Toward Nature-Positive Manufacturing by Adapting Industrial Processes to Pollution Uptake by Vegetation

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Abstract Many studies are conveying the potential of nature-based solutions (NBS) like forests and wetlands to improve the quality of air and water. However, for practical realization of these benefits without formation of pollution hotspots, we need to accommodate the intermittent nature of ecological processes. In this work we show that if emitting activities are designed and operated to adapt to the intermittency of nature's ability to take up emissions, the resulting dynamic techno-ecological synergistic system can be profitable to the emitter while simultaneously reducing damage to society and encouraging ecosystem protection and restoration. Such solutions can also contribute to the desire of many businesses to become nature-positive: the benefits to nature from their activities exceed the harm. We focus on the mitigation of ground-level ozone and its precursor nitrogen dioxide by using the technology of selective catalytic reduction with the nature-based solution of a forest ecosystem. These emissions are from electricity generation for a chloralkali production facility located in Freeport, Texas. The integrated techno-ecologically synergistic system is designed and operated to satisfy hourly air quality constraints while minimizing cost to the business and health impacts on the local community. When the variability of the forest NBS is incorporated in the production schedule of the chloralkali process, the resulting system is found to be economically and environmentally superior to a conventional technology-only solution. A conventional design can approach net-zero impact but at a high cost, while a dynamic techno-ecological synergistic design can have a net positive impact on society and ecosystems, with a small additional cost to the company.

Keywords Process design, Process operation, Ground level Ozone, Sustainability, Ecosystem services, Chloralkali process, Techno-ecological synergy.

Introduction

Despite the widespread availability and implementation of technologies and policies for controlling air pollution, people and the environment across the world continue to suffer from damage due to harmful emissions. In the United States during 2019, anthropogenic activities were estimated to emit 8.95 million tons of NO_x that contributes to formation of ground-level O_3 [1]. Globally, air pollution is the fourth leading risk factor for death, with 3.4 million premature deaths in 2017 attributed to it [2]. An estimated 12800 deaths in the United States could have been avoided if

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O_3 concentrations had been reduced such that their 8-h averages would not have exceeded 70 ppb anywhere in US [3].

Efforts to reduce environmental impacts have mostly relied on technologies for controlling emissions into the environment, usually for satisfying environmental regulations. Such approaches aim to do "less bad." For the emitters and others who benefit from the polluting activity, environmental and social damages due to emissions are often an economic externality since their impact is shared among many in society and the environment, but is not reflected in the emitter's operating cost or profit. Such an approach implicitly assumes that the environment is an infinite sink that can absorb pollutants that are emitted after satisfying regulations with zero damage or no negative effects. [4, 5] Recent work has monetized such externalities of air pollution from various economic activities and compared them with the economic value added by these activities. Several economic sectors such as power generation, chemical refining and manufacturing [6] and agricultural activities [7] are found to have a net negative impact on society. That is, the Gross Economic Damage (GED) calculated by accounting for the impact of air emissions such as the cost of hospitalization, lost days at work, etc. and the value of a statistical human life exceeds the monetary value addition that these activities provide to the economy. Thus, the impact of these activities in society may be "net negative".

In an era of ongoing ecological degradation and increased scrutiny from stakeholders like customers, employees, and governments, such findings about net-negative societal impacts further pressure industry to proactively manage and mitigate such externalities from their activities. Many efforts aim to achieve "net-zero" or even "net-positive" impact, where the activity gives back to society such that the negative impact is nullified or exceeded. Such efforts include systems that emit net-zero greenhouse gases [8] and where the value provided by manufactured products exceeds the impacts of manufacturing at micro or macro scales [9–12]. For specific emissions, using technologies to achieve a goal of net-zero can be expensive, particularly at low concentration of pollutants. Thus, conventional pollution control technologies face a trade-off between their cost and extent of pollutant removal.

In parallel with the interest in net-zero and net-positive impact has developed the interest in the ability of ecosystems to meet human needs [13, 14] and the potential of nature-based solutions [15]. Multiple studies (see [16–22]) have been carried out in the literature to demonstrate the benefit of nature based solutions. With regards to improving air quality, several studies have been conducted in major cities like London [23], New York [24], Houston [25], Florence [26], etc. to quantify the air quality regulation benefits of urban forestry. Compared to conventional or techno-centric methods of low NO_x burner, cap and trade scheme, and selective catalytic reduction (SCR), Kroeger et al. [25] determined reforestation to provide the most economical solution for ozone abatement in Houston. Gopalakrishnan et al. identified industrial sectors [27] and counties [28] across the U.S. where nature-based solution of ecosystem restoration could be cheaper than technological pollution abatement.

These studies convey the promise of nature-based solutions for regulating air quality by comparing annual average values of emissions and uptake. However, they ignore the inherent intermittency of the air quality regulation ecosystem service. Uptake of emissions by vegetation depends on many factors such as wind, temperature, atmospheric concentration, and leaf area index. These factors result in significant intermittency of this ecosystem service, as shown in Figure 1 for the dry deposition capacity over a year of a 20-year-old healthy White Ash tree located in Freeport, Texas. This intermittency is present at multiple time scales ranging from minutes to years. At short time scales, meteorological factors such as wind velocity and atmospheric concentration affect pollutant uptake. At longer time scales, uptake varies during the day and night, and over seasons due to deciduous species shedding their leaves. At the longest time scale, uptake capacity increases with

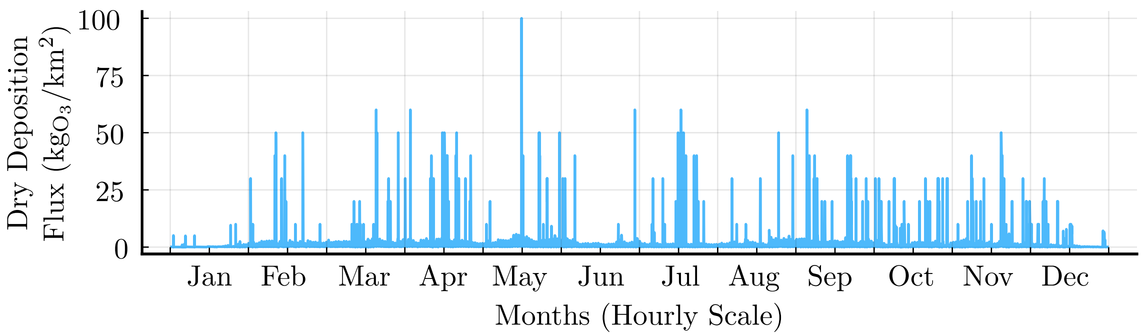

Figure 1: Intermittency of the dry deposition flux for ground-level ozone on 20-year-old White Ash located in Freeport, Texas for 2009. The capacity of this ecosystem to uptake ozone depends on variable meteorological conditions. The flux was calculated using iTree Eco v6 [29].

tree growth and increase in their total leaf area. If vegetation is to contribute to improving air quality, it is necessary to account for such intermittency to prevent the formation of temporal pollution hotspots. These could appear when the capacity of vegetation to take up emissions decreases while the rate of emissions does not change. Ozone alerts in many cities during the summer are an example of such temporal hotspots.

In this work, we develop a novel strategy for integrated design and operation of a manufacturing process, pollution control technologies, and ecosystem services. By applying this dynamic techno-ecological synergy (TES) [30] framework to a chlorine manufacturing process and surrounding vegetation for mitigating formation of nitrogen oxides (NO_x) and ground-level ozone, we show that such an approach that encourages synergies between technological and ecological systems can result in better air quality, cause less societal damage, and increase corporate profit. This demonstrates that if the manufacturing process and pollution control technology account for and adapt to the intermittency of nature, the resulting dynamic TES design can provide a "win-win" and net-positive solution. We compare this novel design and operation strategy with the traditional techno-centric approach of industrial operation at mostly fixed set points of operating conditions and production rate, while relying on only technology for pollution control. The best that is possible with this conventional approach is a net-zero solution, but at a high cost to the company. Thus, our work shows that by seeking synergies with ecosystems and adapting to nature's dynamics, industry and other polluting economic activities may be able to overcome their net-negative impact by protecting and restoring ecosystems to mitigate its emissions and provide co-benefits to society. We also identify areas where future work is needed to make this idea of dynamic TES a reality.

This paper is organized as follows. Mathematical model and methods for a case study are presented in the Methods section. The results from the case study and the tradeoff between societal health cost and annualized cost of production are presented in the Results section. Implication of the results on design and operation methodologies are discussed in the Discussion section.

Methods

As a case study of our approach, we consider an existing chloralkali manufacturing facility located in Freeport, Texas. A chloralkali process is highly energy-intensive, and an onsite coal-fired generator is available at this facility to meet its energy needs. Combustion of coal results in emission of air pollutants like nitrogen dioxide, sulfur dioxide, carbon dioxide and particulate matter. Being located in the ozone non-attainment zone of Houston-Galveston-Brazoria (HGB), we alter the Cl_2

production rate and energy requirement to constrain the generation and emission of precursor NO_2 thus preventing deterioration of air quality due to the formation of ground-level ozone (O_3). Air pollutant emissions from the chloralkali facility necessitate ecosystem capacity to regulate them and thus we refer to these emissions as demand for the air quality regulation ecosystem service. The capacity of ecosystems to abate the air pollutants and regulate air quality is referred as the supply of this ecosystem service.

Our analysis solves an optimization problem based on mathematical representations of the following, 1. Chloralkali production process and its energy requirement, 2. Pollutant emissions and its impact on ambient concentration, 3. Supply capacity of vegetation to mitigate air pollutants, and 4. Economic and external health impact costs of chlorine production. These are modeled as functions of various decision variables to result in a multi-objective optimization problem that can be summarized as,

$$\begin{gathered}\min_{\substack{\text{Reforestation Area } (A^r)\\ \text{SCR Size } (S^{SCR})\\ \text{Cl}_2 \text{ Production Rate } (F^{\text{Cl}_2})}} \quad \text{Cost of Production } (Z^{TAC})\\ \& \\ \min_{\substack{\text{Reforestation Area } (A^r)\\ \text{SCR Size } (S^{SCR})\\ \text{Cl}_2 \text{ Production Rate } (F^{\text{Cl}_2})}} \quad \text{Health Impact Cost } (Z^{\text{Health}})\end{gathered} \tag{1}$$

$$\text{Chlorine production model and its power requirment} \quad P_t = f_1(F_t^{\text{Cl}_2}) \quad \forall\, t \in \mathbb{T} \tag{2}$$

$$\text{Supply-demand accounting for NO}_2 \text{ and O}_3 \begin{cases} D_{it}^E = f_2^i(P_t, S^{SCR}) & \forall\, t \in \mathbb{T},\ i = \{\text{NO}_2, \text{O}_3\} \\ S_{it}^E = f_3^i(A^r) & \forall\, t \in \mathbb{T},\ i = \{\text{NO}_2, \text{O}_3\} \end{cases} \tag{3}$$

$$\text{Air quality constraints} \quad C_{it}^f = f_4(C_{it}^0, D_{it}^E, S_{it}^E) \quad \forall\, t \in \mathbb{T},\ i = \{\text{NO}_2, \text{O}_3\} \tag{4}$$

$$\text{Economic and Health Impact Cost Calculations} \begin{cases} Z^{TAC} = \sum_{t\in\mathbb{T}} f_5(F_t^{\text{Cl}_2}, A^r, S^{SCR}) \\ Z^{\text{Health}} = \sum_{t\in\mathbb{T}} f_6(C_{it}^f, C_{it}^0) \end{cases} \tag{5}$$

where, $F_t^{\text{Cl}_2}$ and P_t are hourly Cl_2 production rate and its corresponding power requirement, respectively. D_{it}^E and S_{it}^E are demand and supply of NO_2 ($i = 1$) and O_3 ($i = 2$) regulation service, respectively. C_{it}^0 and C_{it}^f are baseline and final (post-emission) ambient concentration of air pollutant i at hour t respectively. A complete mathematical formulation of the optimization problem is available in the supplementary information Mathematical Model for Air Quality Regulation. A more generic version of mathematical model applicable to any TES system can be found in the SI in Section Generic Problem Description.

Chlorine production facility and its power requirement

A chloralkali process involves electrolysis of brine (sodium chloride) to produce chlorine (Cl_2) and caustic soda (sodium hydroxide) with a byproduct of hydrogen gas. The major products of this process are widely used as feedstocks in the production of organic chemicals, pulp and paper, water treatment, plastics, etc. The brine electrolysis process is highly energy-intensive and using an onsite coal-fired generator, the existing chloralkali facility needs to meet an annual average chlorine production rate of $2.58\,\text{t}_{\text{Cl}_2}/\text{h}$. The core reaction of chloralkali production that occurs in a membrane electrolytic cell is,

$$2\,\text{NaCl(aq)} + 2\,\text{H}_2\text{O(l)} \longrightarrow \text{Cl}_2\text{(g)} + \text{H}_2\text{(g)} + 2\,\text{NaOH(aq)} \tag{6}$$

In this work, we use a quasi-stationary model of chloralkali production and its power requirement. The hourly chlorine production rate is constrained between a lower bound of $F^l = 1.14\,\mathrm{t_{Cl_2}/h}$ and an upper bound of $F^u = 3.42\,\mathrm{t_{Cl_2}/h}$. The implementation assumes that quasi-steady state operation of chloralkali facility, where cell temperature, concentration, and current density are set in optimal configuration to minimize energy requirement. Using the cell model developed by Otashu and Baldea [31], steady-state specific electricity demand is calculated for complete range of hourly flow rates. In order to maintain computational tractability, the non-linear production rate-power requirement function is approximated as a piece-wise linear function. Hourly power requirement is translated into hourly coal combustion rate by factoring in a coal fired generator's efficiency. For all scenarios considered in this work, the annual chlorine production target is fixed at $2.58\,\mathrm{t_{Cl_2}/h}$. Without loss of generality, the implementation assumes a core reaction yield of 100%. Thus, over the time horizon, all scenarios will have identical raw materials cost with differing cost of energy production and pollution mitigation. Additional information on modeling of chlorine power requirement are presented in supplementary information.

Since instantaneous changes in chlorine production rate are impractical, ramping constraints are added to the model to avoid this impractical operational schedules. Based on historical data [32], chloralkali facilities typically take 4 hrs to ramp up from its F^l to F^u and the implementation allows for same. If needed, the production can shutdown for a day, which would result in zero emission and chlorine production.

The chlorine production rate is allowed to vary every hour between F^l and F^u as

$$F^l y^c_d \leq F_t \leq F^u y^c_d \quad \forall\, t \in \mathbb{T},\ d \in \mathbb{D},\ d = \lceil t/24 \rceil \tag{7}$$

where, y^c_d is the plant's daily operational status i.e. $y^c_d = 1$ if the plant is in operation and $y^c_d = 0$ if the plant is shutdown for a day d. Eq. 7 ensures that production rates are in the feasible region when the power generation unit is on. The annual average production rate is enforced as

$$\sum_{t\in\mathbb{T}} F_t = \sum_{t\in\mathbb{T}} \hat{F} \tag{8}$$

where, $\hat{F}$ is an energy efficient operational point i.e. if the facility is operated at an hourly Cl_2 production rate of $\hat{F}$, the fuel consumed per unit chlorine produced is minimized, as is the operation cost. We assume that chlorine production operates at steady state for the duration of each hour. The energy requirement for chlorine production is calculated using the model described in Otashu and Baldea [31]. The dynamic model is operated at different steady state set points and energy requirement for each steady state flow rate is calculated. This energy requirement is a concave function of flow rate, which is modeled as a piece-wise linear function for computational ease. The hourly chlorine production rates are operational decision variables in the optimization problem. Eq. S10- S14 denotes the piece-wise linear partition of concave energy requirement function.

Demand and supply of ecosystem services

The implementation assumes that coal-fired generator is the sole source of NO_2 emissions in the area. Part of NO_2 emissions can be treated by an SCR (if installed) and the rest is emitted to the surroundings. The SCR is designed according to the EPA Air Pollution Cost Manual [33]. Its capital and operational costs are estimated as a linear function of its size and operation rate. In the presence of solar radiation, NO_2 molecules in ambient air are catalytically converted to O_3 molecules. The number of O_3 molecules produced from one NO_2 molecule is defined as ozone production efficiency (OPE). The implementation assumes a constant OPE [34] during the daylight hours of March through September to account for increase in ground-level ozone formation due to NO_2 emissions and no conversion of NO_2 otherwise. The emission of NO_2 and its conversion to O_3 is considered to be the demand of the air quality regulation ecosystem service.

The following equations (Eq 9–12) describe the calculations of supply and demand of the air quality regulation service. The abatement load (P_t) for emissions resulting from the power generation unit are split between technological (E_t^T) and ecological systems (E_t^E) as,

$$P_t = E_t^T + E_t^E \quad \forall\, t \in \mathbb{T} \tag{9}$$

The amount of pollutant split between technological (when available) or ecological option is an operational decision variable for the problem. The installed SCR capacity should be sufficient to handle the technological abatement load, that is,

$$\begin{gathered} S^{l,SCR} y^{SCR} \leq S^{SCR} \leq S^{u,SCR} y^{SCR} \\ E_t^T \leq S^{SCR} \quad \forall\, t \in \mathbb{T} \end{gathered} \tag{10}$$

The size and availability of the SCR are capital investment decision variables. Demand for the air quality regulation service is calculated as product of the emission load on ecosystems E_t^E and the time varying OPE (θ_{it}) as,

$$D_{it}^E = \theta_{it} E_t^E \quad \forall\, t \in \mathbb{T},\ i \in \mathbb{I} \tag{11}$$

The capacity of vegetation to supply the air quality regulation ecosystem service is quantified by dry deposition of pollutant species on trees. As described by the following equation,

$$S_{it}^E = v_{it}^d C_{it}^f A^r \quad \forall\, t \in \mathbb{T},\ i \in \mathbb{I} \tag{12}$$

the dry deposition of pollutant is a product of its dry deposition velocity (v_{it}^d), pollutant concentration (C_{it}^f) and the land area of reforestation (A^r). We employ iTree Eco v6 [29] to calculate hourly dry deposition velocities for NO_2 and O_3. iTree Eco v6 [29] is a software application suite based on Urban Forest Effect-Deposition (UFORE-D) model used extensively across the United States and internationally to assess the benefits of urban forests. Dry deposition velocities are calculated as an inverse sum of aerodynamic resistance, quasi-laminar boundary layer resistance and surface resistance. Canopy resistance is a function of the density of leaves, thus impacting seasonal behavior to deposition velocity due to leaf-off and leaf-on periodicity. Aerodynamic resistance and quasi-laminar boundary resistance depend on meteorological conditions like temperature, solar irradiance and wind condition. In this work, we obtain deposition velocities for 2009 using local meteorological conditions obtained from the National Climate Data Center (NCDC) for Clover Field Airport, which is the nearest good quality data source to our study site. The base case assumes the vicinity of the manufacturing facility to be barren i.e. zero supply capacity and availability of 15 km^2 for restoration to increase capacity. The cost of reforestation is set at \$75/km^2 [35, 36]. Native species of White Ash is considered to approximate the capacity of the restored forest ecosystem.

Air Quality Index and its Societal Health Impact Cost

US Environmental Protection Agency (EPA) communicates real time air quality using Air Quality Index (AQI) [37]. Scaled from 0-500 with 0 being best, AQI helps quantify the complex impact of air pollution. We develop real-time constraints on change in AQI due to emissions from chloralkali facility. We use retrospective ambient pollutant concentration data for year 2009 to form baseline AQI of our study. The post-emission AQI is determined by considering two scenarios: (1) If the baseline AQI at a selected time point is in the “good” range (i.e. less than 50), then post emission deterioration of AQI by 10 is allowed or until the AQI stays in the "good" range. (2) If the baseline AQI is beyond the "good" range, then no deterioration in AQI is allowed. This restriction prevents aggravation of bad (non-"good") air quality days. Further details about AQI and the algorithm S1 used to determine constraints are provided in the SI.

This work assumes the air quality regulation serviceshed (airshed) to be an ideal continuously stirred tank reactor (CSTR) where the control volume is product of mixing height and airshed area. The airshed refers to the land area where the chloralkali facility is the only source of NO_x and O_3 and sole reason for change in AQI as compared to its historical baseline. For sake of simplicity, we assume a spatio-temporally invariant serviceshed area $A^s = 15\,\mathrm{km}^2$. Using a steady-state CSTR model for pollutant mixing, the final concentration of a pollutant is modeled as

$$C^0_{it} A^s H_t + D^E_{it} - S^E_{it} = C^f_{it} A^s H_t \quad \forall\, t \in \mathbb{T},\ i \in \mathbb{I} \tag{13}$$

where, C^0_{it} is the baseline (retrospective) ambient air pollutant concentration. Accounting for spatio-temporal variation in the airshed along with sophisticated atmospheric dispersion model are being considered in on-going work as a replacement for Eq. 13. The reasoning and implications for this assumptions are provided in Section Permissible change in the Air Quality Index of SI.

The health impact and its monetary valuation due to change in concentration were carried out by using information from the U.S. EPA Environmental Benefits Mapping and Analysis Program–Community Edition (BenMAP-CE) model [38]. Monetary valuation of the chloralkali facility's operation on health of its neighborhood was carried out as described in Nowak et. al. [39]. First, concentration metrics needs to be derived for base case versus operational case. The daily average concentration metric C^{D24a}_d is modeled as,

$$C^{D24a}_d = \sum_{t=24d-23}^{24d} C^f_{it}/24 \quad \forall\, d \in \mathbb{D},\ i = 2 \tag{14}$$

and the daily maximum concentration metrics C^{D1m}_d is

$$C^{D1m}_d \geq C^f_{it} \quad \forall\, t \in \mathbb{T},\ d \in \mathbb{D},\ i = 2,\ d = \lceil t/24 \rceil \tag{15}$$

The change in ambient pollutant concentration metrics due to operation of the manufacturing facility and presence of vegetation are

$$\Delta C^{D24a}_d = C^{D24a}_d - C^{0,D24a}_d \quad \forall\, d \in \mathbb{D} \tag{16}$$

$$\Delta C^{D1m}_d = C^{D1m}_d - C^{0,D1m}_d \quad \forall\, d \in \mathbb{D} \tag{17}$$

where, ΔC^{D24a}_d and ΔC^{D1m}_d are the difference in baseline (retrospective) and final daily average concentrations and daily maximum concentration metrics respectively. They are used to model change in health incidence and its monetary impact (Eq. S32). The daily monetary impact is further aggregated into an annualized health impact cost. Further details for calculating societal health impact cost are provided in Section. Monetary valuation of damages to human health due to air pollution of SI.

The capital and operational costs of SCR are obtained from the EPA Air Pollution Cost Manual [33]. The capital cost of SCR and cost of reforestation are converted to equivalent annualized cost (EAC) [40] using

$$\mathrm{EAC} = \frac{Pr}{1-(1+r)^{-n}} \tag{18}$$

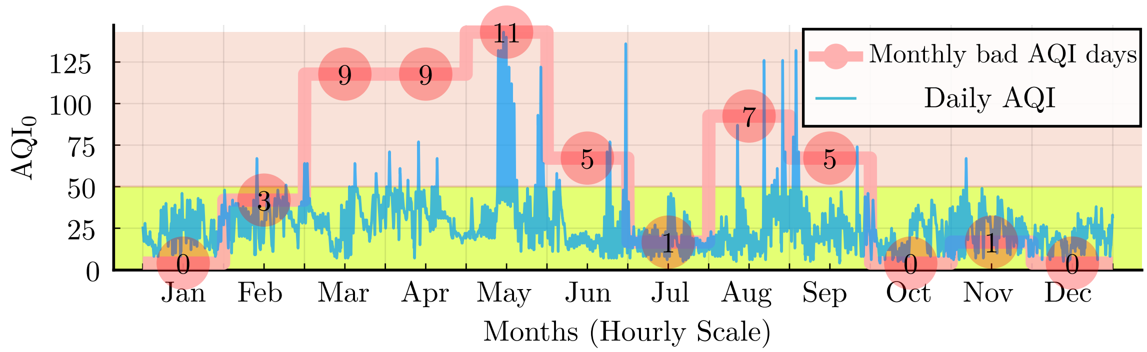

Figure 2: Baseline air quality index (AQI_0) during 2009 in Freeport, Texas when there is no chloralkali plant. A majority of bad AQI days (AQI$>$ 50) occur during hot periods of the year.

where P is the capital cost, r is the discount rate of 7.5% [33] and n is the project lifespan of 20 years. The energy production cost of chloralkali facility, operational cost of SCR and annualized capital investment cost together represent the total annualized production cost.

In this work, the implementation is modeled as a non-convex mixed integer nonlinear programming (MINLP) problem. Using the algorithm AUGMECON [41], the multi-objective optimization problem was cast as an ϵ-constraint problem to determine tradeoff between production cost and social impact cost. The computational modeling was performed in JuMP/Julia [42] and solved using Gurobi [43] to global optimality ($\epsilon = 5\%$). The resulting model has 17520 bilinear quadratic constraints, 143112 continuous variables and 18251 binary variables with an average computational time of 8 hrs (using 4 threads) for each solution on the Pareto curve. The computational code and datasets used in case study can be found at [44].

Results

We consider 2009 to be the *base case* when the chloralkali plant is not operational. The Air Quality Index (AQI) during this year is presented in Figure 2. Multiple not "good" (bad) air quality days occur in the hot summer months when the AQI exceeds 50. After the plant is operational, we consider multiple cases, which are summarized in Table 1. The business as usual case does not consider any AQI constraints and aims to produce Cl_2 at a constant rate. The techno-centric case excludes ecosystems, but allows the production rate to vary for meeting AQI constraints. The techno-ecological synergy case includes technological and ecological systems along with AQI constraints. Solutions for various combinations of annualized production cost and social health impact cost are obtained and described next.

Design for minimum annualized production cost

Business-as-usual scenario. This scenario corresponds to how manufacturing processes operate currently. Here, the sole objective is to minimize annualized production cost and meet the annual mean targeted production of chloralkali $\hat{F} = 2.58\,\mathrm{t\,h^{-1}}$ Cl_2. The AQI constraints, which are introduced in Section Permissible change in the Air Quality Index, are not imposed on the process operation. The facility can be operated at varying chlorine production rates between $1.14\,\mathrm{t_{Cl_2}/h}$ and $3.42\,\mathrm{t_{Cl_2}/h}$ or the production can be entirely shutdown for a day if necessary. The energy generation cost is a significant component of the production cost and the energy requirement per ton of chlorine is minimized if the facility is operated at $\hat{F}$. Any deviation from this production rate

Table 1: Scenarios explored in case studies.

Scenario	Features	Chlorine Production Rate	AQI acronym
Baseline	No plant	No production	AQI_0
Business-as-usual (BAU)	Operation with no AQI constraints	Constant at $2.57\,t_{Cl_2}/h$	AQI_{BAU}
Techno-centric	Operation with AQI constraints. Ecosystems ignored.	Variable hourly production rate	AQI_{Tech}
Techno-ecological synergy (TES)	Operation with AQI constraints. Investment in technology and ecosystems allowed.	Variable hourly production rate	AQI_{TES}

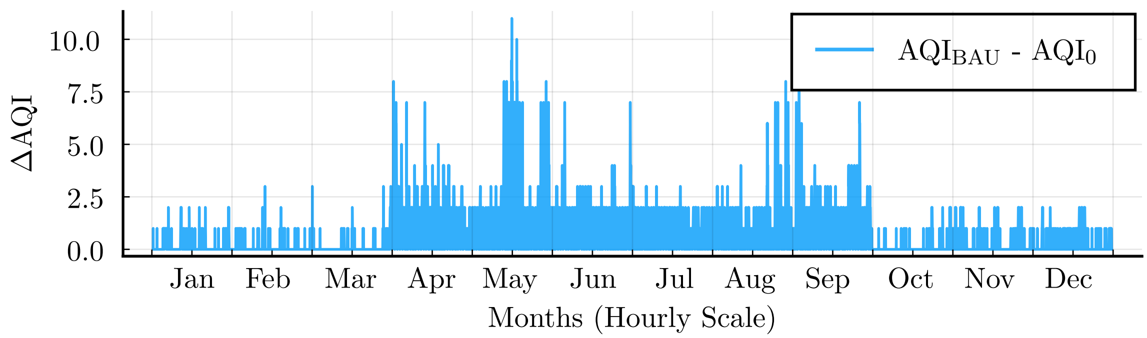

Figure 3: Change in air quality index (AQI) due to business-as-usual (BAU) operation as compared to base case (no manufacturing process). Optimum production rate for BAU is constant, but air quality varies and deteriorates between March and October.

would reduce energy efficiency of the facility and increase the operational cost. Thus, to minimize production cost, the optimal solution under the business-as-usual (BAU) scenario is a constant chlorine production rate of $\hat{F}$. The annualized production and annualized societal health impact costs for this BAU scenario are \$808 k and \$1.7 m, respectively. The BAU case does not have a SCR or any ecosystem capacity in the airshed to mitigate NO_2 or O_3. Thus, any emissions from the facility would lead to an increase in AQI as compared to the historical baseline AQI level.

The change in AQI levels as compared to the baseline scenario due to BAU operation is detailed in Figure 3. This figure shows that constant and predictable production and emission rates do not lead to constant and predictable change in air quality. Greater AQI deterioration is observed in the warmer period of the year as compared to the cooler period. This occurs as the higher solar irradiance and ambient temperature create optimal conditions for ground-level ozone formation. Changing wind conditions and mixing heights also affect the dispersion of air pollutants. Such a BAU scenario is analogous to conventional industry operation. Figure 3 shows that achieving a constant production rate exacerbates poor AQI days whose dispersion and pollutant absorption capacity are already saturated, leading to excessive societal impact. In order to alleviate this impact, in the subsequent scenarios, we impose the AQI constraints in design and operational optimization of the manufacturing facility.

Techno-centric scenario. In this scenario, we let the chlorine producton rate vary, and rely on a selective catalytic reduction (SCR) unit to convert NOx into nitrogen while minimizing cost and satisfying AQI constraints. The resulting hourly production rate and days of process shutdown are depicted in Fig. 4a. The annualized production and societal health impact costs for this scenario are \$923 k and \$1.4 m, respectively. The deviation of production rate from the fixed value, $\hat{F}$ leads to a reduction in energy efficiency and increase in operational cost as compared to the BAU scenario. However, the air quality improves. Ground level ozone formation usually occurs in the summer months leading to a large number of not "good" AQI days in March-Sep. The production of chlorine is shutdown on these not "good" AQI days. Thus, production is lower in the months of April, May and August. In order to compensate for low production during these months and meet the annual targeted production of chlorine, a higher than average production occurs during winter months of October-February. Figure S2a details the change in AQI with respect to the base case for this techno-centric scenario. Note that the largest change of AQI in the optimal solution of this scenario is 4, which is much less than the largest change of more than 10 in the BAU scenario shown in Figure 3. As described in Section S4, this problem is formulated so that on days with not "good" AQI, the manufacturing process does not worsen the air quality. This is ensured by shutting down production. Figure S2b compares the AQI of techno-centric and BAU scenarios. As compared to the BAU scenario, the techno-centric scenario shuts down its production of chlorine on not "good" AQI days. These shutdowns lead to an improvement in AQI as compared to BAU. Since the targeted annual production is the same for both techno-centric and BAU scenarios, production shutdowns in the techno-centric case require additional production in other time periods. Although the AQI constraints are satisfied, increased production in the leaf-off period results in AQI degradation in those periods as compared to BAU, but the air quality does not become worse than the AQI category of "good".

Techno-ecological synergy This scenario includes technological (SCR) and ecological (trees) systems, and obtains synergistic designs that minimize cost while satisfying air quality constraints. While changes in the production rate or capacity of SCR can be used to reduce demand of the air quality regulation ecosystem service (emissions), capital investment in forest ecosystem restoration can be used to improve the supply of this ecosystem service (capacity to mitigate emissions). In this work, we approximate the restored ecosystem by 20 year-old native species of White Ash. We discuss the implications of this assumption in Section Trade-off between social cost and production cost.

For minimizing the annualized cost while meeting air quality requirements, the ecological solution of forest ecosystem restoration is most attractive. The annualized cost of production and societal health impact costs in this scenario are \$903 k and \$1.2 m, respectively, and the production schedule is shown in Fig. 4b. With an available land area (A^s) of 15 km^2, the optimal solution determines an area of 1 km^2 for reforestation (A^r). The contribution of capital expense in the annualized production cost increased due to investment in the ecosystem. Increased supply capacity of ecosystems reduces the number of production shutdown events, especially in the months of February and March as compared to the previous scenarios. This allows the production rates to be optimized for energy efficiency (closer to $\hat{F}$) leading to reduced operational cost and overall cheaper annualized cost of production. Any further increase in reforestation area would lead to higher capital expense with diminishing returns on reduction in operational cost.

Change in AQI due to TES production schedule is illustrated in Fig. S3a. Compared to the techno-centric solution, the TES solution also has the ability to reduce AQI to less than the baseline AQI shown in Figure 2. This is because during production shutdowns, since there are no emissions from the chlor-alkali process, the air quality regulation ecosystem service demanded by this process is zero. Therefore, the capacity of the restored vegetation is available to take up pollutants from sources in the airshed other than the chlor-alkali process. Therefore, improvement in air quality as compared to the base case becomes possible. The improvement occurs specifically on not "good"

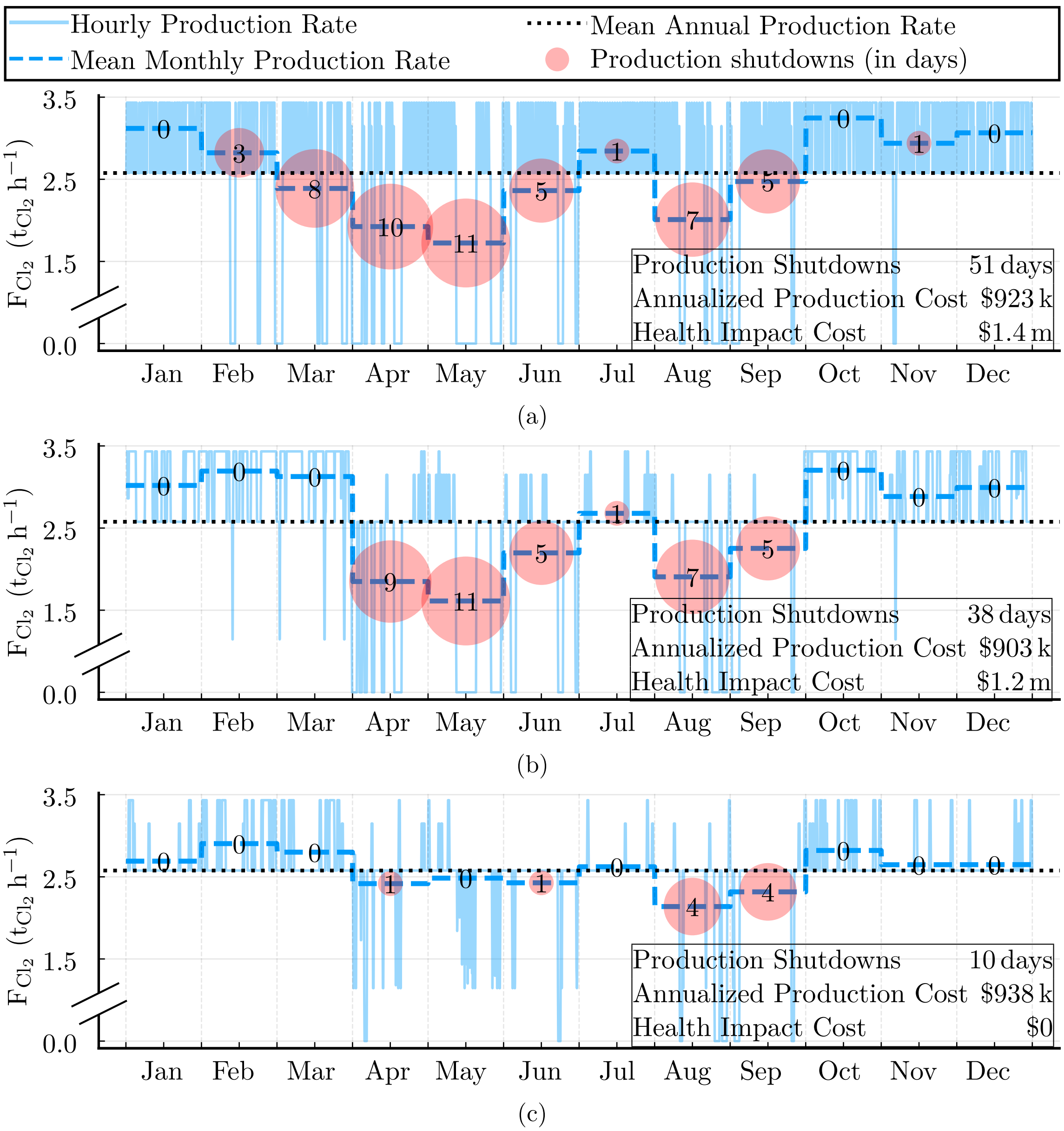

Figure 4: Production schedule, shutdowns, and costs for various scenarios. (a) Production schedule for techno-centric solution. Production is higher in months that do not have poor AQI. Production shutdowns often occur on high AQI days. (b) Production schedule for technology-ecological solution. As compared to techno-centric scenario, production shutdowns are less frequent and product and social costs are smaller. (c) Production schedule for technology-ecological system when optimizing for non-positive social impact cost. Monthly production rates are closer to the energy efficient annual targeted production rate. Production shutdowns are quite infrequent but production cost is higher than other scenarios.

AQI days. Fig. S2b compares the AQI of TES scenario with that of BAU. Due to shift in production schedules, additional chlorine needs to be produced in leaf-off periods. This leads to a deterioration in AQI as compared to constant production BAU case, but imposed AQI constraints are still satisfied.

Despite AQI constraints being met in both, techno-centric and techno-ecological synergy scenarios, emission from the chlorine production facility results in an increased ambient concentration at multiple time periods. The increased ambient concentration causes an increase in incidence rates of air quality related health events. The annualized social cost of chlorine production is \$1.4 m and \$1.2 m in technology only and TES scenarios, respectively. Thus, at lower annualized cost of production and lower societal impact cost the TES solution is both economically and socially superior to techno-centric design and operation, making it a "win-win" solution.

Design for zero social impact cost

Now, along with the AQI constraint set up previously, we add constraints requiring the annualized societal health impact cost to be zero. This constraint does not imply zero health impact cost at all time steps, but the aggregate annualized cost needs to be zero. Under this additional constraint, we find the design that minimizes the annualized cost of production. For techno-centric design and operation, where only investment in SCR and change of production scheduling are allowed, the optimal cost of operation under the new constraints is \$1.05 m. The optimal solution operates at a constant annual average target production rate. Size of the SCR is determined such that all NO_2 emissions from the facility are abated and the demand of ecosystem service for air quality regulation is zero.

In contrast to elimination of demand by taking up all the emissions in the SCR, investments can be made in ecosystem restoration to increase the supply capacity of the air quality regulation service. In this scenario, investment in reforestation and alteration of production schedules are allowed, while imposing the constraints of AQI and non-positive social cost. The optimal TES solution determines a reforestation area of 13 km^2 with an annualized cost of operation of \$938 k. The production schedule is depicted in Fig. 4c. The large forest area provides substantial capacity to absorb emissions, thus allowing for operation closer to the energy efficient targeted annual flow rate. Compared to the TES scenario of optimizing for minimum annualized cost (in the absence of the social cost constraint), the number of production shutdowns have reduced. The daily evolution of social cost is depicted in Fig. S4.

Trade-off between social cost and production cost

We explore the multi-objective tradeoff space of techno-centric solutions versus techno-ecological solutions for the objectives of annual social and production costs. In case of conflicting objectives, a solution in which none of the objective functions can be improved without degrading some of the other objective values is defined as pareto optimal solution. A set of pareto optimal solutions is further defined as a pareto front. An infinite number of solutions can exist on the pareto front and all solutions on it are considered to be equally good. The goal of finding the pareto fronts here is to quantify the tradeoff between two objectives and compare the pareto fronts for two scenarios: techno-centric and techno-ecological.

Figure 5 contains the pareto fronts for the two scenarios considered here. In the techno-centric scenario (curve ABC) only investment in SCR and changes in the operation schedule are permitted. Solution A minimizes production cost and has the highest social impact cost among all optimal solutions obtained under this scenario. Details of this solution are in Figures 4a and S2. Progressing from solution A to solution B reduces the social impact, but the chlorine production rate needs to deviate from the constant energy efficient production rate ($\hat{F}$). This results in added fuel cost and increase in the annualized cost of production. The operational change reduces the ambient concentration leading to a reduced social impact cost. To reduce the social impact cost beyond \$749 k, capital investment needs to be made in purchasing the SCR. Progressing from B to C, the capital investment in SCR increases steadily. Addition of the SCR reduces deviation of the chlorine production rate from its energy efficient BAU operational point. At solution C, the chlorine production schedule resembles that of a BAU schedule, but an SCR that can handle a power generation unit of 11.2 MW is installed. All emissions from combustion are treated by this SCR unit, ensuring no change in ambient concentration and zero social impact cost. This zero social impact design has the highest cost of production for the conventional or techno-centric approach.

For the TES scenario, solution D is the lowest cost solution, and was described in Figures 4b and S3. Progressing from solution D to solution E, additional capital investment is needed in forest restoration. The area selected for reforestation increases from solution D to solution F. Solution E has zero social impact cost and was described in Figure 4c. Both solutions E and C have zero social impact cost, but solution E has lower economic annualized cost of production as compared to that of solution C. Also, the TES solution E is only slightly more expensive than the techno-centric solution A, but the former has zero social impact cost. Further reduction in social impact cost encourages investment in ecosystem restoration to enhance ecological supply capacity and alter production schedule to manage demand. Solution F has the same economic cost of production as solution C but unlike solution C, solution F has a negative societal impact cost, thus providing social benefits. Reducing the social impact cost beyond solution F, requires investment in SCR since no more land is available for restoration. Similar to solution C, solution H has zero ecosystem demand. In addition, solution H has maximum ecological supply capacity, thus resulting in lowest social impact cost i.e. maximum social benefit. From solution D to F, capital investment first occurs in reforestation since the marginal cost of increasing the supply of the air quality regulation ecosystem service is cheaper than that of reducing demand by using the SCR. Details of change in concentration due to operation under solutions D-E-H are presented in Figure S1

The pareto front for the techno-centric scenario conveys that it is not possible to find solutions to the left and below the front. This region is infeasible or unattainable with the available technological options. The pareto front for the techno-ecological solutions is in this technologically unattainable space. This demonstrates how including ecosystems and seeking synergistic techno-ecological designs can expand the design space and yield novel and innovative solutions that have lower production cost and lower health impact cost. Conventional techno-centric approaches cannot find such solutions. However, such solutions need to address the intermittency of the air quality regulation ecosystem service by adapting the manufacturing process and production rate, as described in this work. Thus, the improvement in the two objectives comes at the expense of elevated variability.

Since all solutions on the pareto front are optimal, choosing the best solution is often subjective. The utopia point (purple star on bottom left of Figure 5) represents the best values for both objectives, which for this problem are a cost of production of \$902 k and a social impact cost of \$$-2.2$ m. Ideally, one would want to get as close as possible to a utopian solution. Hence, a solution on the pareto front that is closest to the utopian solution may be considered best.

The reforestation solutions presented in Figure 5 assume that trees are 20 years old. The effect of the age of trees on the TES solutions is depicted in Figure S5 for trees of various ages. Shah & Bakshi [45] demonstrated the feasibility of TES operations while accounting for growth of forest over a project life of 20 years. Regardless of their age, dynamic TES designs provide economically and socially win-win solutions. As the trees grow older, their supply capacity increases, thus enabling

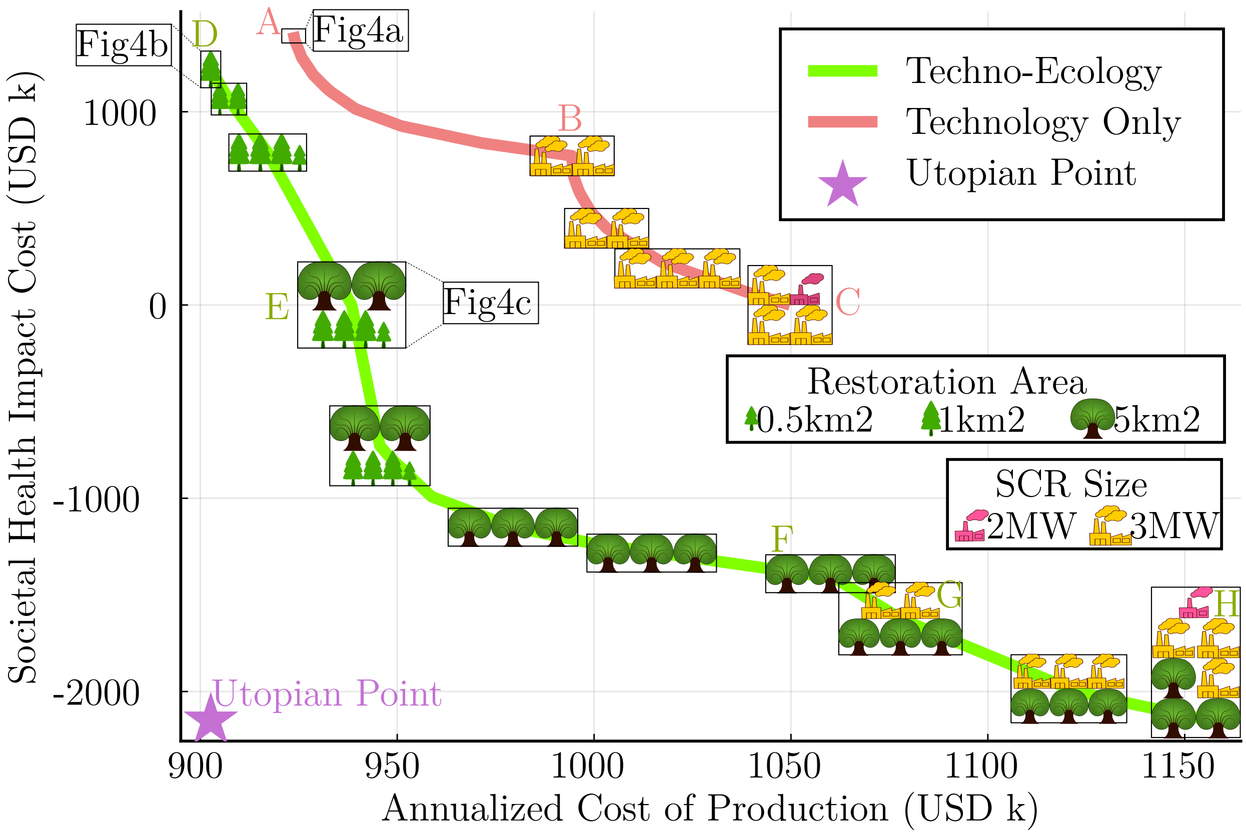

Figure 5: Pareto fronts for techno-centric and techno-ecological systems. Adaptive manufacturing and techno-ecological synergies expands the design space from the techno-centric curve of ABC to the win-win design space of curve DEFGH. The operational schedule of some solutions is depicted in Figure 4.

the solution to approach the utopian point.

Discussion

This work demonstrates the potential benefits if engineering explicitly accounts for its reliance on ecosystems and operates in a manner that adapts to nature's cycles. The emphasis of this work is on economic cost of production and social health impact cost due to ground level ozone. The cost of mitigation and impacts of other criteria air pollutants like particulate matter ($PM_{2.5}$, PM_{10}), carbon monoxide (CO) and sulfur dioxide (SO_2) are ignored. However, forest ecosystems are also capable of taking up these air emissions, so including other air pollutants in the study should provide similar insight into the benefits of TES designs and adaptive operation. The current study also ignores co-benefits of forest ecosystems like carbon sequestration, storm water runoff prevention, and water quality regulation, and its disservices like pollen allergy, damages to pavements and increased biogenic volatile organic compound (VOC) emission. Accounting for these co-benefits and disservices is likely to increase the attraction of nature-based solutions like forests for air quality regulation. This work also shows that if manufacturing and other emitting activities adapt to the intermittency of ecosystems, the benefits of nature-based solutions can be enhanced and industry can operate in manner that reduces its impact and even makes it net-positive. If industry adopts the type of TES design and operation described in this work, it will represent an important step in a paradigm shift in engineering toward working with nature rather than trying to dominate it or taking it for granted. This could transform the engineering-ecology relationship toward synergy instead of antagonism.

The dynamic TES designs obtained in this work rely on meteorological and air quality data in the selected year. Practical application of this approach will need to use real-time data with forecasting models of air quality and feedback control strategies for adaptive manufacturing. In addition, this work considers only a single emission source whereas in practice an airshed is likely to be shared by multiple emitters requiring the ecological capacity to be allocated between them. Liu et.al. [46, 47] discusses different approaches of allocation like economic output, ecosystem ownership, etc. and their implications while explicitly accounting for ecosystems. Additional market based approaches like payment for ecosystem services [48] and cap-and-trade schemes may be required for finding efficient regional TES solutions.

Since TES designs explicitly account for the role of ecosystems and their capacity, they are likely to encourage human activities to stay within the safe operating space [49]. However, for ensuring sustainability of such designs, it is necessary to also consider other ecosystem services, social aspects, and indirect impacts along the life cycle. Incorporating such impacts using a TES-Life Cycle Assessment [47] methodology is subject of future work. In this work, we used a single native species of White Ash for reforestation as a proxy to ecological restoration. For a practical TES based reforestation solution, region-specific native species should be explored such that biodiversity of the region is also restored and principles of ecosystem restoration [50] are followed. Currently, regulatory policies only account for impacts of air pollution on a multi-year annual basis and ignore the supply capacity of ecosystems. Policy planning efforts are required for incorporating short-term health impact exposure and supply capacity of ecosystem services [51]. Without proper monitoring and updates to environmental policy, this approach, like most others, could lead to industry green-washing [52]. Real-time operation of such TES systems would require advances in control algorithms to account for time-varying ecological uncertainties. In future work, we plan to integrate automatic operations with design of TES systems.

Supporting Information The supporting information contains 15 pages, 5 figures, 1 algorithm and complete mathematical model for case study.

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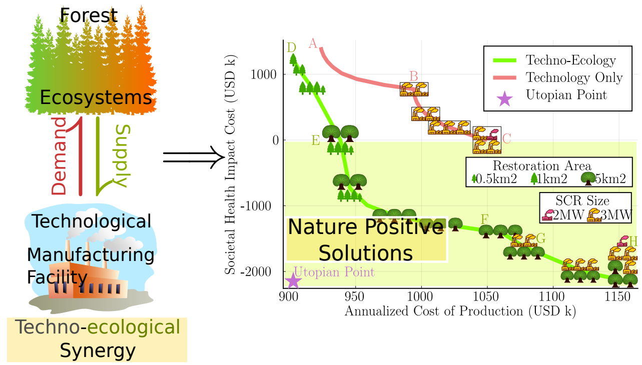

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Synopsis: Accounting for nature's capacity and intermittency while design and operations of manufacturing processes can result in novel net-positive impact solutions.