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Research article

Unlocking the phosphorus circularity potential of corn belt watersheds with biorefinery phosphorus recovery incentives

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ABSTRACT

As global phosphorus (P) stores rapidly decline, P fed algal blooms continue to threaten critical freshwater resources across the globe. In the Midwestern United States (US), particularly the Corn Belt, biorefineries could play a key role in addressing this issue. By recovering P from the byproducts of ethanol production these facilities could reduce the P content of distillers grain feed, thereby reducing P excreted in manures. This process could potentially divert P away from concentrated animal feeding operations (CAFOs) and toward renewable P (rP) fertilizer production utilizing the recovered P. To foster the inclusion of P recovery incentives in state nutrient reduction strategies, this study elucidates the cascading benefits of rP recovery from corn biorefineries in watersheds across six Upper Midwestern states. Incentivizing P recovery in watersheds that contain both biorefineries and CAFOs could foster the production of 107,500 metric tons (MT) rP fertilizer while diverting 26,800 MT P from CAFO wastes each year, nearly double the estimated P reduction potential for municipal wastewater in the analysis region. These estimates can inform nutrient reduction analysts and policymakers in determining P load reduction potential. To further guide incentive strategies, four priority watersheds are highlighted to illustrate P reduction and circularity typologies across the region.

1. Introduction

Agricultural intensification in the second half of the 20th century has led to severe anthropogenic alteration of the global Phosphorus (P) cycle (Yuan et al., 2018). In the United States (US), demand for P fertilizers exceeds domestic production (Desmidt et al., 2015), leading to reliance on imported fertilizer which can impact the resiliency of the US agricultural system (Brownlie et al., 2023). Additionally, overapplication of both fertilizer and manure based P relative to crop needs has made agriculture a primary contributor to P loading of freshwater systems (Robertson and Saad, 2021; Sabo et al., 2021) and the Gulf of Mexico (Alexander et al., 2008) which can cause eutrophication (Dodds and Smith, 2016; Manuel, 2014; Schindler et al., 2016), particularly in the agriculturally intensive Upper Midwest which includes Illinois, Indiana, Iowa, Michigan, Minnesota, Missouri, Ohio, and Wisconsin (Alexander et al., 2008; Iiames et al., 2021).

The unsustainable use of P resources and associated negative water quality impacts has led the US (US EPA, 1998) and Upper Midwestern states (Baumann et al., 2013; IDALS et al., 2017; ISDA and IDEM, 2021; Michigan EGLE, 2021; Missouri DNR, 2014; MPCA, 2014) to develop nutrient loss reduction strategies (NLRS) and an interest in incentivizing a circular P economy (Margenot et al., 2019). Nutrient reduction strategies set P loss reduction goals for both point and non-point sources by leveraging existing regulations for point sources and via voluntary programs for agriculture in the non-point source sector. Current command-and-control regulations for point sources under the Clean Water Act (CWA), such as nutrient limitations for water resource recovery facilities (WRRFs) under the National Pollutant Discharge Elimination System (NPDES) permitting program (US EPA, 2022), have not been adequate in addressing nutrient pollution in all states (State-EPA Nutrient Innovations Task Force, 2009). In the Upper Midwest, this is likely due to agricultural sources contributing an estimated 80% of P loads, with 25% from animal wastes alone (Robertson and Saad, 2021).

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Concentrated animal feeding operations (CAFOs) are one of the few agricultural sources regulated as point sources under the CWA to reduce manure nutrient losses. CAFOs are defined as animal feeding operations (AFOs) that meet a livestock inventory threshold, discharge to waters of the US, or are classified as a CAFO by a state regulatory agency (Miralha et al., 2022). However, challenges to CAFO regulation revisions have allowed states to determine a CAFOs discharge status and NPDES applicability, leading to large variations in implementation (Rosov et al., 2020). This has led most Upper Midwestern states to develop their own permitting programs for CAFOs, which often adopt federal best management practices (BMPs) for manure management including storage and land application standards (i.e., 40 C.F.R. Part 412). While land application of wastes could assist in P recycling, the nitrogen (N) to P ratio of manure can be highly variable (Kumaragamage and Akinremi, 2018) and is still often lower than what is required by crops, leading to overapplication of P (Castellano, 2010; Long et al., 2018; Sadeghpour et al., 2017) and loss of excess P through runoff (Hanrahan et al., 2009; Miller et al., 2011). Even when applying manure based on P, specific conditions are necessary during application to minimize losses based on the timing, location, and application rate (Risse et al., 2006).

Several pre- and post-feeding strategies have been explored to reduce P loss from animal manure. Reduction of P in livestock feeds has been shown to decrease P in livestock excretion from beef and dairy cattle with little to no adverse effects on meat and milk production (Geisert et al., 2010; Wang et al., 2014). Reduction of excreted P can help balance the N to P ratio of manure and minimize losses from land application or other management techniques (Cerosaletti et al., 2004; Ghebremichael et al., 2008; Pomar et al., 2011). P recovery at animal feeding operations has also been proposed to separate manure N from P. Current P recovery strategies from agricultural sources rely primarily on recovery (e.g., struvite-based, calcium-based, or physical separation P recovery) directly from animal waste streams (Martín-Hernández et al., 2021). However, this type of recovery would require de-centralized installation of systems at individual AFOs/CAFOs and proves costly at all but the largest CAFO operations (Martín-Hernández et al., 2022).

Corn ethanol biorefineries are a major, and often overlooked, centralized processor of corn embedded P in the Midwest (Margenot et al., 2019; Ruffatto et al., 2023) uniquely positioned to enable agricultural P circularity in the region (Li et al., 2021, 2023; You et al., 2023). In addition to utilizing nearly 40% of the US corn grain crop (Ramsey et al., 2023), biorefineries also produce a fifth of US cattle feed as distillers grains (Decision Innovation Solutions, 2020). Distillers grains are the remaining grain residues after fermentation at biorefineries which are processed and used as animal feed and are highly concentrated in P. If incentives were directed to biorefineries to perform P recovery, there would likely be cascading benefits to P use efficiency and pollution within watersheds. Previous work has shown that 65% of embedded P in distillers grains can be recovered at dry grind corn ethanol biorefineries as a renewable P (rP) fertilizer by precipitating P as calcium phosphate and phytate from thin stillage (Aguiar et al., 2020; Juneja et al., 2020) while reducing P in distillers grain feed (Ruffatto et al., 2023). Prior feeding trials have shown a linear relationship between distillers grain blend ration and excretion of P in cattle, indicating P recovery could also reduce manure associated P loss from beef and dairy cattle feeding operations.

Though previous work has focused on general (Li et al., 2021, 2023; You et al., 2023) and county-level (Ruffatto et al., 2022, 2023) biorefinery P recovery benefits, there has not been a comprehensive study on recovery co-benefits in watersheds throughout the Upper Midwest and how they fit into nutrient reduction strategies. This study focuses on the biorefinery, livestock, and crop connection on a watershed-level in Midwestern watersheds. The co-benefits of biorefinery P recovery were assessed in the context of corn and soybean fertilizer requirements, the predominant crops of the Upper Midwest, and distillers grain utilization potential at CAFOs, due to their greater risk to water quality (Burkholder et al., 2007). The objectives of this study were to 1) quantify localized biorefinery P recovery and reduction benefits at a watershed-level, 2) comparatively evaluate P reduction potential between CAFO and WRRF wastes in the context of existing reduction strategies, and 3) categorize state-level priority watersheds based on the degree to which corn biorefinery P recovery benefits could be realized locally and explore how co-benefits compare to NLRS goals and progress. Only beef and dairy cattle CAFOs were considered in this watershed analysis (Fig. S1) due to the share of distillers grain fed to these operations (78% in 2023 (RFA, 2023a)), and previously reported relationship between distillers grain consumption and P excretion rates for ruminants (Luebbe et al., 2012; Morris et al., 2018; Spiehs and Varel, 2009).

2. Methods

2.1. Data sources and study-specific terminology

Data sources for input parameters (Fig. 1) related to corn biorefineries, CAFOs, croplands, and WRRFs were limited to governmental and organizational public databases (Tables 1 and 2). The "Upper Midwest" region in this analysis was limited to the 303 8-digit Hydrologic Unit Code (HUC-8) watersheds intersecting Indiana, Iowa, Michigan, Minnesota, Missouri, and Wisconsin due to limited CAFO data for Illinois and Ohio. The term "CAFO" in this analysis was comprehensive of all reported CAFOs based on state-level definitions (SI Section S1), but these CAFOs may not necessarily reflect the federal definition nor have a NPDES permit. Additional detailed information related to each state CAFO dataset, including data descriptions and reporting criteria, can be found in the Supplementary Information (SI Section S2, Table S1). The geographical outlines in this study were generated using ArcGIS (Esri, Redlands, CA) with shapefiles for states from the US Census Bureau (US Census Bureau, 2018) and watersheds from the US Geological Survey watershed boundary dataset (USGS, 2023).

2.2. Corn biorefinery Co-product production

Corn biorefineries utilizing P recovery can generate both a reduced P distillers grain feed and an rP fertilizer as co-products. The amount of distillers grain produced was estimated for 88 biorefineries by converting the ethanol production capacity (i.e., million gallons of ethanol per year) from the Renewable Fuels Association (RFA, 2023b) using 2022 average conversion factors of 2.94 gallons ethanol per bushel of corn (i.e., 0.438 L ethanol per kg corn) and 15.97 pounds of dried distillers grains with solubles (DDGS) per bushel (i.e., 0.285 kg DDGS per kg corn) (Irwin, 2023). The DDGS rate was used as a proxy for total distillers grain production and converted to a dry mass basis assuming 10% moisture (Juneja et al., 2020). The rP production and P reduction potential from distillers grains for each biorefinery was estimated based on a 65% reduction of P in distillers grain from 9.26 to 3.25 mg (mg) P per kg and recovery as rP based on prior process modeling (Juneja et al., 2020).

2.3. Renewable phosphorus ratio and usage

To better understand localized usage of rP generated from corn biorefineries, estimates were generated for P fertilizer application on corn and soybeans in each analyzed watershed. The land area (i.e., hectares) used for corn and soybean production in each watershed was determined by using ArcGIS and cropland rasters from the 2022 USDA Cropland Data Layer (CDL) (US Department of Agriculture Foreign Agricultural Service, 2022). Estimates of state-level crop land area from the CDL were also validated based on historic land area data from the USDA (Table S2). While all other input parameters were limited to the regional boundary of the states analyzed, cropland area was not limited since rP substitution was not directly analyzed for P reductions as part of state nutrient reduction strategies. The P application estimates were generated using percent of cropland treated and phosphate application

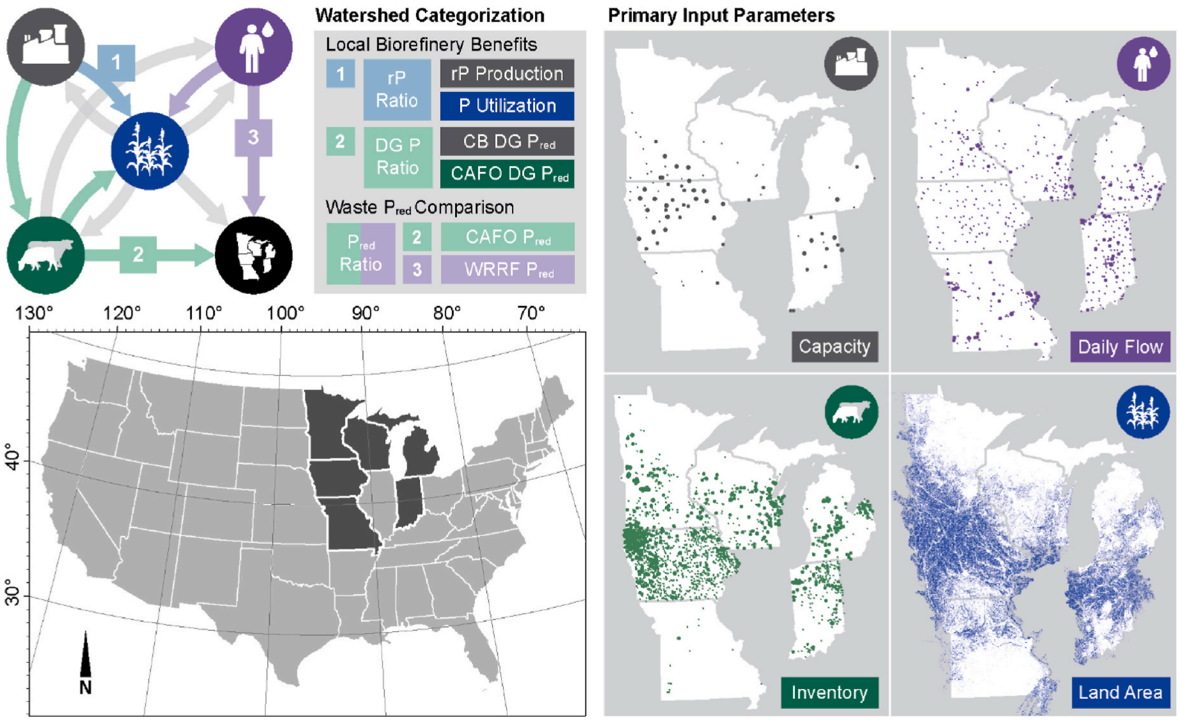

Fig. 1. Schematic of watershed corn biorefinery analysis. Circular phosphorus schematic with highlighted streams for analysis including renewable phosphorus (rP) fertilizer, reduced P distillers grains (DG) from corn biorefineries (CB), and waste streams where P can be reduced. Georeferenced map for US and study area based on an Albers equal-area conic projection. Geospatial data for biorefineries, WRRFs, CAFOs, and crop land area are included with their primary input parameters for the analyses. Illinois was not included due to the lack of public CAFO inventory data.

Table 1
Data sources used for input parameters.

Source	Year	Data Description	Spatial Scale
Biorefinery Distillers Grains and rP Generation			
Renewable Fuels Association Ethanol Plant Locations	2022	Facility ethanol production capacity	Point
Crop P Utilization			
USDA Cropland Data Layers	2022	Corn and soybean land area	Raster (30 × 30 m)
CAFO Distillers Grains Utilization and P Reduction			
State Agencies	Varies	Animal inventories	Point
WRRF P Reduction			
EPA ECHO Database	2022	Facility average daily flow	Point

rate by crop and state from 2010 to 2021 USDA surveys (USDA NASS, 2023) (Table S3) and multiplying by crop land area. Phosphate (i.e., P_2O_5) application rates were converted to P by dividing by a factor of 2.29 based on the molecular weights. An rP ratio for each watershed (i.e., watershed rP generation to crop P utilization) was calculated based on varying the percentage of synthetic fertilizer substituted with rP (i.e. 100, 50, and 25% rP).

2.4. *Concentrated animal feeding operation distillers grains and phosphorus*

To better understand how biorefinery P recovery can create downstream benefits for CAFOs, estimates were generated for P reduction potential at each CAFO. CAFO geospatial data (e.g., livestock types and inventories) were available for 2960 CAFOs across Indiana, Iowa, Michigan, Minnesota, Missouri, and Wisconsin as shown in Table 2 (IDEM, 2020; Iowa DNR, 2023; Michigan EGLE, 2023; Missouri DNR, 2023; MPCA, 2023; Wisconsin DNR, 2023). Only beef and dairy cattle CAFOs were considered (Fig. S1) because of their primary share of the distillers grain market, 78% in 2023 (RFA, 2023a), and their positive relationship between distillers grain consumption and P excretion rates (Luebbe et al., 2012; Morris et al., 2018; Spiehs and Varel, 2009). Inventories of beef and dairy cattle subcategories (i.e., beef cows, beef cattle on feed, other beef cattle, dairy cows, and dairy heifers) were provided or estimated for each CAFO based on state databases. To determine potential distillers grain usage of each CAFO on a dry basis (i.e., 0% moisture), cattle inventory values were multiplied by average dry matter intakes (Table S4) and potential distillers grain inclusion rates (Table S5) based on cattle category. The reduction of P in livestock waste was generated using P excretion equations from the American Society of

Table 2
Geospatial data availability for animal and cattle facilities by state.

State	Source	Last Reported Update	Total Animal Facilities	Cattle Facilities	Cattle Inventory
Indiana	Indiana Department of Environmental Management, Office of Land Quality	April 2020	1782	287	283,612
Iowa	Iowa Department of Natural Resources	February 2023	10,581	2032	2,006,981
Michigan	Michigan Department of Environment, Great Lakes, and Energy	May 2023	290	149	405,833
Minnesota	Minnesota Pollution Control Agency	June 2023	1617	215	600,427
Missouri	Missouri Department of Natural Resources	April 2021	1224	31	27,558
Wisconsin	Wisconsin Department of Natural Resources	June 2023	335	246	530,588

Agricultural Engineers (ASAE) (ASAE, 2005). The ASAE excretion equations estimate that P excretion is directly proportional to dry matter intake and the P content of the feed. Assuming that the dry matter intake does not change when feeding a reduced P distillers grain, the change in P excretion is directly proportional to the change in P content of the feed. The reduction of P in livestock waste was then assumed to be equivalent to the reduction in distillers grain feed from recovery (SI Section S2). The P reduction from CAFOs is considered the P reduction from the waste itself, not including any storage or treatment, and is not necessarily the total P reduction that will occur in loadings to receiving waterbodies. A distillers grain P ratio was generated for each watershed between total biorefinery and CAFO P reduction potential from distillers grain to assess localized reduction benefits. In addition, a prior optimization model for distillers grain distribution was used to estimate the distance between a potential corn biorefinery supplier of distillers grains and CAFOs on a regional and watershed level (Ruffatto et al., 2023).

2.5. *Water resource recovery facility phosphorus*

To compare P reduction potential from CAFO waste to WRRFs, facility-level P reductions were estimated for 632 major WRRFs. Only major WRRFs, or where average daily flow was greater than one million gallons per day (MGD) (3784 m^3/d), were considered due to these facilities representing a 97% share of total WRRF associated P (Ruffatto et al., 2022) and greater likelihood to adopt nutrient standards in a NPDES permit (US EPA, 2016). The most recent 2022 average daily flow rates for WRRFs were used from the US Environmental Protection Agency (EPA) Enforcement and Compliance History Online (ECHO) database (US EPA, 2023). Because P concentrations were not available for facility-specific influent wastewater streams, a typical low-strength total P concentration of 3.7 mg of P per liter (Metcalf and EddyInc., 2015) was used since it was closest to reported (Ruffatto et al., 2022) and estimated (Skinner and Wise, 2019) concentrations. The P reduction estimate was developed based on a typical effluent limitation of 1.0 mg P per liter in Upper Midwestern states as reported by the EPA ECHO database (US EPA, 2023), leading to a total reduction of 2.7 mg P per liter of wastewater.

The P reduction potential from CAFO and WRRF waste streams was compared on a facility and watershed-level. The P reduction potential is only based on that which is reduced from the waste itself (i.e., animal manure and wastewater) and is not necessarily the same as reduction in loading to receiving waterbodies. A P reduction ratio between CAFO and WRRF estimates was generated for each watershed to analyze which source could most contribute to reductions, and where the potential for nutrient credit trading could exist. To analyze the overlap of P reduction potential between CAFOs and WRRFs on a watershed-level, a cumulative histogram of P reduction potential in waste was generated across the log transformed watershed P reduction ratios for each source type. A generalized logistic function (i.e., Richard's curve) was fitted to each cumulative distribution for CAFO and WRRF P reduction based on Equation (1) where Y is the fraction of total P reduction potential from each source, r_x is the log transformed watershed P reduction ratio, X is the portion of total P reduction where no WRRFs exists when fitting the logistic function, B is the growth rate which demonstrates the uniformity of reduction ratios for WRRFs and CAFOs, μ is the shape parameter which affects near which asymptote maximum growth occurs, and M is the positioning parameter which positions the curve on the x-axis relative to μ (Echevarria et al., 2021). The logistic functions were then plotted for both CAFOs and WRRFs.

$$\mathrm{Y}(\mathrm{r_x}) = \frac{1-\mathrm{X}}{\left(1+\mathrm{e}^{-\mathrm{B}(\mathrm{r_x}-\mathrm{M})}\right)^{1/\mu}} \tag{1}$$

A curve centered around a log ratio of zero indicates that P reduction potential between the two sources was geospatially similar and the facilities are relatively co-located within watersheds. However, a stretched curve indicates that the sources are less co-located and tend to not concentrate potential P reductions from waste in similar watersheds.

2.6. *Priority watershed analysis*

To assess the role of biorefineries in state nutrient reduction strategies, priority watersheds were also considered. Priority watersheds are identified by states as hotspots of nutrient pollution loadings, with some states prioritizing for N and P separately (i.e., Minnesota and Wisconsin) and others for overall nutrients (i.e., Indiana, Iowa, Michigan, and Missouri). Though the watersheds which are classified as priority are occasionally updated based on re-prioritization efforts, the watersheds considered in this study are identified in the original state strategies. While most states identify priority watersheds at a HUC-8 level, Wisconsin prioritizes watersheds based on a smaller HUC-10 level. To maintain consistency with other states, this study grouped the HUC-10 watersheds based on their HUC-8 identification but maintains the limited geospatial extent of the original HUC-10 watersheds for analysis. Though the previous analyses mapped watersheds regardless of state borders, this priority analysis limited watersheds to the area inside of the state where they are prioritized, since states lack authority to regulate facilities in other states. Updated calculations were performed for the rP ratio, distillers grain P ratio, and P reduction ratio in all priority watersheds based on state borders. Watersheds were then categorized (i.e., Categories 0 to 5) based on the estimated ratios and how effectively biorefinery benefits could be realized locally (Table S6). Watersheds where the distillers grain and rP ratios were less than one were considered more ideal. A ratio less than one means that all P reduction benefits that the biorefinery could provide would be realized within the watershed. If these ratios were greater than one, that would mean that there is excess distillers grain and rP, requiring transport outside of the watershed. Additionally, four priority watersheds from each category and state were analyzed in the context of their state nutrient strategies. A Minnesota watershed was also chosen where P reductions from CAFO wastes were less than WRRFs (i.e., Category 2) to assess how the addition of AFOs could impact the analysis, since it was the only state to report AFO data.

2.7. *Uncertainty and sensitivity analysis*

Numerous parameters used in this study were based on averages published in literature and have ranges of uncertainty (Tables S3 and S7). A sensitivity analysis was performed to see how each uncertain parameter affected the number of watersheds with P reduction ratios greater than one and rP and distillers grain P ratios less than one (i.e., Category 5 watershed). Latin hypercube sampling was used to generate 20,000 samples based on a triangular distribution with minimum, maximum, and mode for uncertainty for use in a Monte Carlo simulation. Spearman's rank coefficients were assigned to each uncertain parameter based on the sensitivity of the ratios. Further information on the uncertainty and sensitivity analysis is available in the Supplementary Information (SI Section S3).

3. Results and discussion

The subsequent sections leverage available geospatial data to outline biorefinery recovery co-benefits in most Upper Midwestern watersheds, including categorization based on the extent to which benefits can be realized locally and discussion of recovery in the context of current regulatory schemes and NLRSs. Overall, nearly a quarter of priority watersheds would benefit from incentivizing biorefinery P recovery.

3.1. *Biorefinery phosphorus recovery and reduction benefits within watersheds*

Of the watersheds analyzed in this study, incorporation of P recovery at Upper Midwestern dry grind biorefineries have the potential to generate an estimated 107,500 MT rP per year that could be recirculated locally to replace non-local fertilizers (Table 3). While it is possible to substitute synthetic fertilizer with 100% rP, this can potentially limit crop growth (Talboys et al., 2016) and decrease grain yields (Hertzberger et al., 2020) in soils with limited P availability. Since rP from biorefineries is primarily in the form of phytin, the majority (55%) of P is in organic form (i.e., phytate) that requires hydrolysis of phosphomonoester bonds via soil extracellular enzymes to release crop-available inorganic P (Margenot et al., 2019). To avoid early-season P limitation due to insufficient inorganic P and/or mineralization of phytate P (Krey et al., 2013), rP can be mixed with highly water-soluble P fertilizers (e.g., commonly used ammonium or super phosphates) (Margenot et al., 2019).

Reducing rP substitution rate led to an increase in the number of watersheds in which P recovery from biorefineries would exceed local crop demand. When considering a 50% substitution rate of rP for synthetic fertilizer, an estimated 61% of watersheds with biorefineries could utilize all rP fertilizer generated within the watershed (Fig. 2a). When considering bounding substitution rate extremes of 100% and 25%, an estimated 96% and 30% of watersheds with biorefineries can fully utilize rP locally, respectively (Fig. 2b). In addition to added resiliency of generating a local rP, its usage could also create dual P fertilizer use and loss reduction benefits, as slow-release fertilizers have been shown to potentially improve crop P use efficiency (Weeks Jr. and Hettiarachchi, 2019) as well as reduce soluble losses compared to highly water-soluble fertilizers (Hart et al., 2004). This can be particularly beneficial in Upper Midwestern watersheds where application of highly water soluble P fertilizers is a major contributor to off-farm P losses and riverine P export (Robertson and Saad, 2021).

The utilization of reduced P distillers grains in the Upper Midwestern watersheds analyzed in this study could reduce an estimated 26,800 MT P from CAFO wastes and 58,700 MT P from all cattle wastes annually (Table 3 and Fig. S2). The P reduction potential from CAFOs in Iowa alone was estimated to be nearly equivalent to all reductions from WRRFs in the region. The manure P reduction benefits of utilizing a low P distillers grain feed at beef and dairy CAFOs would not be constrained to the watershed where the feed was generated (Fig. 2c, Fig. S2) since more distillers grains are produced than can be utilized locally in most of watersheds analyzed in this study. However, the majority of CAFOs are within a 50 km radius of analyzed biorefineries, indicating excess distillers grains could be utilized by nearby farms to generate reductions, even if not in the same watershed (Fig. 2d). The relative P reduction potentials of CAFO wastes versus WRRF wastes demonstrated here provides a basis for source prioritization within individual watersheds in state NLRSs.

Table 3
Estimated state-wide P recovery potential from corn biorefineries (1000 MT P per year), estimated average P reduction (1000 MT P per year) potential in wastes from total 2017 USDA beef and dairy cattle inventories and from CAFOs fed a distillers grain substitute, and estimated reduction potential (1000 MT P per year) from major WRRFs.

State	P Recovery and Reduction Estimates (1000 MT P per year)			
	Biorefineries	*All Beef/Dairy*	*Beef/Dairy CAFOs*	*WRRFs*
Indiana	18.7	3.1	1.8	2.7
Iowa	53.4	17.2	14.4	2.4
Michigan	5.0	5.9	2.7	3.9
Minnesota	18.2	10.2	3.9	1.4
Missouri	4.2	6.4	0.2	3.7
Wisconsin	7.9	15.9	4.2	1.8
Total	**107.5**	**58.7**	**26.8**	**15.9**

3.2. *Incentivizing corn biorefinery P recovery*

The estimated P reduction potential from waste associated with feeding reduced P distillers grains to CAFO beef and dairy cattle was nearly double that for WRRFs in the watersheds analyzed (Table 3). However, realizing this potential will require incentives due to the higher cost to implement P recovery than profit from selling an rP co-product (Juneja et al., 2020). While preliminary process modeling and technoeconomic analyses indicate the cost of rP production at biorefineries ($1.2–2.3 per kg-P) (Juneja et al., 2019, 2020) would be much lower than chemically recovering P from livestock operations in the region ($11–22 kg-P) (Martín-Hernández et al., 2021; Sampat et al., 2018), no state or federal policies currently exist to directly incentivize renewable fertilizer production.

Nutrient trading is an existing mechanism to incentivize agricultural sources to reduce excess P in lieu of local WRRFs in Minnesota and Wisconsin. However, trading is typically established at the watershed scale, requiring co-location of the sources within the same watershed. One possible pathway to incentivize P recovery from corn biorefineries in the current regulatory environment would be for WRRFs to purchase P reduction credits from CAFOs feeding low P distillers grains to beef and dairy cattle supplied from biorefineries. To understand the potential for nutrient trading to incentivize rP recovery at biorefineries, the colocation of WRRFs and CAFOs was quantified for the analysis region. Unfortunately, the lack of WRRF and CAFO co-location within most watersheds creates a poor physical environment for trading to occur within a watershed-based trading system (Fig. 3a) (Hoag et al., 2017). Individual Upper Midwestern watershed data is available in the Supplementary Information (Table S8).

Due to dislocation between human populations and cattle feeding operations, regulations of P discharge from WRRFs would be insufficient to incentivize widespread production of low P distillers grains at corn biorefineries in Upper Midwestern watersheds. Nearly 80% of estimated WRRF P reduction potential was in watersheds where WRRFs could reduce more P in waste streams than CAFOs (purple shaded watersheds in Fig. 3a and b). Of the 183 watersheds with both cattle CAFOs and WRRFs analyzed in this study, 74% could potentially achieve higher P reductions by feeding low P distillers grains at CAFOs than could be achieved through reductions at WRRFs (green shaded watersheds in Fig. 3a and b). Trading would also be challenging given the uncertainty of P losses associated with manure application, and the difference in scale between WRRFs and cattle farms. While aggregated P reductions are higher from CAFO wastes on a watershed-level, the lower reduction potential from individual feeding operations would require multiple CAFOs to participate in trading schemes to meet required WRRF reductions, adding complexity to trade monitoring but also to command-and-control approaches (Fig. 3c).

3.3. *Incorporating P recovery at biorefineries into priority watershed nutrient reduction strategies*

Due to the limitations of current incentive and regulatory schemes, the implementation of a direct incentive for biorefinery P recovery could generate cascading benefits for P reduction and recirculation within priority watersheds. In contrast to nutrient credit trading, incentivizing biorefinery P recovery through either direct or tax-based subsidies would unlock the ability to partially or fully meet local demands for both distillers grains and crop P fertilizer, as well as contributing to P reduction from animal operations. Priority watersheds were specifically considered for corn biorefinery participation in P reduction and recirculation due to their importance in state NLRSs. Individual priority watershed data (Table S9) and categorization for all Upper Midwest watersheds (Fig. S3) is provided in the Supplemental Information.

To understand typologies of watershed P reduction and recirculation potential in the upper Midwest, priority watersheds were categorized (Fig. 4a and S3) based on colocation of biorefineries with CAFOs

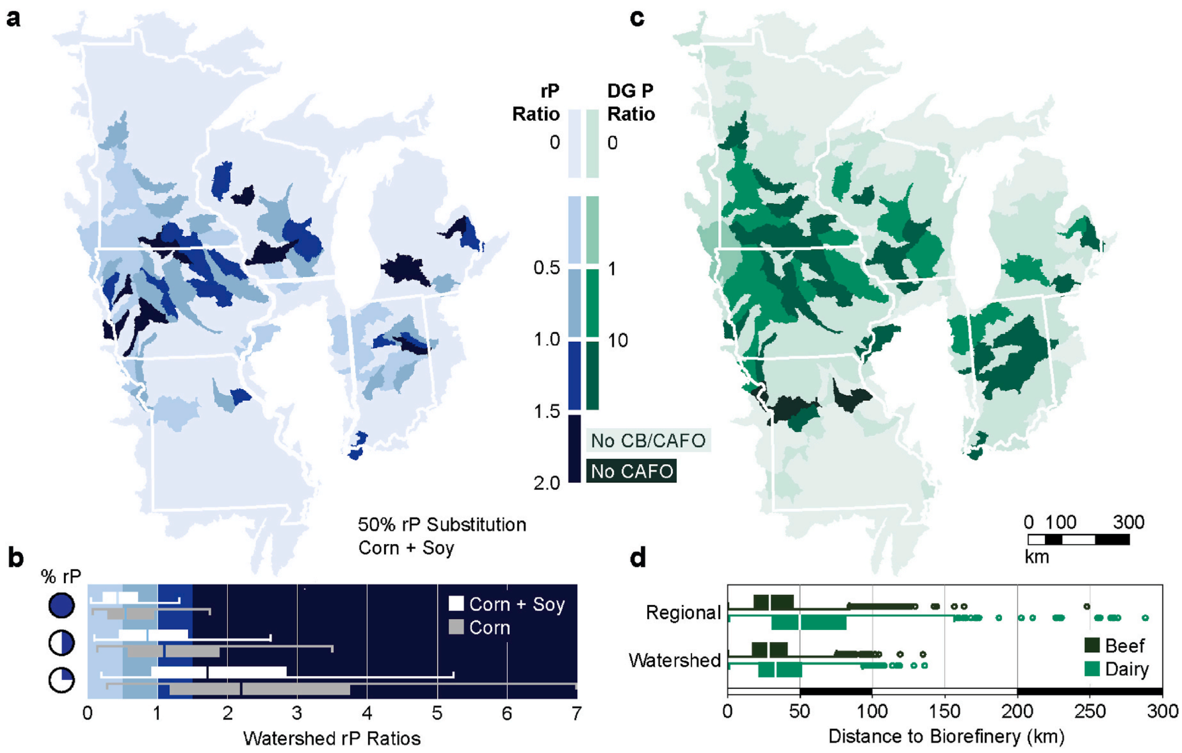

Fig. 2. Corn biorefinery co-product potential. (a) The rP ratio based on a 50% rP substitution of corn and soybean fertilizer, and the (b) range of watershed rP ratios based on varying rP substitution rates (i.e., 100, 50, and 25%) of fertilizer for both corn and corn + soybean. (c) The ratio of P reduction potential in all distillers grains (DG) produced from local corn biorefineries (CB) in each watershed relative to P reduction potential in waste for CAFOs fed distillers grains, and the (d) optimized travel distance of distillers grains from biorefineries to beef and dairy CAFOs on a regional and watershed level. A majority of watersheds with biorefineries can utilize all rP locally, and a majority will generate external P reductions from distillers grains than what can be directly realized in the local watershed.

(Categories 0–1), colocation and reduction potential of CAFOs and WRRFs (Categories 2–5), and local reuse of recovered rP fertilizers (Categories 3–5). Of the 103 NLRS priority watersheds in the Upper Midwest, 78 have either no biorefinery (Category 0) or no CAFO (Category 1). Twenty-five priority watersheds have at least one corn biorefinery and a registered cattle CAFO (categories 2–5, Fig. 4a). Despite representing less than a quarter of all priority watersheds, the estimated P reduction potential in these 25 priority watersheds (5400 MT P per year) accounts for 62% of total reduction potential associated with rP recovery from biorefineries in all priority watersheds. Twenty priority watersheds were estimated to have more P reduction potential from feeding low P distillers grains to CAFOs than possible from WRRFs in the same watershed (Categories 3–5). Nine watersheds fell into category 3, in which P recovery from local biorefineries would exceed local demand for both rP fertilizer and low P distillers grain. Nine watersheds could utilize all rP locally but would generate low P distillers grains production in excess of local cattle CAFO demand (Category 4). Nine watersheds had excess distillers grains production from biorefineries but were capable of utilizing all rP locally (i.e., Category 4). Only two watersheds could realize all the potential benefits of recovery and costs of an incentive program locally (i.e., Category 5). Most category 2–5 watersheds were in Iowa and Minnesota and represent prime candidates for corn biorefinery participation in localized circular P economies. Though Missouri appeared to have no potential watersheds, this was due to the minimal number of registered CAFOs in the state, despite having a large cattle inventory reported in the 2017 USDA Census of Agriculture (USDA-NASS, 2017) due to grazing cattle (Table 3). Four priority watersheds in different categories and states were chosen for further analysis (Fig. S4) in the context of their state nutrient strategies.

3.3.1. *Iowa: The Floyd River Watershed (FRW)*

Iowa is the largest contributor of P loadings to the Mississippi/Atchafalaya River Basin in the Upper Midwest, contributing over 15% of the total load (Robertson and Saad, 2021). The FRW is the largest contributor of P loading from manure in Iowa (Robertson and Saad, 2021). Based on the watershed specific benefits of rP recovery and P diversion from CAFO waste, this analysis identified the FRW as an ideal candidate for incentivizing P recovery (Category 5 rating). The single biorefinery in the FRW may be capable of reducing approximately 900 MT per year of P from distillers grain fed to local cattle CAFOs (Fig. 4b). The high local demand for P fertilizer in the FRW would enable local reapplication of all biorefinery recovered rP within recommended blending ranges, potentially reducing the amount of mined P fertilizer applied in the FRW by approximately 60% (Fig. 4b). The high density of biorefineries in Iowa means that excess distillers grains can be brought into the FRW from other local biorefineries to realize the full P reduction potential of CAFO wastes in the watershed (1500 MT per year).

3.3.2. *Indiana: The Upper Wabash River Watershed (UWRW)*

The UWRW is the largest contributor of P loadings from manure among priority watersheds in Indiana (Robertson and Saad, 2021). The UWRW was classified as a Category 4 watershed for biorefinery P recovery with an estimated CAFO to WRRF P reduction potential ratio greater than one and a rP fertilizer ratio less than one. P recovery at the single local biorefinery would be capable of generating nearly 1800 MT P reductions per year in livestock waste either locally or non-locally, with rP generation being fully utilized meeting nearly 90% of crop fertilizer needs at a 50% rP substation rate (Fig. 4b). The P reduction potential of this biorefinery is much greater than would be realized by feeding local CAFOs low P distillers grains. To reduce agricultural P loadings, Indiana's NLRS incorporates voluntary programs that have generated an estimated 30 MT P per year in reductions in the UWRW

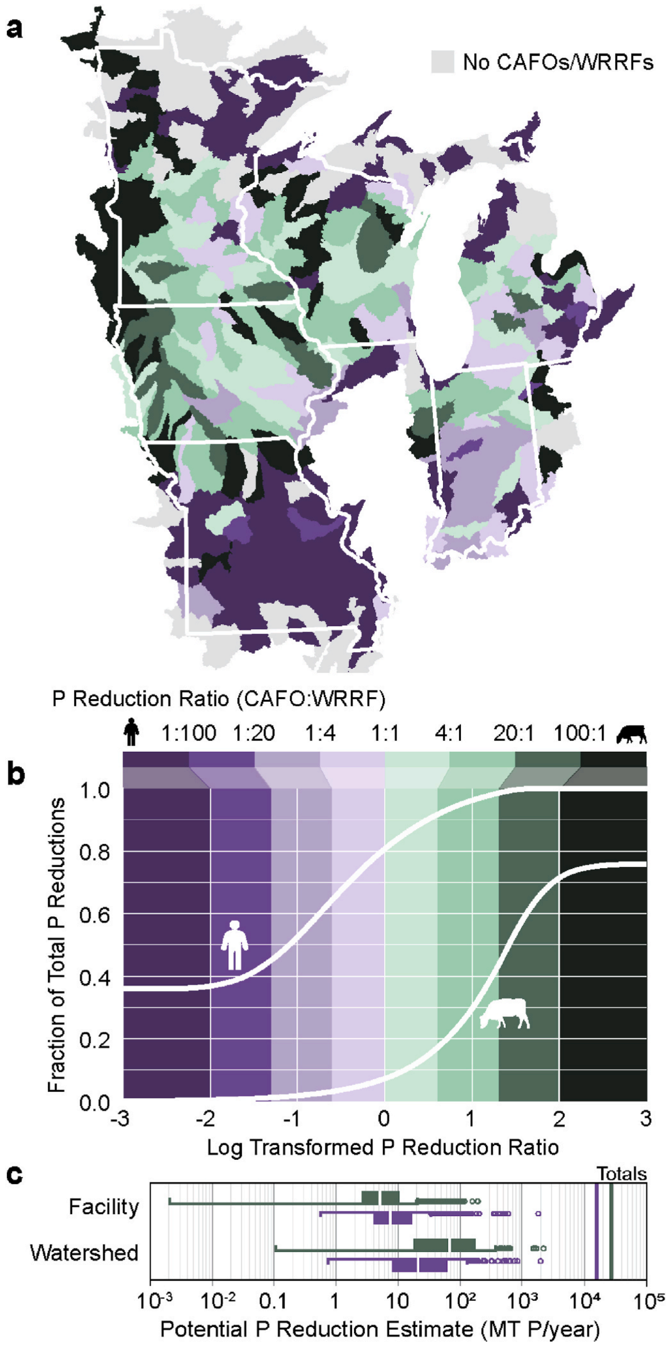

Fig. 3. Potential phosphorus reduction estimates in waste. (a) Phosphorus reduction ratio between estimated CAFO and WRRF P reductions in waste for watersheds. (b) Curves for cumulative fraction of P reductions from WRRF and CAFO waste based on watershed log P reduction ratio. (c) Ranges of waste P reduction potential on a CAFO and WRRF facility and watershed level including regional totals for each. CAFO operations have larger P reduction potential than WRRFs throughout much of Iowa, lower Minnesota, and Wisconsin while overall being relatively displaced geospatially from WRRFs.

since 2013 (ISDA; IDEM, 2021). For CAFO manure application, state strategies have primarily focused on timing of application rather than synchronizing manure N to P ratios to reflect crop N to P demands (i.e., increasing manure N to P).

3.3.3. Wisconsin: The Upper Rock River Watershed (URRW)

Wisconsin was the only state in this analysis that identifies priority watersheds based on a HUC-10 level. However, the HUC-8 Upper Rock River Watershed encompasses seven HUC-10 watersheds listed as priority for P pollution (Baumann et al., 2013). Animal manure is one of the largest contributors to P loading from the URRW (Robertson and Saad, 2021). Wisconsin's NLRS estimates that since 1995, state programs and efforts have reduced an estimated 330 MT P loadings per year from agricultural sources, including CAFOs, throughout the state (Baumann et al., 2013). The URRW was rated as a Category 3 watershed for biorefinery incorporation, where the single biorefinery can produce 1440 MT rP per year, with potential reductions from distillers grains at local CAFOs contributing to 280 MT P reductions in wastes per year. However, rP production exceeds watershed-scale crop demand at a 50% substitution rate (Fig. 4b) but could be fully utilized locally at a 100% rate.

3.3.4. Minnesota: Lower Minnesota River Watershed (LMRW)

The LMRW was the only watershed with a biorefinery in Minnesota given a Category 2 rating, meaning it had lower P reduction potential from CAFO wastes than WRRFs. This is primarily due to the two large urban WRRFs in the watershed and a limited number of CAFOs. Minnesota's NLRS estimated that the LMRW would need to reduce P loads by 40.6 MT P per year to meet state goals and identifies livestock feed management as a potential technique for agricultural P load reduction (MPCA, 2014). As a way of addressing excess P through feed management, the single biorefinery in the LMRW could reduce an estimated 1700 MT P per year from distillers grains. Utilization of low P distillers grain at local CAFOs could result in 67 MT P reduction per year in wastes, which is far less than the estimated 240 MT P per year from WRRFs, but more than 50% of the NLRS target for livestock in the watershed. Additionally, since Minnesota also registers all AFOs, further analysis including AFO locations found that P reductions in all livestock waste could be closer to 500 MT P per year in the LMRW, which is greater than both WRRFs and nearly an order of magnitude higher than the NLRS target. Consideration of AFOs would improve P reduction potential in numerous watersheds throughout Minnesota, and likely multiple other states (Table 3). This P reduction improvement was due to their high density (Fig. S5), which impacts water quality (Miralha et al., 2022). However, AFOs provide a small number of P reductions individually. The LMRW analysis illustrates how directly incentivizing P recovery from biorefineries centralizes P reductions and would not require extensive monitoring or recovery at individual animal operations, which can be both costly and resource intensive.

3.4. Sensitivity analysis and study limitations

This study provides an inventory of watersheds, including priority watersheds, where P recovery from corn ethanol biorefineries could reduce pollution and help foster a circular P economy. However, this inventory of watershed benefits comes with limitations that are important to consider. The use of open-source data from governmental and organizational databases and average conversion parameters created limitations when determining P reductions and recovery. Overall, the availability of more robust facility-level data for biorefineries, CAFOs, and WRRFs would help improve results and reveal potential local variations that are otherwise missed when using standard uncertainty ranges across facilities. A key limitation in this analysis is the inability to directly compare P emissions from WRRFs, CAFOs and fertilizers in all watersheds.

A sensitivity analysis on modeling inputs was conducted to explore uncertainty and model limitations for each analyzed P source and sink (i.e., biorefineries, CAFOs, crop production, and WRRFs). All sensitivity results can be found in the Supplemental Information (Tables S3 and S7). Corn biorefinery distillers grain and rP estimates were limited by the lack of facility-level data on corn to distillers grain conversion and distillers grain P content. To account for this, the P content of distillers grains and P recovery were considered in the sensitivity analysis, where the P content was shown to have a strong correlation with the rP ratio.

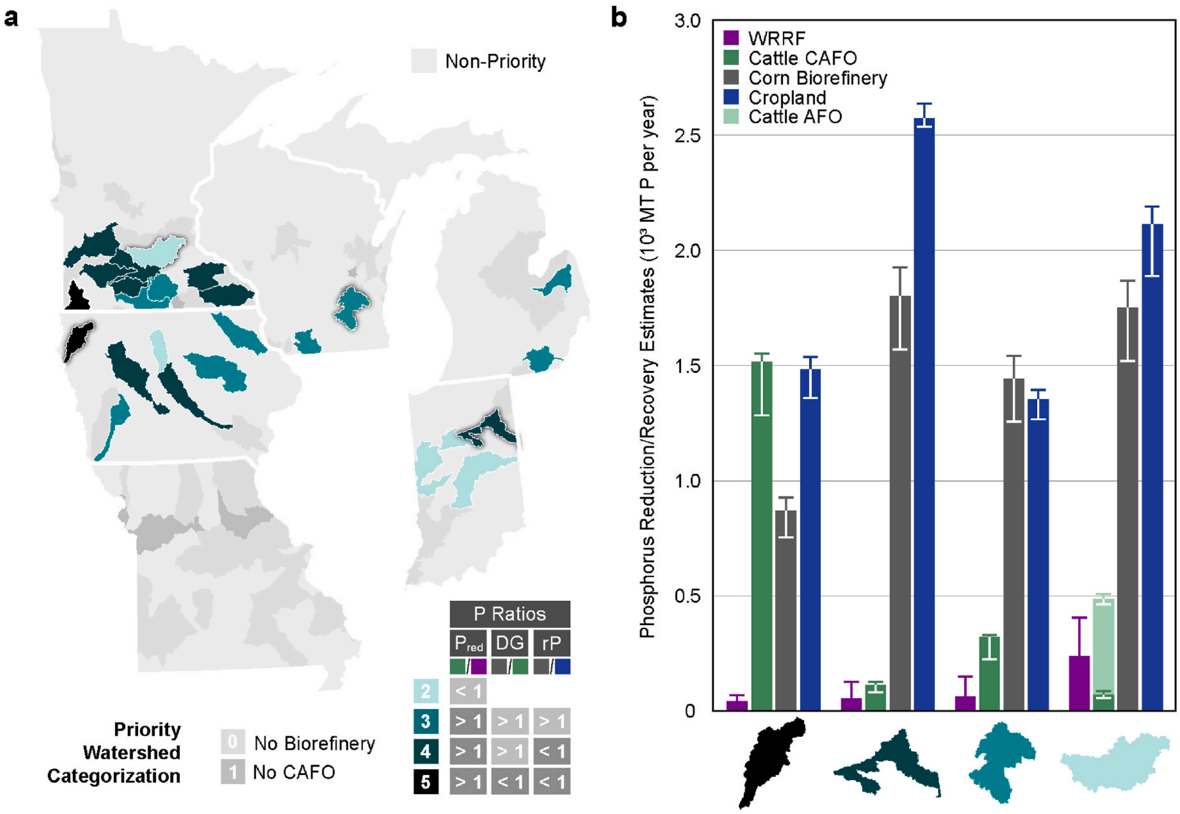

Fig. 4. Priority watershed categorization. (a) Categorization of priority watersheds based on P reduction, distillers grain P, and rP ratios. (b) Data for chosen watersheds in each category including (from left to right) the Floyd River Watershed (10230002) in Iowa, Upper Wabash River Watershed (05120101) in Indiana, Upper Rock River Watershed (07090001) in Wisconsin, and the Lower Minnesota River Watershed (07020012) in Minnesota. Data for each watershed includes estimated P reduction for WRRFs and CAFOs, P recovery/reduction for corn biorefineries, and P utilization for croplands. AFOs are also included for the Lower Minnesota River Watershed. Nearly all watersheds rated Category 2–5 offer some degree of localized benefits from incentivizing biorefinery P recovery.

For CAFO distillers grain usage and waste P reduction estimates, limitations included a complete and consistent inventory of CAFOs between states and actual P loading reductions from waste P reductions. The inventory limitation primarily led to uncertainty in CAFO distillers grain usage. P fertilizer utilization of corn and soybean was limited based on the availability of field specific P application rates. The sensitivity analysis showed that there was a weak correlation between P application rates and the rP ratio, indicating that the uncertainty in application rates had minimal influence. Calculation of WRRF P reduction was limited due to the lack of data on influent P concentrations as most databases, including the EPA ECHO database, only provide effluent concentrations when available. The sensitivity analysis did find that P reduction concentration for wastewater had a strong correlation with the P reduction ratio, where higher P concentrations of wastewater could lead to greater reduction potential from WRRFs and a lower P reduction ratio between CAFOs and WRRFs. The P reduction ratio could also be improved by determining reduction in actual P loadings to receiving waterbodies in the watershed based on the P reduction from wastes. However, while determining P load reductions from WRRFs is more straightforward, determining load reductions from CAFOs would require extensive modeling based on source specific factors and site geology that is beyond the scope of this study.

3.5. Outlook

The Upper Midwest states analyzed in this study account for nearly 45% of total P loadings to the Mississippi/Atchafalaya River Basin (Robertson and Saad, 2021). This study is the first to categorize Upper Midwest watersheds based on localized benefits of P recovery from biorefineries. A total of 66 watersheds in these states with crop and animal agriculture include at least one corn ethanol biorefinery. Incentivizing P recovery at these biorefineries has co-benefits for local agriculture and nutrient cycling by substituting non-local synthetic fertilizer with a renewable fertilizer, while also reducing the P content of locally fed distillers grains and the wastes of cattle that utilize them. Numerous priority watersheds were also identified in Iowa, Minnesota, Indiana, Wisconsin, and Michigan that could benefit from biorefinery P recovery, creating an inventory of priority watersheds that warrant further analysis by policymakers and nutrient reduction strategists for implementation of P recovery at biorefineries.

While this study generated an inventory of potential watersheds for biorefinery participation in P circularity, future work must focus on quantifying state-level incentives required for biorefineries to implement P recovery and working with farmers to foster rP reuse (e.g., agronomic management). Since many states already have incentive programs for voluntary nutrient management measures at agricultural operations, incentive estimates for P recovery can be compared to existing programs. To further improve these P estimates and better inform policymakers, future work should also investigate and incorporate more granular facility-level data (e.g., P content and production rates of distillers grain, watershed specific distillers grain consumption, and WRRF influent P concentrations) to account for local variations in biorefineries, CAFOs, and WRRFs. These data would be especially important as policymakers and local nutrient analysts decide on specific facilities to target for potential subsidies or future regulation. Additionally, as reductions in P concentration in animal waste is not the same as reduction in P loadings to surface waters, further watershed-specific modeling is necessary to fully capture the reduction potential for actual P loadings to further inform proper incentives.

While this work focused on the Corn Belt of the US due to the large number of biorefineries, it can also be applied to other regions of the US. There are numerous corn biorefineries in the Northern Plains states (i.e., North and South Dakotas, Nebraska, Kansas, and Missouri) as well as a select number in western and southern states (e.g., California, Texas, etc) that could benefit from P recovery and CAFO usage of low P distillers grains. Outside of the US, countries such as Brazil and the United Kingdom have also increased the number of corn biorefineries and thus may also capitalize on similar P reuse and reduction benefits. Soybean processing has also been shown to be a potential candidate for P recovery (Juneja et al., 2022; Singh and Singh, 2023), which could further expand the geographical reaches and benefits of P recovery during crop processing.

CRediT authorship contribution statement

Kenneth Ruffatto: Writing – review & editing, Writing – original draft, Visualization, Formal analysis, Conceptualization. **Arghajeet Saha:** Writing – review & editing, Resources, Methodology, Data curation. **Rebecca L. Muenich:** Writing – review & editing, Funding acquisition, Conceptualization. **Andrew J. Margenot:** Writing – review & editing. **Roland D. Cusick:** Writing – review & editing, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Roland Cusick reports financial support was provided by National Science Foundation. Rebecca L. Muenich reports financial support was provided by National Science Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2024.124010.

Data availability

Data will be made available on request.

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