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Designing biofuel supply chains while mitigating harmful algal blooms with treatment wetlands

Tapajyoti Ghosh, Bhavik R. Bakshi*

William G. Lowrie Department of Chemical and Biomolecular Engineering The Ohio State University, 151 W. Woodruff Avenue, Columbus, OH 43210, United States

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ABSTRACT

Preventing harmful algal blooms (HAB) in water bodies is an urgent environmental challenge across the world. This is a side effect from the supply chain of products from agricultural biomass, and renders many bio-based products environmentally unsustainable. Most existing efforts for designing sustainable supply chains aim to reduce the life cycle environmental impact, while ignoring nature's role in absorbing the emissions. Using the framework of techno-ecological synergy (TES), this work explicitly accounts for the role of wetlands in absorbing farm runoff to design environmentally sustainable biofuel supply chains. Application to a twenty-one county region of Northwest Ohio, which is largely responsible for HABs in Lake Erie, indicates opportunities for designing techno-ecological supply networks that are economically and ecologically superior to conventional techno-centric networks. Using the TES framework also provides counterintuitive solutions that encourage intensive agriculture with higher phosphorus runoff if there is enough land available for conversion into wetland ecosystems.

1. Introduction

Over the past two decades, environmental impacts due to manufacturing industries have rapidly come into the limelight. While global warming due to excessive carbon dioxide emissions gets the most attention, studies show that Nitrogen and Phosphorus cycles in nature have been far more seriously affected (Steffen et al., 2015) and in many regions they are disrupted well beyond nature's carrying capacity. The increase in frequency of occurrence of Harmful Algal Blooms (HABs) all over the world in coastal regions, gulfs, estuaries and lakes have been linked to increased nutrient loading (Anderson, 1989; Smayda, 1990). Links between phosphorus loadings and freshwater eutrophication in lakes have been previously established (Schindler, 1977; Schindler et al., 2016). Recently, nitrogen nutrient loading has been found to be one of the leading causes of HABs in coastal ecosystems (Glibert and Burkholder, 2006; Smayda, 1997). Eutrophication is defined as excessive plant and algal growth due to increased availability of one or more limiting factors needed for these organisms to thrive, such as sunlight, carbon dioxide, and nutrients such as phosphorus and nitrogen (Schindler, 2006). It is a slow natural phenomenon that occurs over centuries but anthropogenic activities have accelerated the rate of eutrophication in water bodies around the world due to inflow of huge amount of nutrients in discharged water (Carpenter, 1981). Eutrophication results in dense blooms of foul-smelling phytoplankton that reduce water clarity and harm water quality, destroy marine ecosystems and raise toxin levels in the water. Algae, which occurs at the surface, block light from penetrating into water which results in reduced growth and death of other plants which occur in the littoral zone (Lehtiniemi et al., 2005). High rates of photosynthesis due to algae can deplete dissolved inorganic carbon and tremendously raise acidity levels (Turner and Chislock, 2010). This heavily impairs survival of other aquatic life, especially those which rely on pH levels of water for their physiological functions. One of the major harmful effects of algal bloom is observed when these algae die, and their decomposition results in severe depletion of oxygen levels in water, also known as bottom anoxia. This results in creation of dead zones where other organisms are unable to survive. Severe decline of lake and marine ecosystems directly affect fishing economies. Lake eutrophication has proven to be a stubborn environmental problem. Lakes remain eutrophic for extended periods of time with slow recovery or no recovery at all from eutrophication (Carpenter, 2005). Phosphorus inputs to lakes usually come from sewage, industrial effluents, and runoff from agriculture and urban areas.

Several methods of curbing this environmental problem has been explored, collectively known as best management practices (BMPs). Controlling non-point sources such as agricultural farms is difficult and return of lakes to pre-eutrophic conditions might

* Corresponding author.
E-mail address: bakshi.2@osu.edu (B.R. Bakshi).

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take significant amounts of time. Control measures include diversion of excess nutrients (Edmondson, 1970), altering nutrient ratios (Downing et al., 2001), physical mixing (Huisman et al., 2004), shading water bodies with opaque liners or water-based stains, bio-manipulation and application of algaecides such as copper sulphate (Boyd and Tucker, 2012). Such stop gap end of pipe solutions does not necessarily solve the problem, are expensive to apply and may shift problem outside the system boundary. Methods aimed primarily at reducing agricultural phosphorus include (1) tillage management (conservation tillage), (2) conservation cropping such as crop rotation, double cropping (3) conservation buffers such as riparian forest buffers along major streams (4) constructed wetlands to treat runoff and (5) grassed waterways and novel techniques such as two stage ditches aimed at reducing water flow velocity (Watson et al., 2016). Currently, even technological solutions like treatment devices are being considered to address this problem.

Biofuels introduced primarily to reduce dependence on fossil fuels and life cycle greenhouse gas (GHG) emissions are derived from corn and soybeans. As demand of biofuels have increased, so has the demand for these agricultural products. Reports show that amount of corn used for production of ethanol increased from 0.63 billion bushels in 2000 to 5.28 billion bushels in 2016 (AFDC, 2016). To meet this huge demand, farms have increasingly shifted to intensive agricultural practices that involve applying large amounts of fertilizer to the soil which results in increased nutrient runoffs that flow into large water bodies. It is necessary that raw materials sourced for biofuel production do not address energy availability and greenhouse gas (GHG) emissions by shifting the problem to aquatic pollution. Thus, design of sustainable supply chains for sourcing agricultural biomass for feeding such biorefineries is highly essential. There has been a large amount of literature in the field of chemical engineering for design of supply chains. Eskandarpour et al. (2015) provides a detailed review of all articles in this domain and lists them into the different groups to which they belong. Out of those, 84 articles are listed to have some sort of environmental dimension within their purview. A vast majority of these papers deal specifically with the supply chain (SC) of biomass to liquid fuel conversion processes. De Meyer et al. (2014) provides a detailed review of supply chains focusing specifically on management of biomass supply chains. Nikolopoulou and Ierapetritou (2012) review sustainable supply chain design (SSCD) articles focusing on energy efficiency, waste management and water management. Previously most articles used to focus only on the traditional economic objective for designing supply chains (Akgul et al., 2010; Aksoy et al., 2014; Dunnett et al., 2008). However, as awareness for environmental impacts has increased, researchers have increasingly combined the environmental dimension to supply chain design, thus developing multi-objective optimization problems. Hugo and Pistikopoulos (2005) were one of the first studies to perform a multiobjective optimization by combining LCA with SC optimization for fuels. Guillén-Gosálbez and Grossmann (2009) also combined LCA with SC design but introduced a stochastic MINLP model to account for uncertainty in the design solutions. Mota et al. (2015) used the ReCiPe indicator with SC design while attaching a social indicator to capture social, economic and environmental sustainability. They applied it to SC of a Portuguese battery producer. Santibañez-Aguilar et al. (2014) used a multiperiod multiobjective optimization model to maximize profit and minimize environmental impact using the Eco-indicator99 LCA technique for a biorefinery supply chain in Mexico. You and Wang (2011) designed supply chains of biofuels by combining annualized cost with greenhouse gas emissions. Later, You et al. (2012) extended the study by including economic input output (EIO) models. However, the IO models were used for quantifying social impacts rather than to expand the system boundary of the problem. They applied it for the design of cellulosic biorefinery supply chains focusing on economic, environmental and social sustainability. Yue et al. (2013) demonstrated a life cycle optimization framework where they introduce the concept of functional units under economic and environmental criteria. Corsano et al. (2011) proposed a MINLP optimization problem where a detailed process superstructure of ethanol plants is integrated within the overall SC model to perform sustainability analysis. Zamboni et al. (2009) developed a multiechelon optimization framework which accounted for both environmental and economic dimensions and applied to the design of bioethanol factories in Italy.

While it can be seen from the literature review that researchers are actively focusing on environmental sustainability of supply chains by including multiple objectives in the supply chain design, there are some research questions pertaining to the very definition of sustainability that are yet to be answered. Sustainability is a wicked problem - a class of problems that are very hard to solve due to their in-deterministic nature. A system or process cannot be defined to be sustainable as there is no guarantee of the system not failing in the future and turning out to be unsustainable. Environmental sustainability is exceptionally difficult to determine because of the intricate network of linkages in nature and enormous chance of shifting of impacts between disciplines, spatial areas and through time. While the sufficient conditions for environmental sustainability are yet to be determined, one necessary condition that is included in almost all definitions of sustainable development is for a technological system to be within the bounds imposed by ecological carrying capacity (Bakshi et al., 2018). Overshoots exist when environmental interventions exceed their corresponding ecological carrying capacities. Having just an objective that reduces environmental emissions or resource use focuses just on the technological side of the problem. There has not been any study in the field of SSCD exploring the functioning of ecosystems and their ability to treat the emissions flowing into them from technological activities. Explicitly accounting for such flows results in integration of ecosystems within a design that provide supply chain solutions that are superior from economic and environmental perspectives (Gopalakrishnan et al., 2016).

The research work in this article extends the realm of SSCD by including ecosystem services and ecosystem functioning within the optimization problem through the recently developed Process to Planet – Techno Ecological Synergy (P2P-TES) framework. Along with design of technological processes and supply chains, design of ecosystems to improve remediation of environmental impacts and ensure sustenance of resources is performed in this study. The framework explicitly accounts for flows to and from ecosystems to technological activities. Integration of ecological services within the proposed framework for development of sustainable supply chains not only reduce environmental impact but also promote protection of ecosystems that result in increase of emission re-mediating ecological services. The advantage of using the framework is that it can easily be used to explore BMPs described earlier for addressing phosphorus runoff problem in river waters. In this study, this framework has been applied to an extensive case study in the watershed of three rivers flowing into Lake Erie in northwestern Ohio. This region is currently grappling with extensive water quality problem. Intensive agriculture practiced for production of corn and soybeans in that region requires the use of phosphorus fertilizer. This fertilizer runs off into nearby streams in the watershed of Maumee, Sandusky and Portage rivers and flow into Lake Erie. 11 million people depend on Lake Erie for their water supply. Along with that, the lake supports a substantial industrial sector having a revenue of more than $50 billion (Watson et al., 2016). Numerous studies such as whole-lake experiments at Canadas Experimental Lakes Area conducted to determine the cause of excessive eutrophication have shown that phosphorus is one of the leading causes for harmful algal blooms (Carpenter, 2008; Correll, 1998; Schindler et al., 2016). Michalak et al. (2013) have shown that long-term trends in agricultural practices are consistent with increasing phosphorus loading to the western basin of the lake which in 2011, produced record-breaking nutrient loads which in turn resulted in the largest algal bloom in Lake Erie in recorded history. Excess amount of nutrients in the shallow lake results in algal bloom that decrease water quality, destroy marine ecosystems and raises toxin levels in the water. Eutrophication of Lake Erie has been studied extensively since 1970s (Chapra and Robertson, 1977; Di Toro et al., 1987; Dolan, 1993). To curb this problem, the Great Lakes Water Quality Agreement was implemented by US and Canada which resulted in a rapid return of the lake to pre-eutrophication conditions (De Pinto et al., 1986; Makarewicz and Bertram, 1991). However, this regulation was mostly aimed at point source release of phosphorus with Total Phosphorus Loading (TPL) as the major indicator. Since 1990s, even though TPL has remained below the mandated level of 11 kilo-tonne, soluble reactive phosphorus (SRP) levels have steadily increased and contributed to increasing cyanobacteria, benthic algae growth and return of extensive central basin hypoxia (Carpenter, 2008; Kane et al., 2014). Although total farm land has not increased significantly in Ohio since 1990s, several other factors such as (1) Changing agricultural practices with more till agriculture (2) Increase in fertilizer application frequency and timing (3) application of fertilizer on surface rather than injection into soil and (4) more rainfall and extreme rain events have together increased SRP levels by 200% between 1990 and 2010 (Scavia et al., 2014). This increased nutrient level has been attributed primarily to the Maumee and Sandusky rivers which contribute about 90% of the lake wide TP loads and 92% of lake wide SRP loads (Watson et al., 2016). The watersheds of these river are dominated by agricultural practices which further confirm the sources of TP and SRP.

Sustainable supply chain design of raw material pathways for corn ethanol refineries, process design of the superstructure while focusing on phosphorus flows from corn farms in the region is the major goal of this study. Wetlands are used for treating phosphorus runoff from farms. This problem explored the Food-Energy-Water nexus as it also considers consumers in the region who consume corn as food and are challenged with degrading water quality in Lake Erie. Design solutions and trade-offs between environmental and economic objectives are explored. BMPs of tillage practices and constructed wetlands for treatment of agricultural runoff are explored. The paper is structured as follows. Section 2 contains information regarding the P2P design framework and the TES framework separately which are combined to create the P2P-TES framework. Section 3 describes this framework in details along with relevant optimization formulation. Section 4 describes the application of the framework to the SSCD problem for biorefineries in Ohio.

2. Background

2.1. Process to planet framework

Integration of supply chain design with process design, required the use and modification of a multiscale framework that could incorporate both of these components separately. The Process to Planet (P2P) framework Hanes and Bakshi (2015a) proved to be the rational choice for the foundation of this new modeling system. P2P framework consists of three separate scales – *equipment* for modeling the engineering manufacturing technology or process, *value chain* for modeling life cycle network of the manufacturing processes and *economy* scale for using economic models to capture the life cycle that is not covered by the smaller two scales. Together these three scales allow the incorporation of better environmental impact assessment through hybrid LCA (economy + value chain) in sustainable process design. It is an expansion of conventional process based LCA (Life Cycle Assessment) matrix structure which is defined as

$$Xm = f \tag{1}$$

where X is the technology matrix showing the activity network of the system, m is the scaling variable or multiplier for determining the size of the activities needed to satisfy the final demand f. P2P framework can be represented mathematically as

$$\overline{\underline{X}}\{z\}\overline{\underline{m}} = \overline{\underline{f}} \tag{2}$$

$$\overline{\underline{H}}\{z\} \geq 0 \tag{3}$$

$$\overline{\underline{g}} = \overline{\underline{D}}\overline{\underline{m}} \tag{4}$$

where $\overline{\underline{X}}$ represents a multiscale technology matrix that captures interaction between the economy, value chain and equipment scales. Variable $\underline{z}$ represents decision variables used in at any scale. In sustainable process design z represents decision variables of various equipment in the process flowsheet. Similarly, $\overline{\underline{m}}$ and $\overline{\underline{f}}$ represent the multiscale scaling vector or multiplier and multiscale final demand that contain the sizes of three separate scales and their respective final demands or flows to consumers. Overbars in these equations represent economy scale, underbar represents the value chain scale while no bars refer to the equipment scale. Combination of overbars, underbars together represent multiscale P2P matrices. Eq. (3) collectively represents all mass flow, energy balance and reaction equations that make up the process model of the industrial process with variables such as temperature, flow rate, equipment sizes, heat input, etc. Environmental impact from this multiscale framework is given by Eq. (4) where $\overline{\underline{D}}$ is the multiscale environmental interventions matrix containing impact information for activities at all three scales. It is multiplied with the scaling variables to obtained the total life cycle emission $\overline{\underline{g}}$ for a specified final demand $\overline{\underline{f}}$. The optimization framework for P2P design uses Eq. (4) as the objective function to be minimized subject to constraints of Eqs. (2) and (3). It has been applied to several case studies. Hanes and Bakshi (2015b) showed using the P2P framework how system boundary could be expanded to account for omitted emissions at the economy scale and obtain optimized solutions for process design. Ghosh and Bakshi (2017) demonstrated how P2P multiobjective framework provides win-win solutions over conventional process based LCA when applied to sustainable process design.

2.2. Techno ecological synergy

The Techno-ecological Synergy (TES) framework integrates technological process design and flows of materials(resources and wastes) to and from the environment (Bakshi et al., 2015). Such a framework incorporates ecosystems as unit operations and their services as flows within the model so that necessary bounds and constraints imposed by ecosystems can be modeled and the technological process designed around these bounds. Bakshi et al. (2015) explain that the TES framework tries to address environmental challenges in two ways, encouraging less bad through impact minimization (reducing raw material input and emission levels) while doing more good by means of ecosystem restoration and technological innovation as shown in Fig. 1. TES framework has been applied to designing a residential system (Liu and Bakshi, 2018) and industrial manufacturing site (Gopalakrishnan and Bakshi, 2018) and has been proven to have both economic and environmental benefits – "win win" solutions. Liu et al. (2018a,b) have developed a framework that combines TES and LCA to include

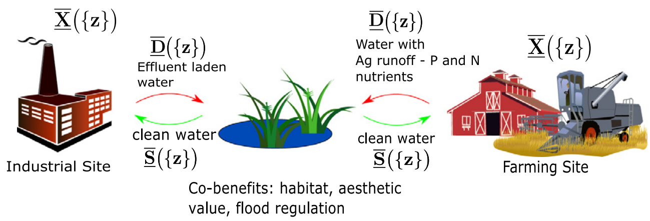

Fig. 1. Technoecological synergy with wetland ecosystems.

ecosystem services in conventional Life cycle Assessment. The computational structure of the TES-LCA framework is expressed as

$$\begin{bmatrix} A & C \\ D & S \end{bmatrix}\begin{bmatrix} m \\ m_e \end{bmatrix} = \begin{bmatrix} f \\ f_e \end{bmatrix} \tag{5}$$

where A is the technology matrix of process based LCA containing economic product flows between technological activities, B is the environmental intervention matrix, which indicates resource use or emissions associated with the technological activities and S is the ecosystem matrix, representing flows between ecological modules in a similar manner to the technology matrix. While technological activity production values are provided in the A matrix, the uptake rate of emissions by ecosystems are provided in the S matrix. C is the management matrix representing the economic product flows from technologies to ecosystems for their maintenance. The objective for this single scale framework is to determine f_e or total environmental impact while accounting for ecosystem services. Its focus is on analysis of a given fixed system and does not involve any optimization or design.

3. Methodology

Motivation behind creating a modeling framework that can perform both process and supply chain design while accounting for ecosystem services and life cycle comes from visualizing the process based LCA matrix structure as a upstream network of any process. Process based LCA represents different activities that are connected with one another and supplies the necessary input flows for the production of the main product. If this upstream network can be alternatively viewed as a supply chain, modifying the problem to design the process based LCA matrix structure evolves into a supply chain design problem. In fact Weidema et al. (2018) have discussed and compared value chain and supply chain and shown how closely they are linked to one another. An initial version of this framework was briefly described in Ghosh et al. (2018). The steps for modifying the P2P framework to the P2P-TES framework is sequentially listed below.

3.1. Modification 1 – including ecosystems in P2P framework

To include ecosystems as unit operations in the different scales, the P2P framework had to be expanded so as to account for flows to and from the ecosystems. Using the TES-LCA framework explained in the Section 2 and combining it with P2P to bring in design variables of process and supply chain, we developed the multiscale P2P-TES framework. While the single scale TES framework was only used for analysis of environmental impacts at the value chain scale, the multiscale P2P-TES framework optimizes a given objective to solve for designs of engineering activities as well as upstream input raw material pathways. Along with three different scales of P2P framework, ecosystems at the different scales are also integrated with technological activities. Flows between ecosystems and technological systems are explicitly included in this framework. The framework is mathematically expressed as shown in Fig. 2. Ecological systems considered in TES can be forests, wetlands, pollinators etc. While sequestering of carbon dioxide can be considered a global ecological service analogous to the economy scale of P2P, deposition and capture of sulphur dioxide particulate matter can be regional services provided at the value chain scale. Wetlands help in treating water locally which contain effluents, heavy metals, organic nutrients and provide back clean water. This service can be obtained at the local site just beside an industry at the equipment scale or may be combined together for watersheds at value chain scale. These ecosystems are components of the $\bar{S}$ matrix. Ecosystems at the equipment scale are represented as unit operations using

$$S(\{z, b\}) \geq 0 \tag{6}$$

At value chain scale, ecosystems are represented like technological activities are modeled – linear model with inputs and outputs proportional to each another in some fixed ratio. The difference is that emission flows from technological systems are inputs to these activities. Such database for ecosystems are not yet available but can be obtained by averaging several ecosystems over a large regional area – such as a watershed. Building models of ecosystems at economy scale is difficult. First step is to obtain monetary values of various ecosystem services provided by nature. There are some databases that provide such information (TEEB, 2016). Next, these ecosystem economic valuations need to be integrated with input output model economic flows that reduces the net economic throughput which in turn results in lower environmental impact through Environmentally Extended Input Output analysis (EEIO) calculations. Every component of the large P2P-TES matrix is explained as follows. $\bar{X}(\{z\})$ represents the network of technologi-

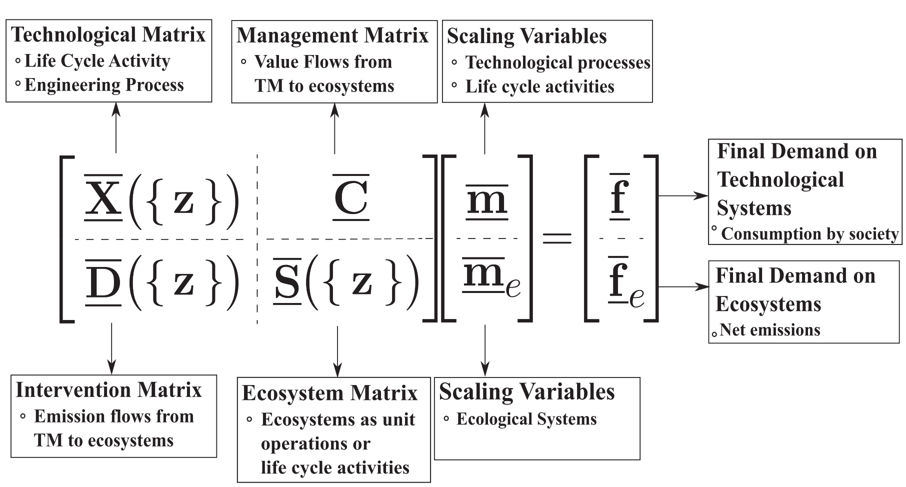

Fig. 2. Multiscale matrix structure, equations and representation of the P2P-TES framework.

cal activities in the system and is known as the technology matrix (TM). $\underline{\overline{D}}(\{z\})$ represents the emissions matrix, included separately to denote the flows from technological systems to ecosystems shown in Fig. 1. $\underline{\overline{S}}(\{z\})$ is analogous to the $\underline{\overline{X}}(\{z\})$ matrix except that it contains ecosystems at different scales. This matrix represents the ecosystem services obtained from natural systems, such as air quality regulation and water provisioning by forests, water treatment through wetlands etc. which is given back to the technological systems as shown in Fig. 1. $\underline{\overline{C}}(\{z\})$, known as the management matrix represents flows of materials that are necessary for maintenance of ecosystems from the technological systems. Mathematically, the major difference between this equation and Eq. (5) is that the individual terms in the matrices are all multiscale rather than single scale. Also, these terms include variables of engineering process design z since the objective of this framework is to perform optimization for design solutions. $\overline{\underline{f}}$ is the final demand for technological systems and $\overline{\underline{f}}_e$ denotes final demand on ecosystems. $\overline{\underline{f}}$ contains demand of useful products which are consumed by society whereas emissions or environmental impacts are expressed as demand of ecosystem services in $\overline{\underline{f}}_e$. The matrix structure enabling integration of these different components is shown in Fig. 2.

3.2. Modification 2 – introduction of spatial variables

The P2P framework is setup as an optimization problem for achieving different objectives as per the concerned stakeholder. Design variables are only restricted to the equipment scale where they are used to determine process parameters. In this framework, spatial decision variables are introduced into the three scales such that the problem can be solved for choices of suppliers, economic sectors as well as search for locations for the primary process. These variables denoted as b can be binary when choices are mutually exclusive or continuous. With this modification, P2P-TES framework can now be mathematically represented as

$$\begin{bmatrix} \underline{\overline{X}}(\{z,b\}) & \underline{\overline{C}}(\{z,b\}) \\ \underline{\overline{D}}(\{z,b\}) & \underline{\overline{S}}(\{z,b\}) \end{bmatrix} \begin{bmatrix} \underline{\overline{m}} \\ \underline{\overline{m}}_e \end{bmatrix} = \begin{bmatrix} \overline{\underline{f}} \\ \overline{\underline{f}}_e \end{bmatrix} \tag{7}$$

In previous design studies, the $\underline{\overline{X}}$ matrix was fixed. It represented the network of technological activities in the system. The number of activities and their products are previously determined and they always existed within the matrix. With this modification the $\underline{\overline{X}}$ matrix becomes variable. Activities within this matrix may or may not be included based on the values of spatial b variables. If for a certain activity, its corresponding binary spatial variable is 0, that activity is removed from the technology matrix. The activity gets included when its corresponding b has a value of 1. Due to the presence of spatial variables in the technology matrix, associated $\underline{\overline{D}}(\{z,b\})$, $\underline{\overline{S}}(\{z,b\})$ and $\underline{\overline{C}}(\{z,b\})$ also get modified with their corresponding b variables. Solving Eq. (7), the unknown scaling variables $\underline{\overline{m}}$ and b are determined.

3.3. Environmental impact assessment

P2P-TES framework, built on the matrix structure form of LCA is used for environmental impact calculation. Final demand matrix in Eq. (7) is demand of valuable products by society manufactured by the system under study. The first step is to solve for technological scaling variables $\underline{\overline{m}}$ using

$$\underline{\overline{X}}(\{z,b\})\underline{\overline{m}} = \overline{\underline{f}} \tag{8}$$

Emission flows from the system is given by

$$\overline{\underline{f}}_e = \underline{\overline{D}}(\{z,b\})\underline{\overline{m}} \tag{9}$$

If ecosystems are considered to take up emission flows from technological activities, then Eq. (9) gets modified into

$$\overline{\underline{f}}_e = \underline{\overline{D}}(\{z,b\})\underline{\overline{m}} - \underline{\overline{S}}(\{z,b\})\underline{\overline{m}}_e \tag{10}$$

In an environmentally sustainable system $\overline{\underline{f}}_e$ should be 0, which denotes that there are no net emissions or demand of ecosystem services. This condition is mathematically represented as

$$\overline{\underline{f}}_e = 0 \tag{11}$$

$\underline{\overline{m}}_e$ denotes the scaling variables to determine size of ecosystems while $\underline{\overline{m}}$ represents size of technological systems. These are similar to scaling variables in conventional process based LCA. The net environmental impact is obtained as

$$\overline{\underline{g}} = \sum_n Q^n \overline{\underline{f}}_e^n \tag{12}$$

which represents the sum of final demand to ecosystems. Q is the characterization factor matrix. It contains the impact categories such as acidification potential, global warming potential etc. for every environmental flow. Using Eq. (12), the different environmental flows are lumped together by converting them into midpoint indicators for various impact categories. If required, the midpoint indicators can be summed up to calculate endpoint indicators. The P2P-TES framework includes not only direct environmental impacts in the life cycle but also considers the supply of ecosystem services to mitigate such impacts. Incorporation of ecosystem services allows design of technological systems such that supply and demand of these services are balanced and do not exceed limits, making the system unsustainable. Solving Eq. (11), as mentioned earlier, technological scaling variables $\underline{\overline{m}}$ are determined. Along with that, size of ecosystems required for mitigating impacts can be determined by solving for ecological scaling variables $\underline{\overline{m}}_e$. If these variables are known, then using Eq. (12), the net environmental impact can be calculated rather than minimized.

3.4. Objective functions

$$\textbf{Environmental objective} \quad Z_1 = \overline{\underline{g}} \tag{13}$$

$$\textbf{Economic objective} \quad Z_2 = \underline{\overline{X}} p_x + \underline{\overline{C}} p_c \tag{14}$$

The design solution is obtained by optimizing relevant objective functions depending upon the scope of the problem. Environmental objectives capture the life cycle impacts from all the different scales using Eq. (12). Economic objective functions depend primarily upon the stakeholders. The first term of Eq. (14) captures the economies of technological activities at all the different scales, from raw materials, transportation and plant operation. The second term denotes the cost of maintenance of ecosystems paid by stakeholders. This can be cost of land, or regular upkeep of forests or wetlands.

3.5. Optimization formulation

$$\textbf{Minimize} \ Z_1, Z_2 \tag{15}$$

$$\textbf{subject to} \quad \begin{bmatrix} \underline{\overline{X}}(\{z,b\}) & \underline{\overline{C}}(\{z,b\}) \\ \underline{\overline{D}}(\{z,b\}) & \underline{\overline{S}}(\{z,b\}) \end{bmatrix} \begin{bmatrix} \underline{\overline{m}} \\ \underline{\overline{m}}_e \end{bmatrix} = \begin{bmatrix} \overline{\underline{f}} \\ \overline{\underline{f}}_e \end{bmatrix} \tag{16}$$

$$H(\{z,b\}) \geq 0 \tag{17}$$

$$S(\{z,b\}) \geq 0 \tag{18}$$

$$\underline{\overline{m}} \geq 0 \tag{19}$$

$$\underline{\overline{m}}_e \geq 0 \tag{20}$$

The scaling variables are multiscale and relate to the technological and ecosystems at different scales. Presence of variables in the equipment scale allows the framework to be used for process design. In the value chain, it allows choosing between suppliers of raw materials and required inputs which proves supply chain design capabilities. Variables at the economy scale can be used for policy design. In the current work, we explore only the supply chain and process design multiscale problems.

4. Case study

As explained in Section 1, the northwestern region of Ohio and eastern Indiana is grappling with a eutrophication of Lake Erie causing HABs and severely impeding drinking water supply. Several industries that depend on Lake Erie are also suffering due to this. One of the ways of addressing this environmental problem is to reduce the phosphorus load of the lake. Development of a biofuel supply chain network that depends on agricultural feedstock as raw materials results in chances of exacerbation of the phosphorus run off problem. Thus, it requires adaptation of sustainable agricultural practices and choosing those farms that follow those methods. The P2PTES framework is applied to this region for a problem designed as follows.

4.1. Problem description

21 counties in the northwestern part of Ohio are selected in the watershed of the Maumee, Portage and Sandusky rivers. The problem is solved at county scale with information of corn production, corn usage by consumers as food and phosphorus runoff at different counties. The location of farms, corn ethanol refineries, consumers as well as ecosystems are assumed to be at the centroid of the counties. The framework described in Methodology is general but for purposes of this case study, we are not considering the economy scale within this problem.

A complete overview of the system under study is shown in Fig. 4. There are three primary players - Refineries, farms and consumers. Farms produce corn resulting in agricultural runoff laden with phosphorus nutrients. Corn is consumed as food by consumers and as raw material by refineries for production of bioethanol. Bioethanol produced is used to satisfy the bioenergy demand of the consumers in that region. To reduce phosphorus in runoff water, ecosystem services provided by constructed wetlands are considered in this study. The wetlands are assumed to be present near the farms so that runoff water flow can be directed into them. The goal of the problem is to determine the location of biorefineries in this region, as well as farms from which both refineries and consumers source their corn supply. These solutions depend on the objective being considered, such as minimization of phosphorus run off in water, minimization of cost for corn-ethanol production etc.

Corn production information is obtained from USDA (2015) for the different counties shown in Fig. 3. From USDA, it is found that all 21 counties considered had corn production. Thus, farms are present in all the counties. To explore the effect of different farming practices, counties are assumed to practice different forms of

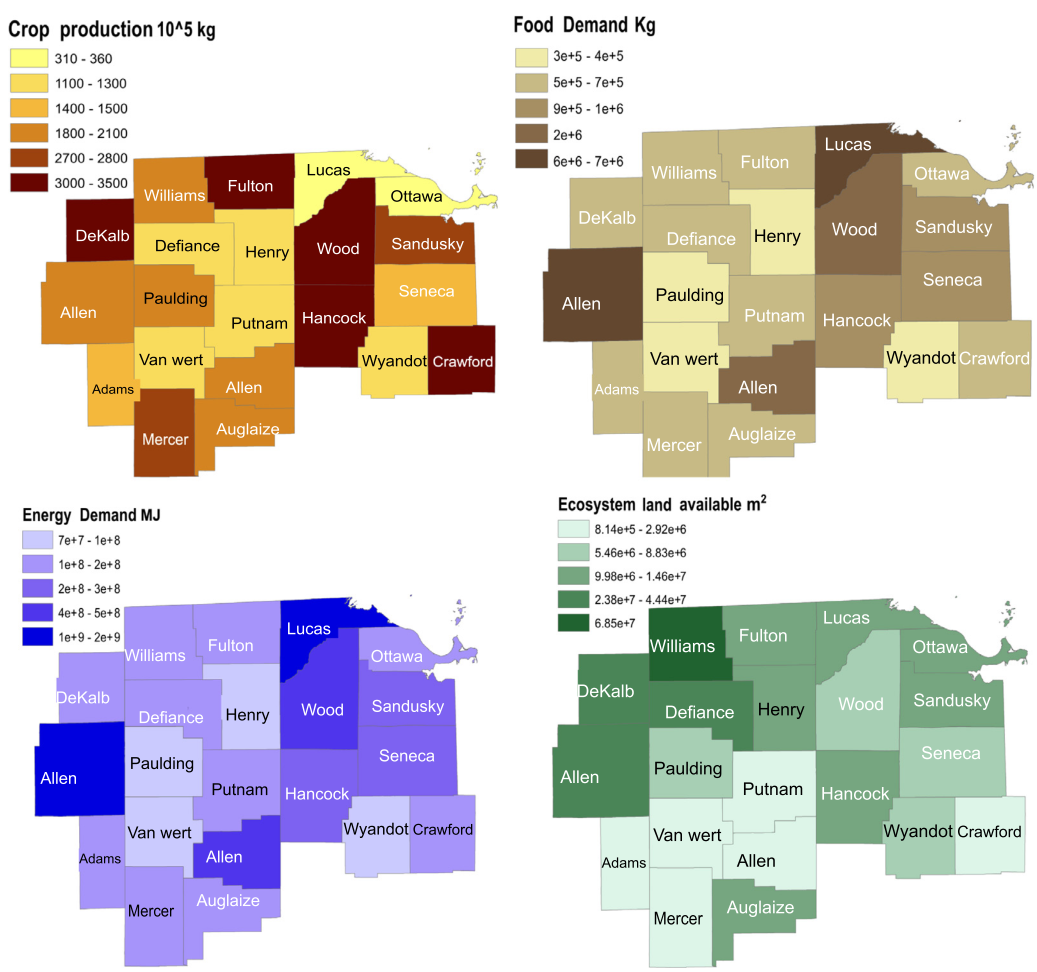

Fig. 3. County scale information of crop production, biofuel energy demand, crop production and ecocystem area available in 21 counties in Ohio.

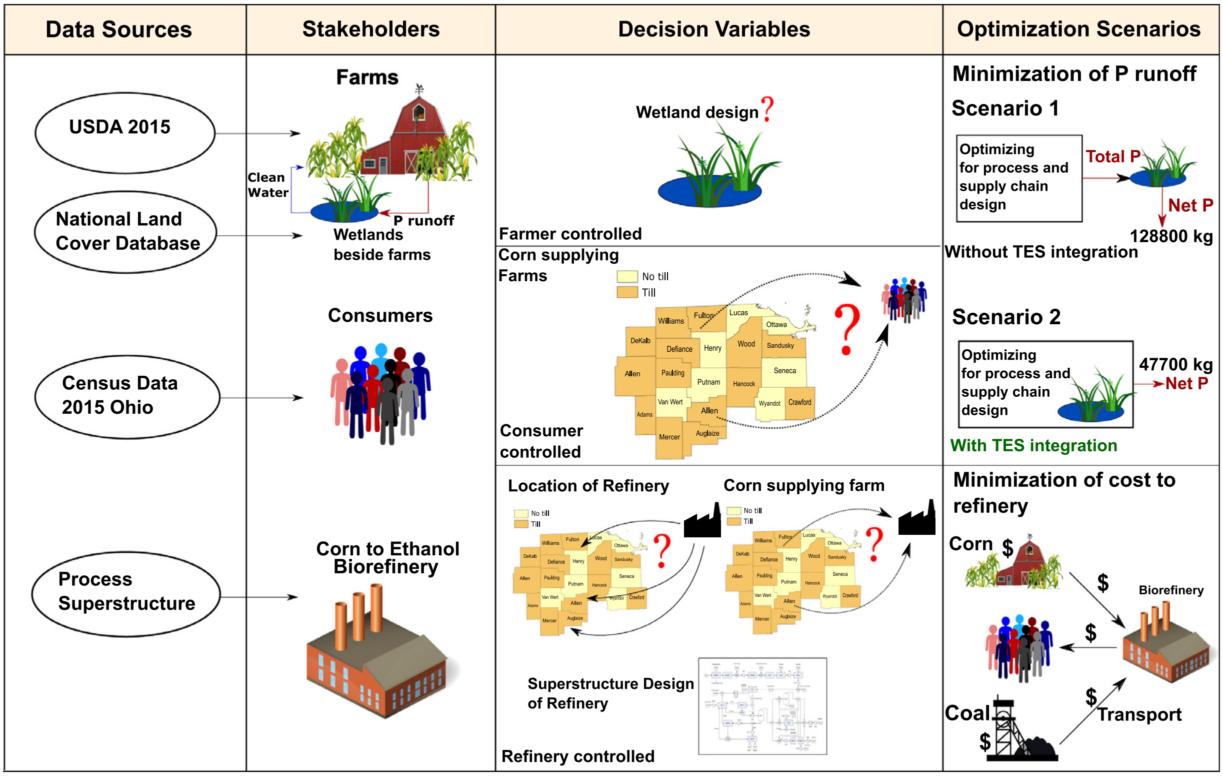

Fig. 4. Overview of case study describing data sources, stakeholders, decision variables of different stakeholders and optimization scenarios explored in study.

agricultural practices as shown using different colors for the counties in Fig. 4. The farming choices are expected to affect the supply chain choices from where the biorefineries source their corn as feed as shown in Fig. 4 decision variables column. As no till agriculture results in lower production of corn, it is considered that no till corn is priced higher to recuperate losses for the farmers. However, no till agriculture results in lower phosphorus levels in agricultural runoff.

Using the countywise population information (Census, 2015) and statewise demand of corn as food and energy from biofuel (EIA, 2015), the countywise demand for ethanol-based energy and corn consumption by residents are derived. This information is mapped in Fig. 3. While different methods can be applied for reduction of phosphorus runoff, in this study we explore the use of wetlands for removal of phosphorus from agricultural runoff water. For this service, land needs to be available to be converted into wetland. For such purposes, in this study, we considered barren, swamp and shrubland areas in these counties to be available for conversion. These converted wetland areas are also considered to be at the centroid of the counties. The available land for different counties are shown in Fig. 3. Amount of different types of available area is obtained from National Land Cover Database (NLCD, 2011) through ArcGIS 10.6 software.

Bioethanol refinery location is determined through solving this problem as shown in Fig. 4. The fundamental engineering model (Hanes and Bakshi, 2015b) of the corn to ethanol plant is based on a 50 million gallon capacity plant. After obtaining the total bioethanol energy demand of consumers in this region from US Energy Information Administration (US-EIA) (EIA, 2015), it is observed that corn ethanol produced by two 50 million gallon capacity refineries would be enough to satisfy the corn ethanol demand of this entire region. Hence, the choice of binary variables is such that the refineries can be placed at any of the counties with a maximum of two biorefineries in the entire region for satisfying the demand of corn ethanol. The plant capacities have been assumed to be fixed at 50-million-gallon value because in real plant operation, a plant generally operates at its designed intended capacity. The biorefineries can choose their corn supply from any of the farms in the 21 counties. Along with design of the supply chain, the process design of the corn to ethanol refinery is also included in the system as shown in Fig. 4. Variables which are optimized for this process design are listed in the Table 2 in SI.

A major assumption is that trade with entities outside the system boundary of this region is not considered in this study. In reality, a major part of the corn produced in this region would be exported outside these counties. Similarly, ethanol produced by the refineries would also be exported. However, as we are delimiting our system to this location, the consumption of corn and ethanol is limited to consumers in this region. This assumption also makes sure that infeasible solutions do not appear in the optimization problem because the total production of corn in this region is much more than the possible consumption by bio-refineries and consumers in this region.

Due to the presence of multiple players (farms, consumers and refineries) in this problem setup shown in Fig. 4, the optimization objectives need to be modified to cater specific goals within the purview of the problem. The three major stakeholders in this problem are the consumers, mainly based in and around the region of Toledo in Ohio. These people are the most affected by the declining water quality in Lake Erie due to eutrophication. Consumers have the power to enact laws or policies to monitor the amount of phosphorus flowing into Lake Erie through the rivers. The second stakeholder are farmers. Their main goal is to produce and sell as much corn as possible that accounts to increased revenue. However, the farmers have control over their farming methods that can help reduce phosphorus runoff into water streams - such as reducing phosphorus application, reducing corn production, less intensive agricultural practices, no till agriculture, wetlands to treat water, catchment areas along river banks, etc. The third stakeholders are the corn ethanol refineries. All the refineries are considered together as a single entity. Major goal of refineries is to produce as much as bioethanol demanded by the users in this region. These refineries can improve their profits by buying cheaper corn from farmers, which is their main raw material. Process design and operating parameters as listed in Table 2 in SI. are within control of this agent. Supply chain decisions are also taken by the biorefinery agent. In this case study, our focus is on the design of corn ethanol refineries, their supply chain while trying to minimize environmental impact through phosphorus run off reduction which is directly affecting the consumers by degrading their water quality.

4.2. Wetland ecosystem models

Wetland ecosystems can break down and absorbing pollutants like phosphorus and nitrogen nutrients, heavy metals, suspended solids. They can also reduce biological oxygen demand and destroying microorganism like algae. Various industries such as paper and pulp mills, meat processing facilities, and petroleum refineries use constructed wetlands as treatment units to remove oil and grease, heavy metals, chemical oxygen demand and other pollutants. These wetlands provide a cost-effective alternative to conventional treatment units as they do not need regulation, maintenance and operating energy costs. Viability of ecosystems for treating wastewater has been studied previously (Kadlec, 1995; 1997; Kadlec and Wallace, 2008). Wetland operations are modeled using first order plug flow reactors. They have an exponential profile between inlet and outlet flows. These equations are used to find the surface area of wetlands needed to treat a certain concentration of wastewater based on reactor conditions such as temperature.

However, for purposes of this study, it was difficult to use the PFR model, primarily due to lack of information about the phosphorus concentration in runoff water from farms at the scale of individual counties. Thus, to circumvent this problem, the first order models are converted to zero order models by plotting wetland treatment data from Kadlec (2016) and regressing a log-based model to develop a relation between wetland area and phosphorus uptake. The values obtained from the equation are found to be in concordance with experimental data obtained from wetlands already constructed in Ohio. Detailed information about the wetland model is provided in the SI.

4.3. MINLP problem formulation

A multiobjective non linear optimization problem is developed for solving this design problem. The 21 counties are defined by a set **C**. The set of 21 farms pertaining to every specific county is defined as **F**. Similarly the sets of consumers and possible refineries in these counties are defined as **P** and **R**. Ecosystems are considered to be present alongside every farm and their set is defined as $\mathbf{F_E}$.

4.3.1. Corn ethanol refinery

$$\overline{\underline{X}}_{k,k}(\{z,b\}) \;=\; fc_{eth}(H(\{z\}))\ s.t.\ k \in \mathbf{R} \tag{21}$$

$$H(\{z\}) \geq 0 \tag{22}$$

Eq. (22) denotes the combination of fundamental models to describe the process superstructure of a technological activity such as a corn to ethanol conversion process. It comprises of mass, energy balances and all other variables that determine the conversion of raw materials to a useful product. $fc_{eth}(H(\{z\}))$ is the outflow of ethanol from the process superstructure of the wet corn-to-ethanol technology represented as $H(\{z\})$. The conversion technology model has been adopted from Karuppiah et al. (2008). Few parts of the process have been linearized for ease of optimization. Process variables are provided in the SI.

4.3.2. Refinery location

$$\exists!\overline{\underline{X}}_{k,k}(\{z,b\})\ :\ b_k = 1\ s.t.\ k \in \mathbf{R} \tag{23}$$

$$\sum_k b_k \leq 2 \tag{24}$$

Eq. (23) represents the existence of a refinery if the binary variable b associated with that region is equal to 1. b_k and $\overline{\underline{X}}_{k,k}(\{z,b\})$ have a one-one mapping relation to each other. Eq. (24) makes sure that a maximum of two refineries can be incorporated in this system. Thus, the variable k actually relates to two refineries only. In Fig. 5, this points to the ethanol production cell. Out of the 21 counties, only two will be chosen for refinery placement as explained in Section 4.1.

4.3.3. Consumer demand of food

$$FD_j = \sum_i \overline{\underline{X}}_{i,j}(\{z,b\})\ s.t.\ i \in \mathbf{F}, j \in \mathbf{P} \tag{25}$$

where FD_j is the food demand of the jth consumer. As shown in 5, Eq. (25) denotes the flow of corn as food material from ith farm to the jth consumer. This constraint makes sure that the amount of corn flowing from all farms to a specific consumer equals the corn demand of that consumer.

4.3.4. Consumer demand of bioethanol

$$BD_j = \sum_k \overline{\underline{X}}_{k,j}(\{z,b\}) \tag{26}$$

$$\sum_j \overline{\underline{X}}_{k,j}(\{z,b\}) \leq fc_{eth}\ s.t.\ j \in \mathbf{P}, k \in \mathbf{R} \tag{27}$$

where BD_j is the bioethanol demand of the jth consumer. $\sum_k \overline{\underline{X}}_{k,j}(\{z,b\})$ denotes the flow of ethanol as biofuel from sum of kth refineries to the jth consumer. As shown in 5, this equation refers to the row sum for every consumer column in the ethanol consumption part of $\overline{\underline{X}}$ matrix. This constraint makes sure that the amount of ethanol flowing from all refineries to consumers of a certain county equals the bioethanol demand of all consumers in that county. fc_{eth} is the flow of ethanol output from a refinery obtained from the fundamental engineering model. Eq. (27) makes sure that total amount of bioethanol consumed from each biorefinery does not exceed its production.

4.3.5. Corn demand of biorefinery

$$CD_k = \sum_i \overline{\underline{X}}_{i,k}(\{z,b\})\quad s.t.\ i \in \mathbf{F}, k \in \mathbf{R} \tag{28}$$

$$CF_k = fc_{corn} \tag{29}$$

where CD_k is the corn demand of the kth refinery. $\sum_i \overline{\underline{X}}_{i,k}(\{z,b\})$ denotes the flow of corn from sum of ith farms to the kth refinery. This constraint makes sure that total amount of corn from all selected farms to a specific refinery equals the corn demand of that refinery. Eq. (29) relates the corn demand from the supply chain to the corn feed input flow fc_{corn} in the process superstructure of the refinery. This flow information relates to the corn consumption by refineries cell in Fig. 5. It must be noted that the flow information depends on whether a particular refinery in a county has been chosen to be located or not. If there is no refinery, then flows do not occur.

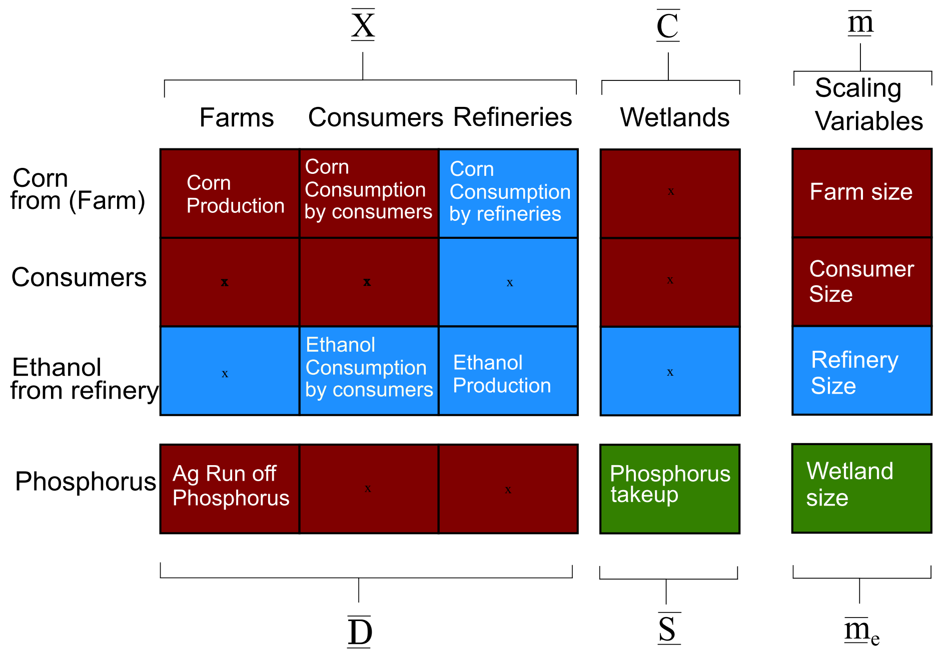

Fig. 5. $\overline{X}$ matrix for the corn ethanol problem, Flows in cells with **x** marks are not considered in this study. Consumers do not have any product that sell to Refineries or Farms.

4.3.6. Energy demand of biorefinery

$$ED_k = \overline{X}_{coal,k}(\{z,b\}) \ s.t. \ k \in \mathbf{R}. \tag{30}$$

It is assumed in this problem that the refineries obtain its energy for operation from coal. However, the coal supplier is not included within the system and is modeled as being supplied from outside the system boundary. Thus, the impact of using energy from coal does not affect the solution. The coal supplying sector is included in the $\overline{X}$ matrix to capture the transportation costs of coal to the refinery. Since it is an external sector to the system boundary and incorporated separately, it has not been included in Fig. 5. Transportation of fuel can constitute a large part of industry operating cost and can have a profound effect on its location. In this case study, as one of the design decisions was determination of biorefinery location, it was necessary to consider fuel transport from a selected source. However, this fuel source need not be coal. It can be replaced by other fuel sources that might impact refinery location. Hence, in this case study, focusing only on environmental impacts of nutrient runoff and HAB, does not consider impacts from the fuel use and its extraction.

4.3.7. Wetland ecosystems

$$PU_l = \overline{S}_{l,l}(\{z,b\}) \ s.t. \ l \in \mathbf{F_E} \ ; \ i \rightarrow l. \tag{31}$$

where PU_l is the phosphorus uptake by the l_{th} wetland from agricultural water by the i_{th} farm. i and l have a one-one mapping relation. The wetland information is inputted into the $\overline{S}$ matrix shown in Fig. 5.

4.3.8. Management of ecosystems

These flows are not modeled in this present case study. If present, they would have indicated the flow of material from farms to the wetlands for their maintenance and efficient operation. Although empty, this is denoted as $\overline{C}$ in Fig. 5.

4.3.9. Size of processes

$$\underline{m}_i \leq 1 \ s.t. \ i \in \mathbf{F} \tag{32}$$

$$\underline{m}_j = 1 \ s.t. \ j \in \mathbf{P} \tag{33}$$

$$m_k = 1 \ s.t. \ k \in \mathbf{R} \tag{34}$$

$$(\underline{m}_e)_l \leq 1 \ s.t. \ l \in \mathbf{F_E} \tag{35}$$

As seen, from Fig. 5, the $\overline{X}$ matrix contains information about the different technological activities. In this case study, information for farming activities are provided at their 2015 county level production obtained from USDA (2015). Eq. (32) limits farming scaling variables to 1 ensuring that maximum production of corn within the system model is less than or equal to the 2015 county level corn production. The upper limit on the farming scaling variable denotes the constraint that total farm activity is lower than the maximum production of farm in a certain region. For refineries, the actual data for a 50-million-gallon ethanol plant is provided to the technology matrix. Thus in Eq. (34) the scaling variable value of 1 makes sure that refineries in this study are fixed at the 50 million gallon capacity. Consumer scaling variable of 1 in Eq. (33) fixes the size of consumers in a certain region to 2015 population levels. Population level and total farm production information is provided to the $\overline{X}$ matrix. Similarly Eq. (35) ensures that the size of wetlands in a certain region does not exceed the maximum available barren land area available in that region.

4.3.10. Environmental impact

$$g_{phos} = \sum_i \underline{\overline{B}_i \overline{m}_i} \ s.t. \ i \in \mathbf{F} \tag{36}$$

$$g_{phos} = \sum_i \underline{\overline{B}_i \overline{m}_i} - \sum_l \underline{\overline{S}_l \overline{m}_{e_l}} \ s.t. \ l \in \mathbf{F_E} \ ; \ i \rightarrow l. \tag{37}$$

where B_i denotes the phosphorus flow from the ith farm, m_i is the scaling multiplier of that corresponding farm as shown in Fig. 5. Eq. (36) is the case where ecosystem services are not considered. Eq. (37) integrates ecosystem services along with technological activities. The environmental impact flows (first term) are remediated by the "cleaning" services provided by the wetland (second

Table 1
Summary of results for different optimization scenarios.

Objectives	P2P TES integrated design	Total phosphorus run off (kg)	Net phosphorus run off (kg)	Cost to refinery ($)	Farms chosen	Refinery Locations
Minimization of phosphorus runoff	No. Wetlands considered to be used as end of pipe solution.	175,900	128,800	9.71E+07	Lucas, Henry, Van wert, Mercer, Putnam, Wood, Wyandot, Seneca, Ottawa	N/A
Minimization of phosphorus run off	Yes	261,300	47,700	9.64E+07	Lucas, Williams, Henry, Van wert, Putnam, Wood, Wyandot, Seneca, Ottawa,Dekalb	N/A
Minimization of cost to refinery	Yes	236,800	105,400	9.63E+07	Lucas, Fulton, Defiance, Paulding, Henry, Van wert, Mercer, Auglaize, Putnam, Wood, Wyandot, Seneca, Ottawa, Sandusky, Allen, Dekalb	Sandusky, Van wert

term). As farms only considered to have wetlands beside them, ecosystem indices are mapped one-to-one with farm indices.

4.3.11. Cost to biorefinery

$$p_{cost} = \sum_{i,k} \underline{\overline{X}}_{i,k}(\{z,b\}) p_{corn} + \sum_{i,k} \underline{\overline{X}}_{i,k}(\{z,b\}) T_{i,k} p_{tc} + \sum_{k,j} \underline{\overline{X}}_{k,j}(\{z,b\}) T_{k,j} p_{te} + \underline{\overline{X}}_{coal,k}(\{z,b\}) T_{coal,k} p_{tcoal} + \underline{\overline{X}}_{coal,k}(\{z,b\}) p_{coal} \ s.t. \ i \in \mathbf{F}, \ j \in \mathbf{P}, \ k \in \mathbf{R} \tag{38}$$

In this equation, the total cost to the biorefinery is obtained by adding the cost of corn (first term), the cost of transportation of corn from farms to refineries and cost of transportation of ethanol from refinery to consumers (second term) and the cost of coal transportation (third term), and the cost of coal (fourth term). Such a function forces transportation distances to be shorter and refineries to be more energy efficient. This was sufficient to solve for the locations of biorefineries and supplying farms. Investment cost for refineries includes land, labor and capital equipment costs. When refineries change their location from one county to another, these quantities would change only if variation in prices of land and labor from region to region are considered. Obtaining and using such information was outside the scope of this study. Thus, considering these costs for the biorefinery in this case study along with the operating cost would not affect the supply chain design decisions for determining refinery locations. Hence investment costs are not considered in this study. p refers to prices. $\sum_{i,k} \underline{\overline{X}}_{i,k}(\{z,b\})$ represents the quantity of corn flow between farms and refineries. The transportation cost depends on the distances between the chosen supplier farms and the refinery and consumers whose information is contained in the transportation matrix T which contains distances between the centroids of different counties. Distance and quantities of flow are combined with necessary price parameters p_{tc} for corn, p_{te} for ethanol and p_{tcoal} for coal to find total transportation cost.

4.4. Results

The optimization objectives of the problem are shown in Fig. 4 in optimization scenarios section. Initially the problem is solved for minimization of the two objectives separately. Implications of farming practices explained in Section 4.1 results in a trade-off between these two objectives. For every scenario, the process design, farm choices are observed and explored. Explanation of why changes occurred due to changing objective functions are provided. Next, the same problems are solved while including ecosystem services by considered conversion of free land available as explained in Problem description into wetlands. The wetlands are expected to treat the excess phosphorus in the water. The objectives are then compared with each other to explore tradeoffs and see if using wetlands and harnessing their ecosystem services results in "win-win" solutions for designing the biofuel network. Summary of different optimization results are provided in Table 1.

4.4.1. Minimization of phosphorus runoff

The optimization problem is defined as

$$Z_1 = g_{phos} = \sum_i \underline{\overline{f}}(phos)^i_e \ s.t. \ i \in \mathbf{F} \tag{39}$$

$$\text{subject to} \quad \begin{bmatrix} \underline{\overline{X}}(\{z,b\}) & \underline{\overline{C}}(\{z,b\}) \\ \underline{\overline{B}}(\{z,b\}) & \underline{\overline{S}}(\{z,b\}) \end{bmatrix} \begin{bmatrix} \underline{\overline{m}} \\ \underline{\overline{m}_e} \end{bmatrix} = \begin{bmatrix} \underline{\overline{f}} \\ \underline{\overline{f}}_e \end{bmatrix} \tag{40}$$

$$H(\{z,b\}) \geq 0 \tag{41}$$

$$S(\{z,b\}) \geq 0 \tag{42}$$

$$\underline{\overline{m}} \geq 0 \tag{43}$$

$$\underline{\overline{m}_e} \geq 0 \tag{44}$$

$$\sum_i \underline{\overline{B_i m_i}} - \sum_l \underline{\overline{S_l m_{e_l}}} \ \geq \ 0 \ s.t. \ l \in \mathbf{F_E} \ ; \ i \ \rightarrow \ l. \tag{45}$$

$$\underline{\overline{m_e}} \leq \underline{\overline{m}} \tag{46}$$

Two major constraints in this formulation are Eqs. (45) and (46). Eq. (45) models the assumption that phosphorus cannot flow between counties. This is a geographical constraint that makes sure that phosphorus runoff from one county cannot be treated by wetlands of another county. This is because phosphorus runoff, even though occurring throughout the watershed, its interaction with wetlands happens within a small local region. The minimum possible phosphorus flow in a county can be 0. Eq. (46) is an allocation determination constraint. Suppose a farm in a specific county has a scaling variable less than 1. That means in the context of the farm, the production of the farm is lower than its 2015 production value. Thus, amount of ecosystems available for uptake of phosphorus flow is also limited by that number. This makes sure that even though a farm is not used or is used less than its maximum production, the amount of wetland for runoff treatment is attributed accordingly.

4.4.2. Without ecosystems

In this scenario, integration of ecosystems are not considered during optimization and design. Mathematically this can be

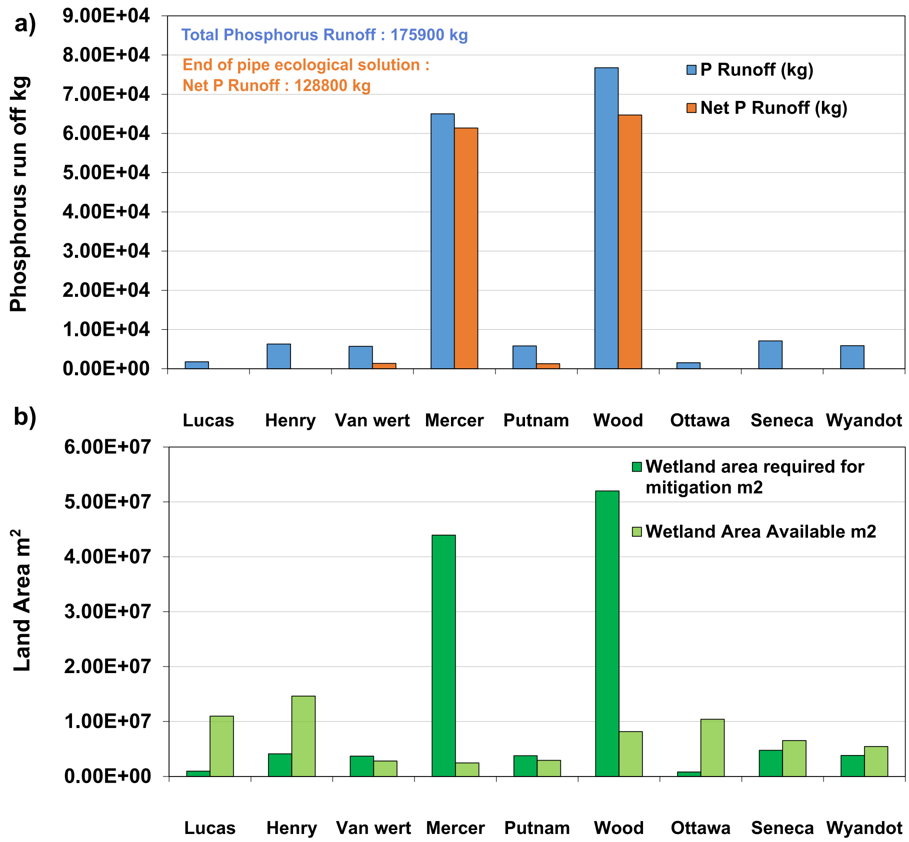

Fig. 6. (a) Total and net phosphorus runoff from different counties selected in supply chain design optimization. Net phosphorus runoff obtained from end-of-pipe solution. (b) Wetland area required for total phosphorus removal compared to barren land available for conversion to wetlands.

represented as modification of the above optimization formulation with

$$\overline{m_e} = 0 \tag{47}$$

Minimization of g_{phos} results in optimization solutions that focus on improvement of corn to ethanol transformation ratio through the process design of the plant. Along with that, no till agriculture practicing farms are chosen by the biorefineries and consumers to source required corn. Without the ecosystems, the optimization solution first selects all the counties which practice no till agriculture. This is because for the same amount of corn production, no till releases much less phosphorus to runoff compared to till agriculture. However, the farms in these regions are not able to satisfy the demand of corn by biorefineries as well as consumers. Thus along with the no till farms, two till practicing farms from counties Wood and Mercer are chosen to satisfy the remaining corn demand as seen in Fig. 6. The reason these two counties are chosen is because the phosphorus outflow per kg of corn there is the least compared to other till agriculture practicing counties as determined by the crop production and phosphorus runoff data. However, their individual runoff values are quite high compared to no till farms as seen from Fig. 6a. The sum of all the blue bars in this figure gives the total phosphorus run off of 175,900 kg. Fig. 8a is a visual representation of the entire supply chain. The graph is read using the colored bands flowing between nodes of farms, consumers and refineries. Source of flow is obtained by matching the color of the band with circumference segment of same color. Bands and segments of different colors denote destination of flows. In this problem, the choice of placement of refinery is not modeled. The objective function in this scenario is phosphorus runoff from the farms The placement of biorefineries did not affect the objective function because biorefineries did not have any outflow of phosphorus in its waste water. So only the choices of farms in this scenario are described in the results. This is the reason why refineries in Fig. 8a are generic and named 1 and 2. Corn ethanol production from two biorefineries are enough to satisfy the demand of biofuel energy from the consumers in that region. The width of the bands in Fig. 8a represent the fraction of corn being consumed from the farms by refineries and consumers. Farm Wood supplies the maximum of corn among all the farms. After all the no-till farms are used to their maximum capacity, Wood county is the next best farm choice with lowest phosphorus per unit mass corn according to available data. Mercer county is more phosphorus intensive and occupies a much smaller percent of the network as it is not required to its full capacity and chosen only to satisfy the remaining demand of corn after all other selected farms haven been completely used. The coal supplying sector is considered to be outside the system boundary.

4.4.3. Ecosystems as end of pipe solutions

Rather than being a separate optimization scenario, this is just calculation of net phosphorus runoff given by the equation

$$g_{phos} = \sum_i \underline{f}(phos)_e^i \; s.t. \; i \in \mathbf{F} \tag{48}$$

$$\overline{m_e} = \overline{m} \tag{49}$$

outside the optimization problem. In this analysis scenario, rather than optimizing, using the decision variables obtained in the without ecosystems scenario, Eq. (48) is calculated while using values of m_e obtained from Eq. (49). The results described in without ecosystems scenario are for the situation where the problem is

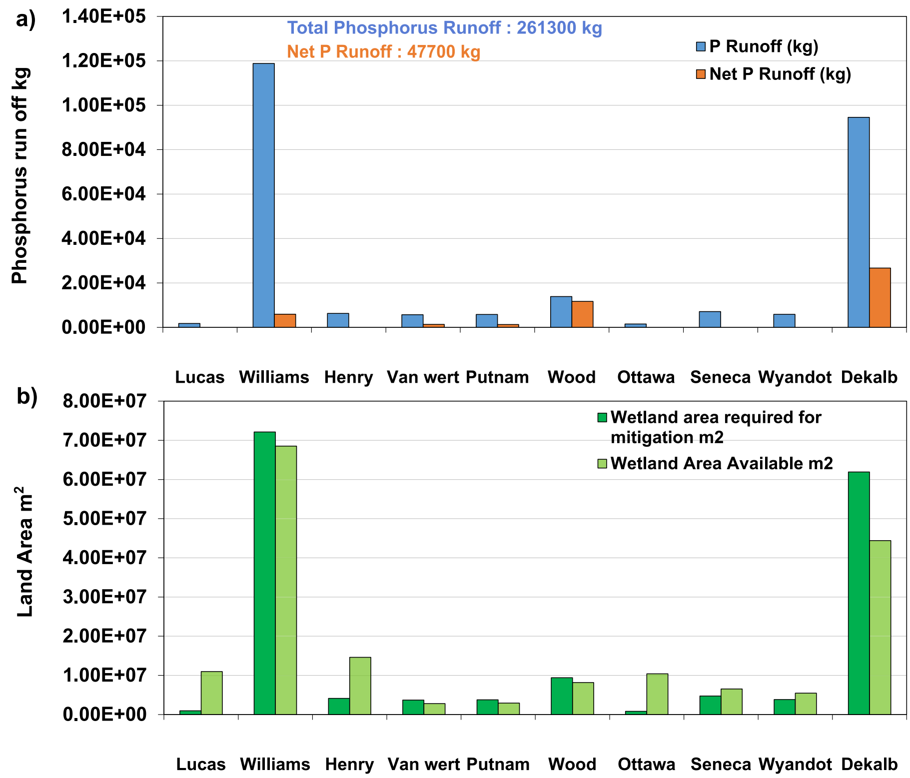

Fig. 7. (a) Total and net phosphorus runoff from different counties selected in supply chain design optimization. Net phosphorus runoff obtained using P2P-TES integrated framework. (b) Wetland area required for total phosphorus removal compared to barren land available for conversion to wetlands.

solved using a conventional supply chain framework like conventional P2P framework. It does not explicitly account for ecosystem services provided by wetlands. However, if after solving this problem, wetlands are harnessed for reduction of phosphorus runoff, the following results are seen. Using Eq. (49), the farms that are chosen from optimization are allowed to use their available land area for ecosystems to treat runoff. As seen from Fig. 6b, Van wert, Mercer, Putnam and Wood counties all other counties do not have enough land area available for conversion to wetlands which can take up phosphorus. This results in a net phosphorus runoff of 128800 kgs from the entire region. Actual and net phosphorus run off is compared in Fig. 6a. The sum of orange bars in this figure give the net phosphorus runoff.

4.4.4. Ecosystem services integrated into design

In contrast to the above scenario, the same problem is now solved with the P2P-TES framework that integrates ecosystem services explicitly into the design. This is basically solving the optimization problem with Eqs. (39)–(46). Rather than choosing the no-till farms which have lower phosphorus runoff, farms with higher land area available for conversion to wetlands is chosen. This results in a much higher total phosphorus runoff of 261,300 kg as compared to 175,900 kg in the previous scenario. However, due to the availability of required area for wetlands in most of the counties, as seen from the bottom graph in Fig. 7a, the net phosphorus run off is reduced to 47,700 kg by the wetlands. It is also shown in the top bar chart in Fig. 7a which shows a huge difference between total and net phosphorus run off. Williams, Dekalb and Wood are three till agricultural practicing farm counties that are chosen in this supply chain design. All these counties have large amount of land available for wetland construction. Williams and Dekalb was not chosen in the previous solution because they have a high total phosphorus runoff as seen from Fig. 7a. They are chosen in this solution because the presence of large wetlands reduce the net phosphorus runoff significantly. This is a superior solution in terms of phosphorus runoff when compared to the previous one and could only be obtained by using P2P-TES integrated framework for design. Fig. 8b shows the supply chain design for this optimization scenario. Dekalb and William farm supplies large amount of corn as seen from the width of colored bands starting from them and going to refineries. The reason for this can be seen from Fig. 7b. Large amount of wetlands enable take up of lots of phosphorus from runoff resulting in choosing these farms. Compared to the previous scenario, Wood is not chosen as much because of its relatively low availability of unused land for ecosystems. As mentioned in the without ecosystem scenario, in this optimization scenario, the location of refineries did not matter since phosphorus runoff is not affected due to that decision.

4.4.5. Minimization of cost to biorefinery

In this scenario, the objective function is changed to

$$Z_2 = p_{cost} \tag{50}$$

The transportation components whose cost is considered in this objective function are (1) Transportation of corn from farms to biorefineries (2) Transportation of corn from farms to consumers for consumption as food. (3) Transportation of produced bio-ethanol from refineries to consumption by consumers (4) Transportation of coal to refineries. Along with these, coal and corn cost is also added. As mentioned in Problem description, the price of corn from till agriculture is higher than that of non-till farms. Along with that, farther the transportation distances, more is the cost for transporting materials to and from the refineries. The prices

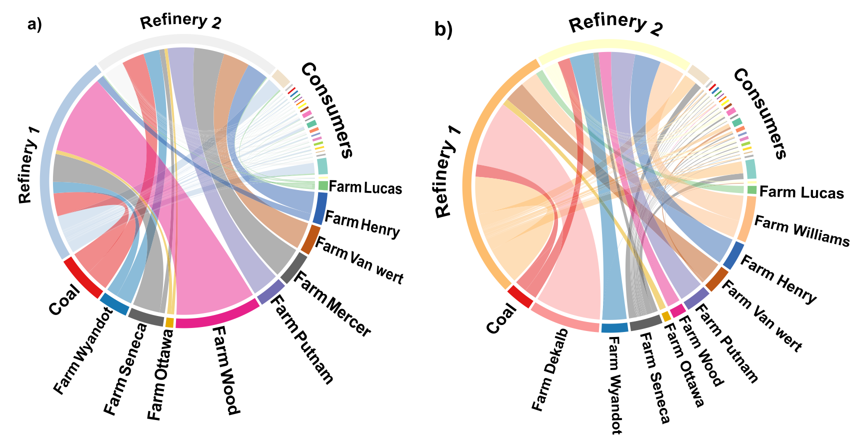

Fig. 8. Network graphs showing connection of flows between chosen farms, refineries and consumers, quantity of flows for (a) Conventional design without ecosystems (b) P2P-TES integrated design with wetlands. Source of flow is obtained by matching the color of the band with circumference segment of same color. Bands and segments of different colors denote destination of flows.

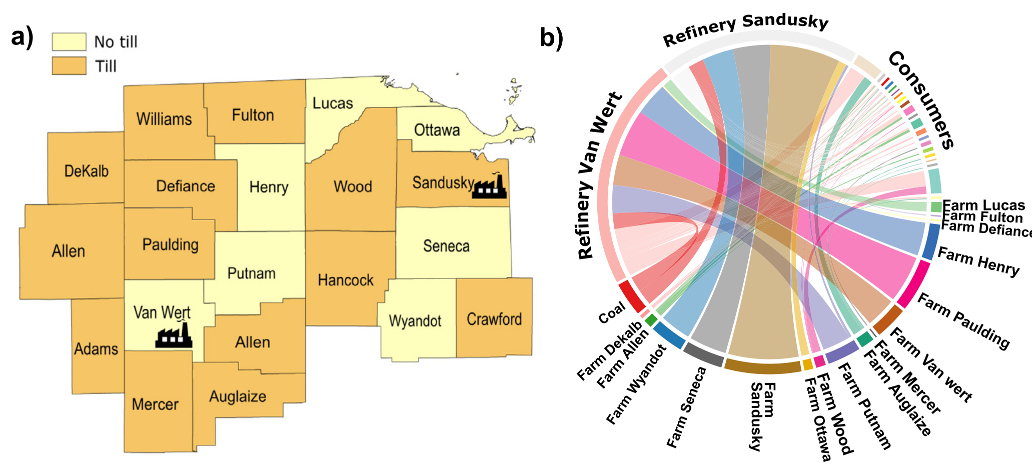

Fig. 9. Biorefinery placement and supply chain design for minimizing cost of corn consumption, energy consumption and transportation of corn and coal to refinery and ethanol from refinery to consumers. The industry symbol shows the location of refineries.

from all these different sources are added up to give the total cost to the refineries for corn ethanol production. Eqs. (40)–(46) are part of the optimization formulation for this scenario. The results are presented in Fig. 9a. The bio-refineries are placed at strategic counties that minimizes the total cost from all sources mentioned above. Along with that, farms are also chosen that have lower selling price for unit mass of corn. Minimization of cost also results in changes in the process design of the refineries to become more energy as well as mass efficient. However, in this scenario presence of ecosystems does not affect the system since wetlands have only been considered to treat phosphorus and hence does not change the cost objective function. Fig. 9b depicts the complete supply chain design. To lower transportation costs, refinery Van wert sources majority of its corn from nearby farms of Paulding, Henry, Putnam and Van wert itself. Similarly, refinery Sandusky sources its corn mostly from Ottawa, Seneca, Wyandot and Sandusky itself. This information can be explored by tracing the colored bands starting from similar colored circumference segments and going to different colored segments. Due to lack of space, the names of consumers counties are not provided. However, results showed that refinery Van wert supplied ethanol to consumers in surrounding counties of Lucas, Fulton, Williams, Defiance, Henry, Paulding, Van wert, Mercer, Auglaize, Dekalb and Allen. Similar connections are observed for refinery Sandusky supplying surrounding counties with ethanol. All these connections are in agreement with the sole objective of reducing costs, of which transportation cost is a major contributor.

4.4.6. Tradeoff between phosphorus runoff and cost to biorefinery

As observed from the optimization scenarios of phosphorus runoff and cost reduction, there will be a trade-off when both the objectives g_{phos} and g_{cost} are minimized simultaneously. The trade-offs can be explored using a multiobjective optimization approach visualized using a Pareto curve in Fig. 10. Movement along the pareto graph results in improvement of one objective with degradation of the other. At the right extreme of the pareto the design decisions choose designs that reduce the cost to the biorefinery by placing them in such a way to reduce transportation costs. On the left side of the pareto, phosphorus runoff is minimized. Thus, those farms which have less intensive agricultural practices as well as large wetland area available are chosen. It is also observed that inclusion of wetlands results in expansion of design space and win-win solutions by shifting the pareto front from the red to the blue line. Thus, for the same cost to the biorefinery, a much lower level of phosphorus runoff can be obtained. Movement along with pareto front results in change of supply chain design as shown from the two network graphs in Fig. 10. Its can be seen from these graphs that location of refineries as well as choice of farms for supplying corn varies for different values of the objective functions.

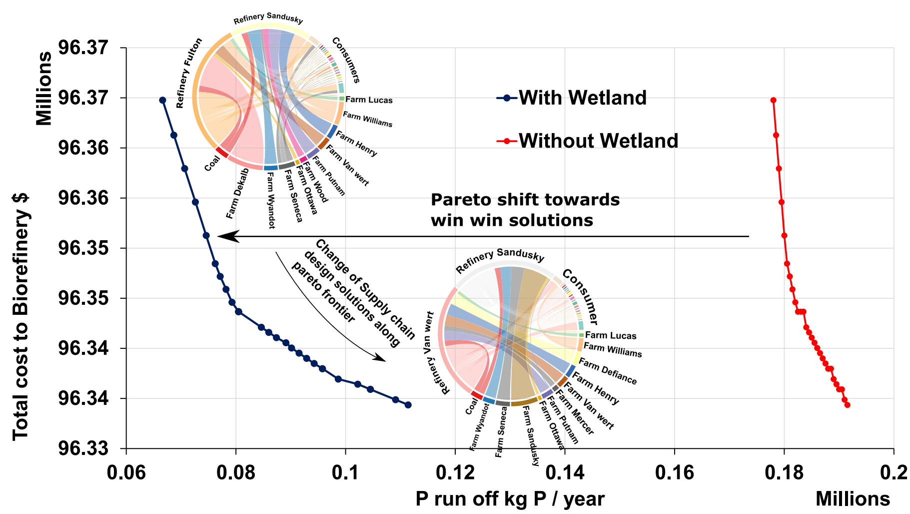

Fig. 10. Pareto frontier showing trade-off between phosphorus runoff and cost to refinery. Network diagrams visualizing complete supply chain changes along pareto frontier showing different designs obtained within solution space.

5. Conclusion

In this article, a novel sustainable process and supply chain design framework which also integrates synergies between technological and ecological systems is presented and used to design supply chain network of bioethanol manufacturing plants while trying to address nutrient runoff from farms which causes HABs in Lake Erie. The major objective of this framework is to determine location of biorefineries, choice of farms and also consider ecological flows – resource use and environmental interventions so that the design is much more robust and satisfies one of the necessary conditions for environmental sustainability. It is observed from the results, that ecosystems can provide a viable solution to the phosphorus runoff problem if properly maintained and adopted by farming communities. Along with phosphorus removal, wetlands provide additional ecosystem services of sequestering carbon dioxide, nitrogen removal and improving aesthetic value of local regions.

Even though the P2P-TES framework is completely general, the case study was refined using certain assumptions for easier application. One of the major disadvantages of this study is the scale at which it is done. Information at the county scale is too aggregated to have any directly applicable results. What this means is that the study needs to be done at a much finer scale with more details if at all the results can be directly useful to refinery operators and farmers in that region. For this reason, currently work is ongoing for applying the P2P-TES framework at a much finer level. With more detailed grids, information at a single or multiple farm level can be used for this study. Along with that, use of such detailed land use information enables determination of exact location of wetlands. In the present study, wetlands, farms are all considered to be at the centroid of the county which is a convenient assumption. For future work, due to consideration of much finer grids, exact location of farms and land availability for wetland construction immediately beside or close to that farm can be confidently determined. The other major future work is to bring in system dynamics of ecosystems over an yearly period to better model their working efficiency.

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