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Phosphorus (P) recovery from corn biorefineries is promising for mitigating environmental impacts and promoting the P circular economy

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ABSTRACT

The intertwined issues of eutrophication and phosphate mineral resource scarcity have prompted the necessity for phosphorus (P) recovery. Corn biorefineries are considered a promising source for recovering P. We investigated the environmental impact and economic benefits of P recovery technology in corn biorefineries considering the sidestream P recovery and downstream animal manure nutrient reduction, and marginal impacts associated with economic scales. The results show that the P recovery technology for corn biorefineries can mitigate more than 70% of the mineral resource scarcity and avoid about 40% of eutrophication. While the economic benefits of P recovery technology are not reflected in small plant capacity, the environmental impacts reduce and economic benefits increase as economic scales increase. This study shows the co-benefits of P resource recovery and life-cycle eutrophication mitigation and the economic gain of P recovery for larger-scale corn biorefineries.

1. Introduction

Phosphorus (P) is an indispensable nutrient for supporting life (Conley et al., 2009; Scholz et al., 2013). Yet, available P resources are now facing a crisis because the phosphate rock reserves are being depleted (Alewell et al., 2020; Walan et al., 2014). The P paradox has been a major concern in many regions (e.g., the US corn belt) around the world (Lougheed, 2011; MacDonald et al., 2012; Metson et al., 2016). While P mineral stocks are becoming increasingly scarce, P levels in the aquatic environment are often high, thus leading to eutrophication problems, which seriously threaten the ecological environment and human health (Khan and Ansari, 2005; Némery, 2016). Therefore, timely efforts are needed to address the issues of the P paradox. In particular, P recovery has been widely taken as a promising approach to supplement P resources and mitigate eutrophication (Dawson and Hilton, 2011; Sarvajayakesavalu et al., 2018). For example, P resources recovered from wastewater have been investigated in different P-containing flows (e.g., wastewater effluent, digester supernatant, sewage sludge, and sewage sludge ash) (Egle et al., 2016), by adopting different technologies, such as struvite crystallization (Vinardell et al., 2023), alkaline precipitation (Mielcarek et al., 2023), absorption and electrochemical desorption (Wang et al., 2023). Among a variety of P recovery paths, P recovery from corn biorefineries has been considered a promising route, given the high P concentration in the steepwater of the corn wet milling process and thin stillage of the corn dry grind process (Juneja et al., 2020, 2019). Yet, the environmental and economic impacts (especially the marginal impacts associated with economic scales) of P recovery in corn biorefineries remain key knowledge gaps for its sustainable development and P circular economy.

Life cycle assessment (LCA) enables comparison between different production cases (Li et al., 2019) and has been widely applied in environmental impact assessment of P recovery technologies from different feedstocks (e.g., sewage sludge (Pradel and Aissani, 2019; Sorensen et al., 2015), wastewater (Orner et al., 2022; Sena et al., 2021), manure (Bryant and Coats, 2021; Orner et al., 2021; Pedizzi et al., 2018; Temizel-Sekeryan et al., 2021), meat and bone meal (Tonini et al., 2019)). From the perspective of system boundaries, studies on P recovery from manure or wastewater have investigated side stream P

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content change in coproducts and suggested research needs for including the downstream impacts of P flow on the environments (Li et al., 2021b; Tarayre et al., 2016). For example, Temizel-Sekeryan et al. (2021) investigated P recovery from dairy manure and suggests eutrophication impact can be reduced by 78% due to the reduced P content in digested manure as a fertilizer. For economic analysis, techno-economic analysis (TEA) is a well-established approach to evaluate the economic feasibility (e.g., break-even analysis, internal rate of return) of P recovery technologies in different application scenarios (e.g., P recovery from the complex pharmaceutical wastewater) (Bonatsos et al., 2020; Li et al., 2021a; Shukla et al., 2022). Yet, the current TEA studies on P recovery technologies have little consideration for the break-even analysis of recovery products across different economic scales.

Corn is relatively high in P content compared with other common grains (Hernandez et al., 2005; Sun et al., 2022). Especially, the coproducts (e.g., corn gluten feed (CGF), distillers dried grains with solubles (DDGS)) from corn biorefineries have excessive P which cannot be digested for ruminant animals (Juneja et al., 2019; Rausch et al., 2005), leading the excess P discharged by animal manure into the aquatic environments. Therefore, P recovery from corn biorefineries not only recovers nutrients as potential fertilizers but also reduces P content in coproducts (e.g., DDGS, CGF) for animal feeds, which has the potential to reduce P pollution discharged by animals (He et al., 2017). At present, there have been studies on the distribution of P content and molecular structure in different production streams of corn biorefineries, but mainly focus on the P flow inside the corn biorefinery plants (Alkan-Ozkaynak and Karthikeyan, 2012; Liu and Han, 2011; Noureddini et al., 2009; Rausch et al., 2005). However, the impacts of P recovery in corn biorefineries and their associated downstream P reduction in animal manure are still lacking in consideration, resulting in the environmental impact being incomplete. Studies have called for a more comprehensive assessment (e.g., extending system boundary) of P recovery technologies to reveal the true environmental impacts of P recovery technologies, such as using an end-user perspective (Lam et al., 2022). In addition, traditional LCA studies commonly assume that environmental impacts are proportional to the scale of production. Yet in reality, the performance of P recovery technologies at different economic scales (i.e., different capacities) can result in nonlinear marginal impacts (Pizzol et al., 2021; Qin et al., 2021). In this context, extending the system boundary to the downstream P discharge in animal manure and taking different economic scales into account is necessary to reveal more realistic environmental and economic marginal impacts.

To evaluate the feasibility of P recovery comprehensively, we applied LCA and TEA to compare the environmental and economic performance of full-scale corn biorefineries with and without P recovery technologies. With an extended system boundary to downstream animal manure, we used the process model (i.e., SuperPro) to simulate the production processes and establish life cycle inventories for different plant capacities. Based on this, we summarized the environmental impacts of P recovery technologies at different plant capacities from two levels of environmental assessment (i.e., midpoint and endpoint). Considering the simultaneous costs and revenues generated by P recovery, we continued to evaluate the economic impact by focusing on the minimum selling price (MSP) of P recovery coproducts for a break-even analysis at different economic scales.

2. Methods

2.1. P recovery technologies in corn biorefineries

Two of the most widely used corn biorefinery processes were considered in this study: the wet milling process producing starch, and the dry grind process producing ethanol as the main product. CGF and DDGS are the coproducts of the aforementioned two kinds of corn biorefineries respectively, which are commonly used as animal feeds. The P recovery technology is applied in different specific production processes in wet milling and dry grind corn biorefineries. For wet milling biorefineries, most of the P is steeped in the steeping step. In the base case, about 70% of P remains in the concentration of the steep water and is mixed with the suspension to produce CGF, resulting in high P content of CGF product (Rausch et al., 2005). For dry grind biorefineries, about 76% of the P remains in the thin stillage (Alkan-Ozkaynak and Karthikeyan, 2012; Juneja et al., 2020). DDGS are obtained by mixing wet distiller's grain and thin stillage, thus burdened with high P content. Given that the P in corn exists mostly in the form of phytate, the specific P recovery technology is to add the alkaline hydroxide ($NaOH + CaCl_2$) into the chosen high-P streams from corn to achieve optimal pH and Ca:P ratio. Thin stillage and the steepwater were mixed for 5 min and centrifuged to convert the excessive P into the P-containing complex precipitations with Ca-phytate ($C_6H_6Ca_6O_{24}P_6$) as the main component (Juneja et al., 2020, 2019). The treated thin stillage and treated steepwater (mixed with insoluble solids) were then processed to conventional processes. The production processes and reference P recovery flows are shown in Fig. 1 and Table S1. Detailed information about the production processes was further described in Supporting Information (SI) Section S1.1. The P content of CGF and DDGS produced by the conventional processes is about 12 mg/g and 5–10 mg/g, both of which are higher than the generally recommended level of P for animal feeds (i.e., 3–4 mg/g) (Noureddini et al., 2009; Rausch et al., 2005; Spiehs et al., 2002). After adding the P recovery units to the key steps of the corn biorefineries, the P content of CGF and DDGS can be ultimately reduced to 2.4 mg/g and 3.2 mg/g respectively, enabling the P content of these two feeds to be controlled at the level of the normal requirements of ruminants (Juneja et al., 2020, 2019).

2.2. Environmental life cycle assessment

We compared the life cycle impacts of traditional corn biorefineries (base cases without P recovery) with P recovery cases to evaluate whether the P recovery technologies have better environmental performance for certain environmental impacts. The system boundary considered in this study includes the upstream production processes of all the required chemicals and energy, the corn processing processes, the use of CGF and DDGS as animal feeds, and the downstream nutrient emission with animal manure (Fig. 1). The corn biorefineries in this study have multiple end-products, which can result in product allocation issues. Due to the focus of our study on P recovery technology which not only affects the full-scale corn biorefinery production but also influences the quality and yield of coproducts (i.e., CGF and DDGS), we chose the functional unit as 1 MT of corn processed in corn biorefineries, as the inputs are independent with final products (Cherubini and Strømman, 2011; Li et al., 2020), thus it is suitable for the analysis to compare processes with the same input raw materials (corn) in this study. For instance, existing LCA studies on biorefinery also reported selecting input biomass as a proper functional unit to avoid complex allocation (Uihlein and Schebek, 2009). Since the purpose of this study was to compare the environmental impacts of the two cases for corn biorefineries, both of which are identical in terms of the corn farming process, thus the system boundary does not include the farming and transportation of corn. We also considered the loss of coproduct yields (e.g., CGF, DDGS) caused by P recovery in the system boundary. A more detailed description of system boundary and environmental impact allocation methods was provided in SI Section S1.2 and Section S1.3.

The detailed foreground inventory was generated based on process simulation using SuperPro Designer (Intelligen, Inc) (Buitrago-Tello et al., 2022). Specifically, we modeled the production processes of corn biorefineries without P recovery (base cases) and with P recovery (P recovery cases), respectively, for obtaining related inventory data including raw materials (e.g., corn, sulfur, ammonia), energy consumption (i.e., electricity, natural gas), equipment (e.g., conveyors, tanks, pumps), products (e.g., starch, CGF, ethanol, DDGS), wastes (e.g., wastewater) and additional required inventory to compensate the

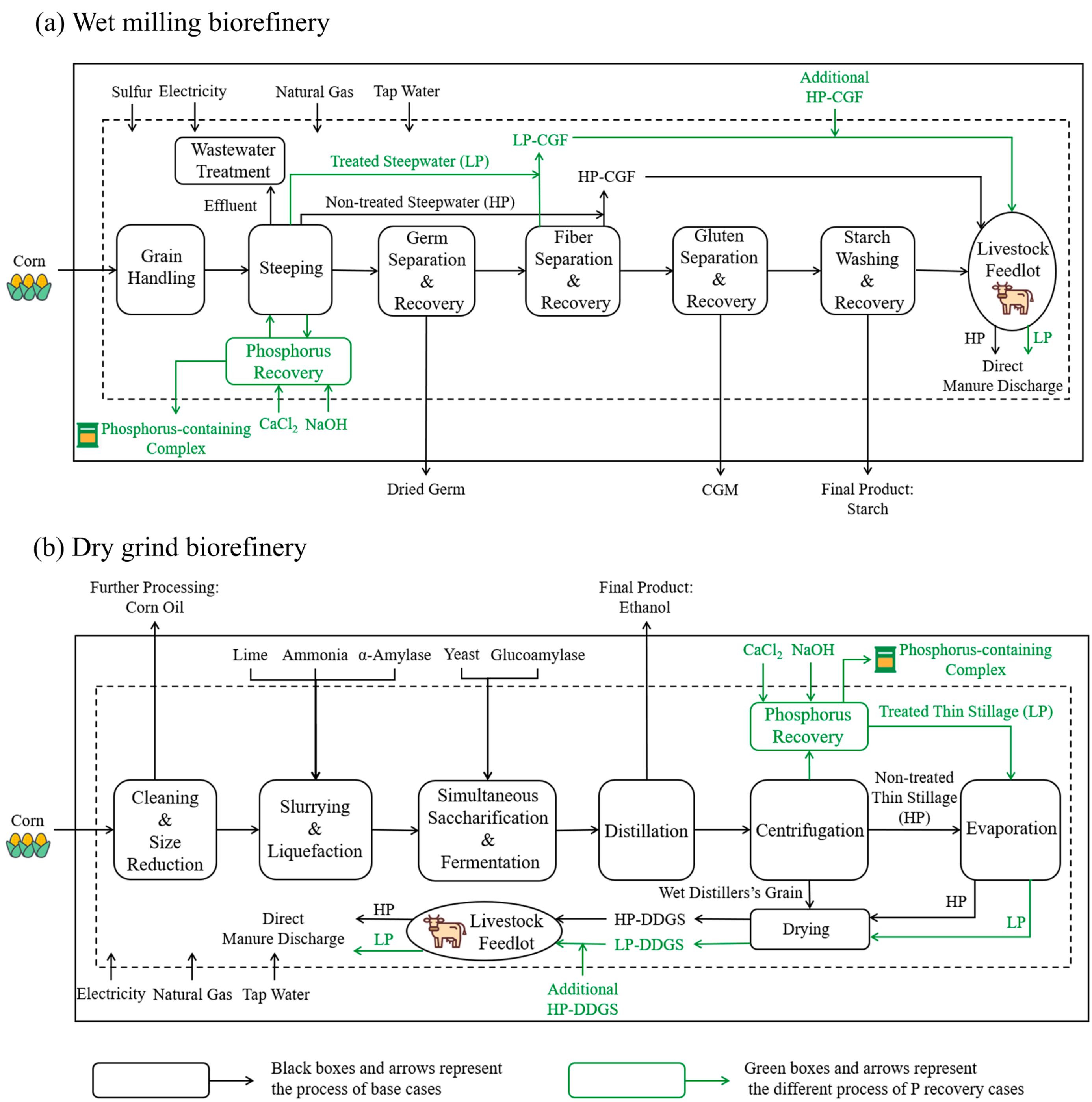

Fig. 1. Detailed production process and system boundary for (a) wet milling biorefinery and (b) dry grind biorefinery. CGF = corn gluten feed. CGM = corn gluten meal. DDGS = distillers dried grains with solubles. HP = high phosphorus. LP = low phosphorus.

reduction of CGF and DDGS yields in P recovery cases (i.e., high-P CGF and high-P DDGS production) (correspond to flows in Fig. 1). Detailed foreground inventory information can be found in SI Section 1.4 and Table S1. To evaluate the marginal life cycle impacts subject to economic scales, we modeled five common plant capacities for both wet milling (i.e., 0.67, 0.91, 1.70, 2.10, 5.00 MMT corn/yr) and dry grind biorefineries ((i.e., 0.35, 0.70, 1.05, 2.10, 2.63 MMT corn/yr). The treatment of wastes from corn biorefineries is well worth considering. Accordingly, the wastewater discharge of corn wet milling biorefineries can be adjusted according to the production capacity of the plant (Juneja et al., 2019). The P content of the direct animal manure discharge was calculated using the well-established equations developed by ASAE "Standard for Animal Manure Production and Characteristics" (ASAE, 2005), in which existing research data and regression analysis were used to identify the relationship between diet feed composition (e.g., P content) and the manure characteristics (e.g., nutrient excretion). The detailed calculation formulas and parameters for estimating how animals' manure responds to diet feed with different P content levels were provided in SI Section S1.5.

In the P recovery case, the optimal ratio of Ca to P was found to be 1.5 and the optimal pH was 9 based on the laboratory-scale experiments (Juneja et al., 2020, 2019), which could be scaled up accordingly to obtain the input data of calcium chloride and sodium hydroxide and the output data of P-containing complexes (Table S1). In addition, the new equipment required for P recovery units was also included. All the foreground inventory simulated by SuperPro Designer (Intelligen, Inc) was then connected to the ecoinvent 3.6 cutoff database to generate the complete life cycle inventory. A detailed explanation of the choice of background data providers in ecoinvent 3.6 cutoff database was attached in SI Section S1.6 and Table S2.

The software openLCA 10.3.1 was used and the potential environmental impacts were analyzed using ReCiPe 2016 (version: Hierarchist) (Huijbregts et al., 2017), which provides a state-of-the-art and harmonized method to convert life cycle inventories to specific midpoint and endpoint environmental impact values and has been well applied in many fields (Dekker et al., 2020; Lakho et al., 2022). The performance of activities at different scales in terms of life-cycle impacts can vary in a nonlinear manner due to economies of scale (Pizzol et al., 2021). To reveal the possible nonlinear relationships, we analyzed the trend of marginal environmental impact changes across different economic scales (i.e., plant capacities), thus providing a more comprehensive and credible assessment.

2.3. Techno-economic analysis

We performed techno-economic analysis (TEA) to compare the economic performance of P recovery in corn biorefineries. The TEA in our study was based on economic data for the year 2018 in US dollars ($) and included mainly capital costs, operating costs, and product revenues (Kern et al., 2017). Capital costs were derived from capital investment and construction costs. The depreciation period for equipment is assumed to be 20 years. Operating costs consist of raw materials, energy consumption, labor and depreciation. We set operational days of 330 days for corn biorefineries. Product revenues are from main products (i.e., starch, bioethanol) and coproducts (i.e., CGF, DDGS, P-containing complexes). The net present value (NPV) and internal rate of return (IRR) were conducted in the analysis to compare the economic feasibility between the base cases and the P recovery cases considering a project lifetime of 20 years (SI Section S1.7). P content in low-P CGF, low-P DDGS and P-containing complexes obtained from the P recovery cases are different from that of the base cases, which might have uncertain prices given by different markets and policy incentives. We conducted a break-even analysis to estimate the minimum selling prices (MSP) of the coproducts (i.e., CGF, DDGS) and the P-containing complexes by setting equal NPVs of base cases and P recovery cases. The economic feasibility of P recovery was evaluated by comparing the MSPs of the coproducts as low-P animal feeds and P-containing complexes with the current market prices in base cases (i.e., 108.8 $/MT for high-P CGF, 153.0$/MT for high-P DDGS). We also took different economic scales into account for a better understanding marginal economic impacts of MSP across economic scales (i.e., different plant capacities).

2.4. Sensitivity analysis

LCA and TEA results may vary significantly given that foreground and background data have inherent variabilities. For comparative purposes, considering the uncertainty of all inventory data is not necessary and may complicate the interpretation of results, because comparative LCA studies share many common inventory data (Mendoza Beltran et al., 2018). Instead, we considered $\pm$10% changes in the key parameters in the animal manure P process (i.e., the proportion of CGF or DDGS in animal feeds, milk yield of dairy cows, and feed intake of each dairy cow), which would have considerable impacts on the final comparative results. In addition, the P recovery would impact the yields of main and coproducts (e.g., starch and CGF for wet milling, ethanol and DDGS for dry grind), in which different LCA allocation methods (i.e., mass and economic allocations) may have also impacted the results. Therefore, we conducted a sensitivity analysis for these influencing factors to determine whether they could potentially alter the final results. This helped us to gain a more dialectical understanding of whether the implementation of P recovery technologies in corn biorefineries would result in overall or situational environmental benefits. Details of sensitivity analysis on animal manure P process and allocation methods can be found in SI Section 2.3. An important source of long-term uncertainty for TEA analysis is the expected selling prices of P recovery coproducts (i.e., CGF, DDGS, and the recovered P-containing complexes) which will depend on the unknown behavior of the market and government (external driving force). We investigated and discussed this impact by considering $\pm$10% price fluctuations of animal feeds (i.e., CGF and DDGS) and the known price fluctuations of P fertilizer (DAP) in 2015–2019 for P-containing complexes.

3. Results and discussions

3.1. Environmental impacts shifting with the P recovery technology

The environmental impacts of all midpoint impact categories for the P recovery cases in wet milling and dry grind biorefineries were compared to the base cases without P recovery (Fig. 2). The results show P recovery technologies are environmentally superior across some of the midpoint impact categories, such as mineral resource scarcity (reduced by more than 70%) and freshwater eutrophication (reduced by about 40%), due to the benefits of P recovery products and reduced P discharged by animal manure. However, we found the issue of environmental burden shifting exists between the P recovery cases and the base cases. Particularly, the P recovery cases have resulted in more land use (163% higher for the wet milling process and 85% higher for the dry grind process) than the base cases. This is mainly because the precipitation for P recovery can take away part of the fibers from the nutrient stream, resulting in a reduction in animal feed yield. The supplemental animal feeds production process contributes most to the increased land use of P recovery technologies (SI Section S2.1, Fig.S1). The significant land use impacts of corn-related products have also been pointed out by other studies (Cai et al., 2016; Pieragostini et al., 2014; Yang et al., 2012). For example, Pieragostini et al. (2014) showed that corn farming can contribute up to 91% of the total land use, which supports our findings that the production of supplemental animal feeds contains a large amount of farmland use, indirectly increasing the land use of P recovery technology. Similarly, the increase in water consumption was observed for the P recovery cases, also due to the yield loss of coproducts (CGF and DDGS as animal feed). It is suggested to future endeavors in P recovery technology development should focus on minimizing the yield loss of coproducts while maximizing P recovery products to mitigate the trade-offs of environmental burden shifting. After considering the impact of P recovery on all midpoint environmental impact categories, we identified the three midpoint environmental impact categories that were most affected by the P recovery technology (i.e., mineral resource scarcity, freshwater eutrophication and land use) given the above results of the percentage change analysis (Fig. 2). Because the focus of this study is P recovery technology, the three selected midpoint categories were then investigated in depth in the following results and discussions, while the remaining less-affected midpoint categories would not be further analyzed.

3.2. The importance of downstream animal manure nutrient reduction and P recovery potential

As the impacts of P recovery on eutrophication and mineral scarcity were the key consideration in this study, we provided a detailed analysis of the two midpoint impacts with detailed process contributions. Fig. 3a represents the process contribution of the mineral scarcity impact, indicating that the P recovery case offers the wet milling biorefinery an environmental advantage over the base case without P recovery. The recovered product (i.e., P-containing complexes) can offset traditional fertilizer made from phosphate rock, thus considered a P resource (Ruffatto et al., 2022). For wet milling biorefinery, the recovered P

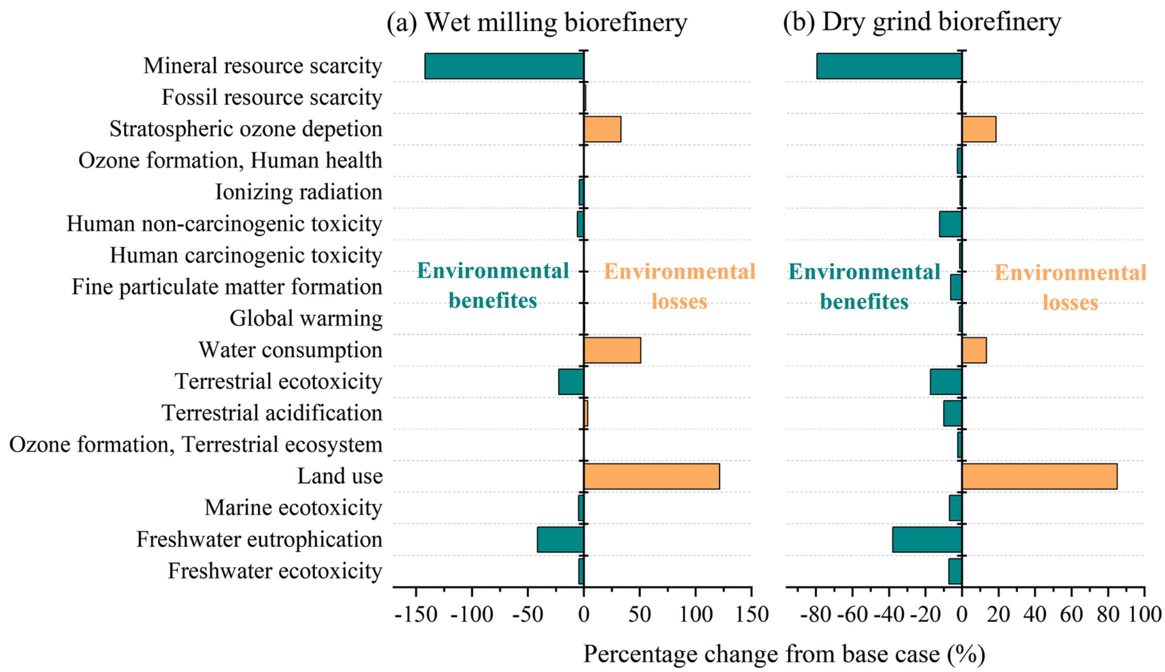

Fig. 2. Relative change of P recovery case from base case for ReCiPe 2016 (version: Hierarchist) midpoint categories at the minimum plant capacity (0.67 million metric ton corn input for wet milling and 0.35 million metric ton corn input for dry grind). (a) wet milling biorefinery; (b) dry grind biorefinery. Negative percentage change indicates P recovery technologies have relative environmental benefits, while positive change means relative environmental losses, as compared to base cases with P recovery.

offsets significant mineral resource use in other life cycle stages, resulting in a net mineral scarcity benefit with −0.47 kg P per FU. While for the dry grind biorefinery, the P recovery case also resulted in a significant reduction of 79.1% in mineral scarcity impact, decreasing from 2.25 to 0.47 kg P per FU (Fig. 3b). Dry grind biorefinery consumes 0.72 kg P per FU more mineral scarcity impact on equipment than wet milling biorefinery, so the recovered P from wet milling biorefinery can cover more mineral resource consumption compared to dry grind in terms of P recovery cases.

As P discharge is one of the driving factors for the eutrophication issues of various water bodies (Khan and Ansari, 2005; Némery, 2016), freshwater eutrophication is also one of the focused environmental impacts in our work. Fig. 3c-d shows that the freshwater eutrophication impacts under the P recovery cases are significantly lower than the base cases, with a 41.8% reduction for the wet milling biorefinery and a 37.9% reduction for the dry grind biorefinery. Moreover, as shown in Fig. 3c-d, the above reduction in freshwater eutrophication impact is mainly dominated by the reduction of animal manure P content. The animal feeds derived from corn biorefineries (i.e., CGF, DDGS) contain phytin P, a calcium magnesium salt of phytate, which cannot be digested by non-ruminant animals (e.g., diary), resulting in the downstream animal manure containing very high P content and cause freshwater eutrophication. The potential of direct P recovery from livestock waste has been investigated before (Martin-Hernandez et al., 2021), but the indirect impact of reduced P content in manure has not been considered. Gerrior et al. (2022) found out that the reduction of freshwater eutrophication impact from dry grind corn biorefinery is mainly due to the replacement effect of DDGS on corn feeds and recovered P product on commercial fertilizer. The necessity of connecting corn biorefinery production with downstream animal food systems was suggested in other studies on nutrient cycling (Algren et al., 2021), but quantitative analysis referring to downstream animal manure was lacking. Different from previous studies, we considered animal manure discharge within our system boundary. We found that though the offset effect from the P-containing complexes on P fertilizer does exist, the contribution of animal manure P discharge has a dominant role in reducing environmental life cycle eutrophication. Therefore, the benefits of freshwater eutrophication mitigation that P recovery technologies can bring may be underestimated before.

3.3. Nonlinear environmental impacts induced by economic scales

The P recovery technology in this study was conducted on a laboratory scale, and the optimal pH condition (pH = 9) and Ca:P ratio (Ca:P = 1.5) were determined in previous studies (Juneja et al., 2019, 2020). As reported, only these two major unit operations in the front end of the process are required to make the change for P recovery in corn biorefineries. We simulated the production processes of corn biorefinery and P recovery on different economic scales based on the optimal operational conditions by SuperPro based on the commercial corn biorefinery plants in the US and found that the amount of recovered P can steadily increase with the expansion of economic scales (SI Section S4, Fig. S6c-d) as shown by Juneja et al. (2020), indicating the scalability of P recovery technology. While P recovery itself has scalability, the environmental and economic impacts of P recovery per functional unit might change due to the expansion of economic scales. Fig. 4 shows the endpoint environmental impacts per functional unit gradually decrease with plant capacity increasing. For example, the normalized impacts on human health reduce from 1 to 0.93 in wet milling biorefineries. This is because the electricity energy efficiency of corn biorefineries increases as the scale increases (Section S2.2, Table S3) given the important contribution of electricity, especially for human health (Section S2.2, Fig. S2).

We note that the decreasing trend of environmental impacts tends to level off gradually with the expansion of common economic scales (0.67~5.00 MMT corn/year for wet milling, 0.35~2.63 MMT corn (40~300 Mgal ethanol)/year for dry grind). In the small-scale stage, the environmental impacts of corn biorefineries show a noticeable scale effect. Although the consumption of variable costs such as natural gas in the plant increases steadily with plant capacity, the fixed inputs (e.g., equipment) do not need to change substantially, thus increasing the production efficiency of corn biorefineries. As the economic scale

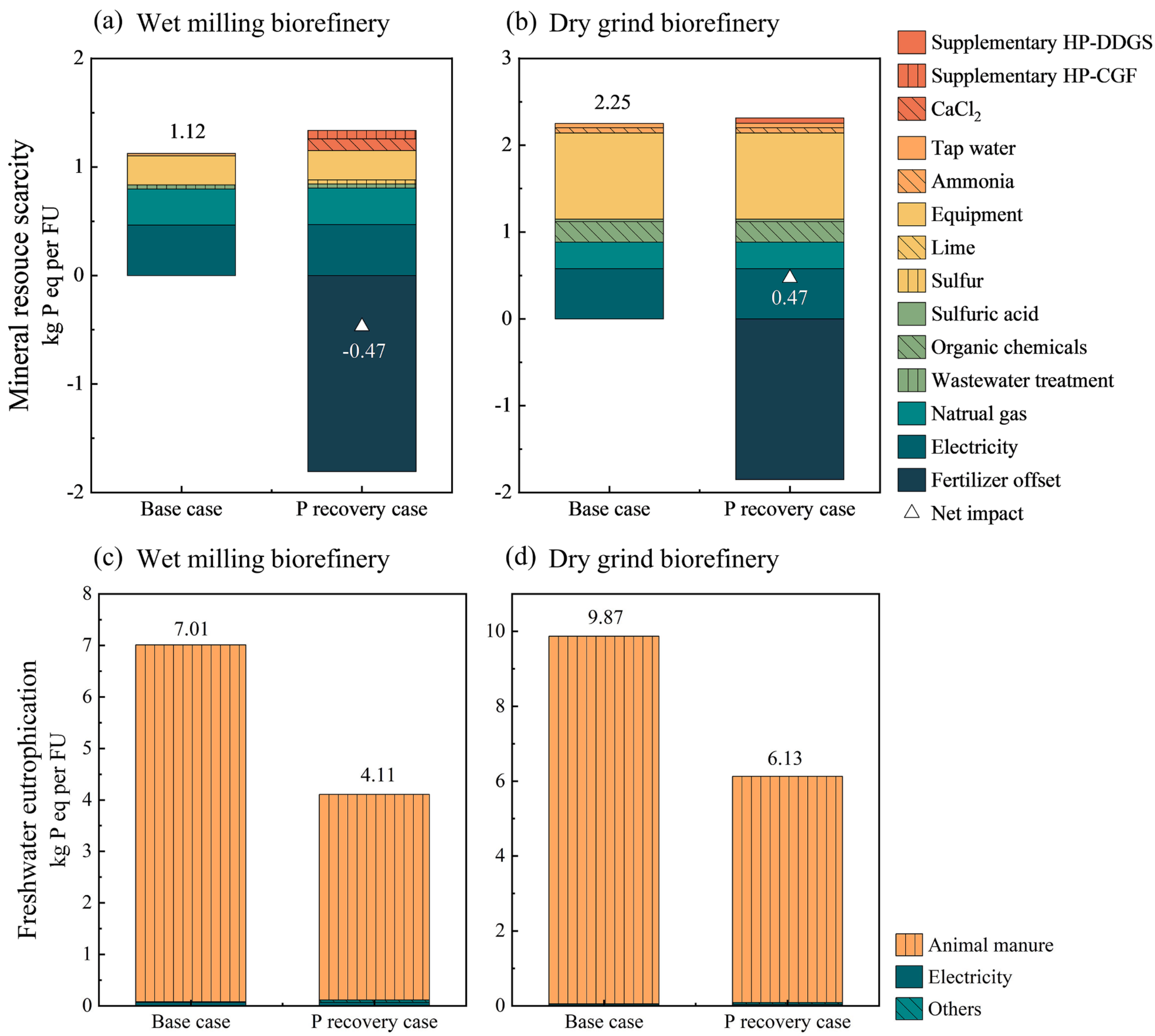

Fig. 3. Eutrophication and mineral scarcity impacts and key contribution analysis at the minimum plant capacity (0.67 million metric ton corn input for wet milling and 0.35 million metric ton corn input for dry grind). Mineral resource scarcity impact in (a) wet milling biorefinery and (b) dry grind biorefinery; freshwater eutrophication impact in (c) wet milling biorefinery and (d) dry grind biorefinery. Negative impacts indicate net environmental benefits in the category, while positive impacts indicate environmental losses. HP = high-phosphorus (P). CGF = corn gluten feed. DDGS = distillers dried grains with solubles. FU = functional unit. Note that for mineral scarcity, we converted the unit of kg Cu-eq to kg P-eq based on the conversion factor provided in the ReCiPe 2016 (version: Hierarchist) method, given that the focus of this study is P recovery.

continues to increase, the previous equipment can no longer meet the requirements of production and the fixed inputs have to be increased. This impact on equipment is ultimately reflected in the changes of electricity energy efficiency (Section S2.2, Table S3), thus dominating the nonlinear trend of environmental impacts. Therefore, with the increase of economic scales, the environmental impacts of large-scale plants are gradually reduced. Pizzol et al. (2021) also focused on the nonlinear environmental LCA impacts with technologies scaling, of freight transportation and showed a similar trend of decreasing environmental marginal impacts with our study.

Besides, Fig. 4 shows that the gaps of ecosystems and resource impacts between the base and P recovery cases are essentially stable with different plant capacities, which means that the critical environmental benefits of P recovery for ecosystems and little impact for resources hold across economic scales. Although the human health impact difference between the P recovery and base cases varies in different plant capacities, the gaps are still generally quite small compared to those of ecosystem impact. Our results are also supported by Tonini et al. (2019) who also highlighted the environmental and health advantages of a variety of P recovery technologies (e.g., recover P from sewage sludge, manure, and meat and bone meal) over P mining from phosphate rocks. We performed a sensitivity analysis in terms of selected parameters involved in animal P content calculation (Table S4) and different environmental impact allocation methods (Fig. S3). A detailed description of sensitivity analysis was provided in SI Section S2.3. The results of sensitivity analysis show that the P recovery technologies are generally environmentally friendly based on the endpoint impact analysis across different economic scales.

3.4. Minimum selling price of P recovery product and coproducts across the economic scales

In addition to the environmental impacts, we investigated the economic feasibility of the P recovery technologies by estimating the MSP of animal feed coproducts and P recovery products across the economic scales (Fig. 5). We first analyzed the impacts of P recovery technologies

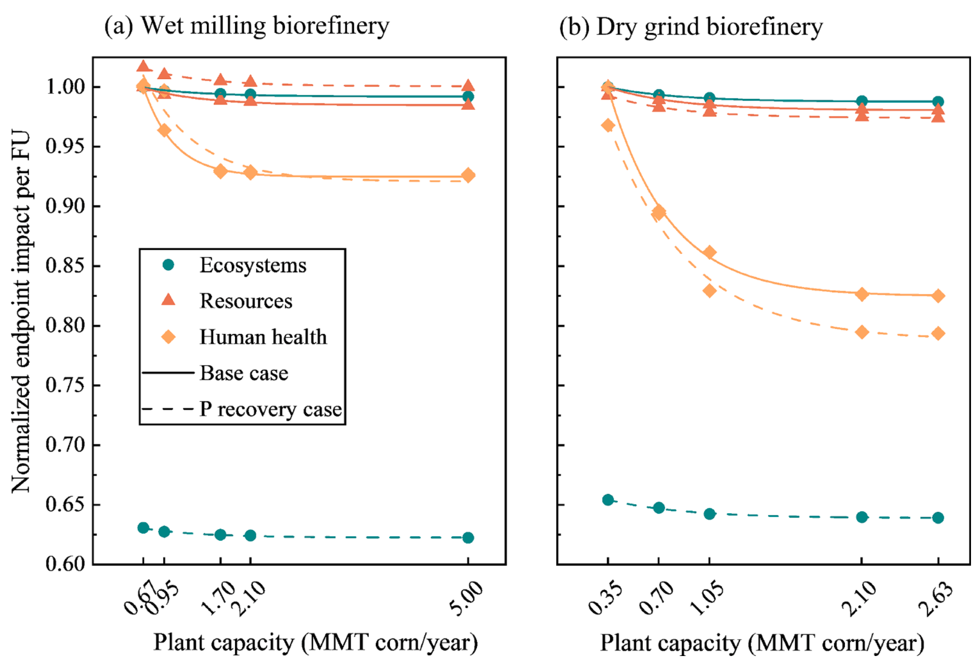

Fig. 4. Normalized endpoint environmental impact change with different plant capacities for (a) wet milling biorefinery and (b) dry grind biorefinery. The normalization endpoint impact was calculated as the impact at a given plant capacity divided by the same endpoint impact at the minimum plant capacity of the base case. MMT = million metric tons. FU = functional unit.

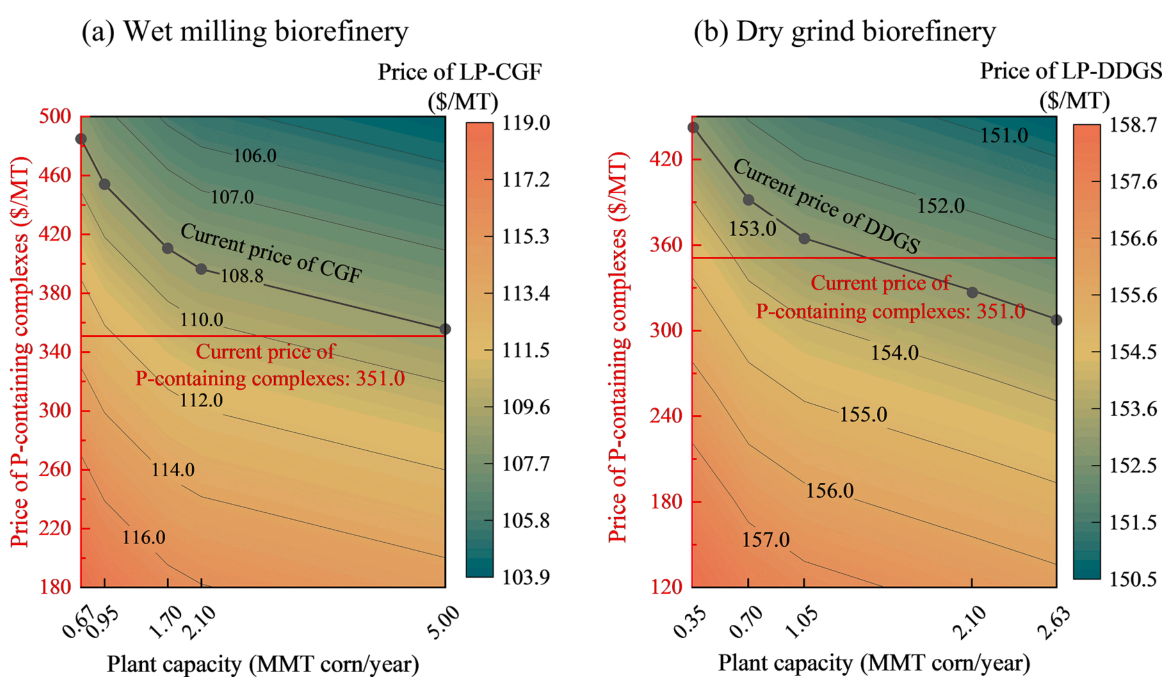

Fig. 5. Minimum selling price (MSP) of the P recovery product and coproducts across different economic scales (i.e., different plant capacities) (a) wet milling biorefinery and (b) dry grind biorefinery. The color bar on the right side of each subplot shows the price of the animal feed generated from P recovery cases. Every point in the plot is the MSP of P-containing complexes given the price of animal feeds to reach the break-even equilibrium between the base cases and P recovery cases. LP-CGF = corn gluten feed with low P content; LP-DDGS = distillers dried grains with solubles with low P content; MT = metric ton; MMT = million metric ton.

on the capital cost, operating cost, and revenue of the two kinds of corn biorefineries at a single economic scale (0.67 MMT/yr corn input for the wet milling biorefinery and 0.35 MMT/yr corn input for the dry grind biorefinery, respectively) (SI Section S3.1 and Table S5). The results show that higher revenues shown in the P recovery cases compared to the base cases are mainly contributed by the changes from three co-products (i.e., CGF, DDGS, and P-containing complexes). Although the IRR of P recovery cases (29.02% for wet milling, 7.89% for dry grind) is smaller than base cases (30.48% for wet milling, 8.01% for dry grind) in the smallest plant capacities (Table S5), the complete economic impacts of the P recovery cases cannot be simply defined based on only a single scale given the potential nonlinear marginal impacts subject to different economic scales.

When the prices of animal feeds or P-containing complexes are fixed, the MSP of the coproduct is observed to decrease with increasing plant capacity (Fig. 5). Specifically, the MSP of P-containing complexes can be lower than the current price of similar P fertilizer (DAP) (351.0 $/MT) with low-P DDGS sold at the current price when the plant capacity is larger than about 1.5 MMT corn/yr (Fig. 5b). This indicates that although the P recovery technologies do not reflect economic advantages over the base cases at the smallest scale, the economic efficiency of the P recovery cases relative to the base cases keeps increasing as the economic scales expand. The main reason is that the marginal investment expenditure caused by the additional P recovery units decreases as the unit production increases, while the revenues of the P recovery cases over the base cases increase steadily with the scaling up of recovered P fertilizer. Therefore, the net income of the corn biorefineries under the P recovery cases increases. Overall, the economic benefits brought by the P recovery technologies are increasing as plant production scales up, which implies that larger-scale corn biorefineries have more potential to be profitable through P recovery.

Since the new products (i.e., low-P CGF, low-P DDGS, P-containing complexes) obtained from the P recovery cases can reduce P discharge from animal manure by reducing the P content of animal feeds, they can be recognized as environmentally friendly products and have the potential to sell for better prices than conventional animal feeds and P fertilizers with policy incentives (e.g., subsidy) (Wang et al., 2018; Yi et al., 2021). The current market price of high-P CGF is 108.8 $/MT. If the low-P CGF produced by the P recovery technologies is also sold at the same price, the MSP of the P-containing complexes should still be 355.6 $/MT for the maximum plant capacity for wet milling biorefinery (Fig. 5a), which is higher than the price (351.0 $/MT) of the commercially available P fertilizer with similar function (DAP). But if the price of low-P CGF can increases (e.g., 110.0 $/MT) when supported by economic incentives, the MSP of P-containing complexes can be reduced to less than 351.0 $/MT at some large economic scales. In other words, with policy incentives for low-P animal feeds, P recovery for the corn wet milling biorefineries have chances to gain economic benefits over the base cases if the P-containing complexes are still sold at the same price as other similar P fertilizers, which will stimulate the industrial stakeholders to apply P recovery technologies in their plants. At the same time, the P-containing complexes directly recovered by the P recovery technologies are also a kind of environmentally friendly new fertilizer. If it can also be promoted and sold at a more profitable price under policy support, the economic feasibility of the P recovery technologies will be more sufficient.

The economic analysis and results for the dry grind biorefineries were found to be similar as shown in Fig. 5b, that is, the economic benefits of P recovery will increase with the increase of economic scales, especially under the conditions of policy incentives. Despite policy incentives creating potential profit opportunities for P recovery, the market is also an important factor for our price analysis. Detailed analysis of price fluctuations affected by the market was provided in SI Section S3.2 (Fig. S4-S5).

3.5. Implications

Recovering P as fertilizer has been reported as a potential route for minimizing the pressure of P resource depletion (Liu et al., 2023). To estimate the potential of P recovery and demonstrate the practical implications of the P recovery technologies, we estimated P recovery potential on US national scale by interpolating the amount of P recovery product with plant capacities from US Energy Information Administration (EIA, 2018). Details about estimating P recovery potential for all US corn biorefineries with different plant capacities are provided in SI Section S4 (Fig. S6). The results show that if the P recovery technologies evaluated are widely disseminated, the P-containing complexes recovered from corn biorefineries in the United States can supply approximately 30.3 million acres of corn farmland for fertilizer use. Note that the actual corn harvest area in the United States is 84.7 million acres in 2017 (USDA, 2017). Therefore, the recovered P from corn biorefineries can cover 35.8% of P fertilizer used in corn farmland, which can effectively mitigate the problem of food security threatened by phosphate rock depletion. Ruffato et al. evaluated the P recovery potential of corn biorefineries in the US. as an estimated 229 thousand tons of recovered P per year, while our estimation is about 284 thousand tons of P per year, which both studies have similar estimates (Ruffatto et al., 2022). The difference may come from the different numbers of corn biorefineries covered between the two studies. Therefore, P recovery in corn biorefineries is demonstrated as a very promising route through P cycling to offset nonrenewable P resources used for agriculture.

P recovery in corn biorefineries was also shown to become more economically favorable after accounting for policy incentives tied to green low-P coproducts as animal feeds (i.e., CGF and DDGS) and P fertilizer (i.e., P-containing complexes precipitated by P recovery). Further investigations on designing effective policy incentives to support the sustainable green development of P recovery technologies from corn biorefineries are expected. For example, reasonably increasing the prices of low-P coproducts as animal feeds and P-recovered products merit further investigations. Also, including nutrient trading as part of the economic benefits of P recovery benefits is worthy of considering to comprehensively quantify the indirect benefits of P recovery (Sneeringer, 2013). Besides, although P recovery was focused on our study, other nutrient recovery technologies can also be evaluated using similar approaches by considering broader system boundaries and different scales of production. Overall, we expect more comprehensive assessments for nutrient recovery technologies and offer guidance to the development of a circular economy based on their relative advantages.

4. Conclusions

In this study, we investigated the environmental and economic impacts of P recovery from the two most common corn biorefineries (wet milling and dry grind) by considering the impacts of different economic scales and downstream impacts of the P recovery on animal manure nutrient reduction. The results indicated that environmental burden shifting exists, where mineral resource scarcity (i.e., P resource depletion) and freshwater eutrophication are mitigated after P recovery while the impacts of life-cycle land use increase. By considering the economic scales, P recovery cases in corn biorefineries present steady overall environmental advantages with increasing economic scales in a nonlinear manner which is because the updates required for equipment to match with economic scale expansion weaken the scale effect in environmental impact. As for the economic analysis based on MSP, the economic benefits of P recovery cases over base cases become more apparent as economic scales increase, due to the possible decreasing marginal cost of P recovery and the potential faster growth rate from P recovery revenue. In summary, this study shows the co-benefits of mitigating eutrophication impacts and P resource depletion and the gain of economic revenue of P recovery for larger-scale corn biorefineries, indicating its great potential for promoting P circular economy.

CRediT authorship contribution statement

Jiaqian You: Methodology, Software, Formal analysis, Visualization, Writing – original draft. **Shaobin Li:** Conceptualization, Methodology, Validation, Writing – review & editing, Supervision, Funding acquisition. **Nengwang Chen:** Writing – review & editing, Resources. **Xiaolin Yang:** Writing – review & editing, Methodology. **Chinmay Kurambhatti:** Data curation, Writing – review & editing, Validation. **Ximing Cai:** Writing – review & editing, Funding acquisition. **Vijay Singh:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

We have shared our inventory data in the Supporting Information. Further data can be available upon request.

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Supplementary materials

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