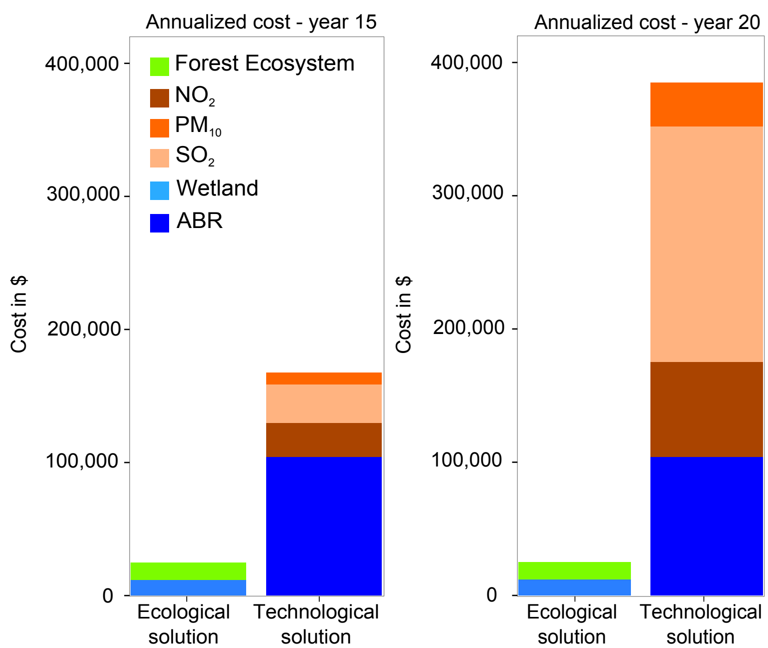


Figure 8: Demand and supply of ecosystem services



(a) Annualized cost at year 15 (b) Annualized cost at year 20

Figure 9: Annualized cost for technological and ecological solutions