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Journal of Environmental Quality SPECIAL SECTION
CELEBRATING THE 350TH ANNIVERSARY OF DISCOVERING PHOSPHORUS—FOR BETTER OR WORSE

Toward a Regional Phosphorus (Re)cycle in the US Midwest

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Abstract

Redirecting anthropogenic waste phosphorus (P) flows from receiving water bodies to high P demand agricultural fields requires a resource management approach that integrates biogeochemistry, agronomy, engineering, and economics. In the US Midwest, agricultural reuse of P recovered from spatially colocated waste streams stands to reduce point-source P discharges, meet agricultural P needs, and—depending on the speciation of recovered P—mitigate P losses from agriculture. However, the speciation of P recovered from waste streams via its chemical transformation—referred to here as recovered P (rP) differs markedly based on waste stream composition and recovery method, which can further interact with soil and crop characteristics of agricultural sinks. The solubility of rP presents key tensions between engineered P recovery and agronomic reuse because it defines both the ability to remove organic and inorganic P from aqueous streams and the crop availability of rP. The potential of rP generation and composition differs greatly among animal, municipal, and grain milling waste streams due to the aqueous speciation of P and presence of coprecipitants. Two example rP forms, phytin and struvite, engage in distinct biogeochemical processes on addition to soils that ultimately influence crop uptake and potential losses of rP. These processes also influence the fate of nitrogen (N) embodied in rP. The economics of rP generation and reuse will determine if and which rP are produced. Matching rP species to appropriate agricultural systems is critical to develop sustainable and financially viable regional exchanges of rP from wastewater treatment to agricultural end users.

Core Ideas

- There is high potential for recovering P (rP) from point sources for agricultural reuse.
- rP speciation depends on recovery source and method, interacts with soils and crops.
- Engineering, agronomic, and economic considerations of rP are context-specific.

The global P cycle has been substantially altered by human activity in the past century (Bennett et al., 2001). This anthropogenic P cycle is mediated by distinct kinetic and spatial manipulation of primary P, in which humans expedite the chemical and physical weathering of primary P into concentrated, water-soluble forms at a rate that outstrips natural weathering by nearly an order of magnitude (Liu et al., 2008; Rockström et al., 2009) and globally redistribute this P in the form of fertilizer at the rate of 20 Tg P annually (Van Kauwenbergh, 2010). Biogeochemically, this can be conceptualized as a targeted engorgement of the nonoccluded P pool (Walker and Syers, 1976) in which primary P from a handful of geological hotspots are transferred to soils in agricultural landscapes largely across western Europe, East Asia, and North America (Schipanski and Bennett, 2012), which have been accruing P since the advent of P fertilizers in the mid–20th century (MacDonald et al., 2011, 2012). Major fluxes in the anthropogenic P cycle are governed by the balance of P inputs and exports at the agricultural landscape or watershed scale. Fertilizer is the chief P input, and P is exported intentionally as harvested crop products and unintentionally largely as losses via erosion and runoff (Bennett et al., 2001; Chianu et al., 2011). Phosphorus losses from agricultural lands have led to significant impairment of surface waters due to eutrophication and subsequent hypoxia (Scavia et al., 2014; Stevenson et al., 2008).

In the United States, 45% of P exported from agricultural fields occurs in three aqueous waste streams with high potential for recovery: biofuel grains (10%), net processing losses (27%), and human diets (8%) (MacDonald et al., 2012). We define this recovered P (rP) as P recovered from waste streams via its chemical transformation. Generally, this entails transforming P into low-water-solubility solid phases (e.g., Ca, Fe, and Mg precipitates) to enable its separation from largely aqueous waste streams. This is in contrast to unprocessed waste stream P contained in organic matrices that are directly reused in agriculture (e.g., crop residues, manure, wastewater-derived biosolids).

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Abbreviations: CAFO, concentrated animal feeding operation; EBPR, enhanced biological phosphorus removal; FAO, Food and Agriculture Organization; ILNLRS, Illinois Nutrient Loss Reduction Strategy; MAP, monoammonium phosphate; NPDES, National Pollutant Discharge Elimination System; rP, recovered phosphorus; TMDL, total maximum daily load; WWTP, wastewater treatment plant.

Furthermore, separation of rP from hydrated organic matrices is essential to reducing the energy intensity of transport between urban sources and agricultural sinks (Trimmer and Guest, 2018). A key feature of rP is that the low water solubility that enables its generation entails trade-offs for its agricultural utility because low water solubility can limit P crop availability. Although not defined as such, rP has been variously proposed for potential reuse in agriculture as a means to increase P use efficiency, abate point source P mitigation costs, meet crop P demands, and/or increase resilience to fertilizer market dynamics (Cordell et al., 2011; Metson et al., 2016; Scavia et al., 2014; Sharpley et al., 2016; Simons et al., 2014). Barriers to the recovery and reuse of P in waste streams are technological, logistical, and economic, in particular, the costs of reuse that scale, often nonlinearly, with distance between rP sources and sinks (Sharpley et al., 2016; Trimmer et al., 2017; Trimmer and Guest, 2018).

The region of intensive grain production in the US Midwest known as the Corn Belt is uniquely positioned to harness large fluxes of colocated recoverable P in urban and industrial waste streams to meet the large collective P demand by maize (*Zea mays* L.) and other crops (Clampitt, 2015; Metson et al., 2016). In the Corn Belt, 74% of maize P needs could be met by rP generated at the county level, and Corn Belt states could potentially satisfy from up to 46% (Illinois) to 128% (Nebraska) of maize P needs using rP generated in-state (Metson et al., 2016). The full P demand of the Corn Belt could be met with relatively low-to-moderate spatial reallocation of rP (65–519 km; mean, 302 km), assuming similar transportability of rP forms. However, such assessments do not take into account the type of rP despite the diversity in speciation of P recoverable from diverse waste streams (Karunanithi et al., 2015), which entails variation in crop availability of recovered P species (Havlin et al., 2013).

Realizing the potential for regional P recycling necessitates consideration of interactions among rP sources, engineering of rP capture, and characteristics of recipient agricultural sinks (e.g., soils and crops), which we hypothesize will enable optimally matching rP sources and sinks to fulfill the proposition of "Feeding the Corn Belt" (Metson et al., 2016). In addition to achieving nutrient use efficiency and supporting point source mitigation, rP in certain contexts may be able to reduce P losses from the agricultural sinks that are themselves nonpoint sources of this eutrophying element. Thus, the generation and reuse of rP offers a potential triple win: reduce point source P discharges, meet crop P needs, and potentially reduce P losses from agricultural nonpoint sources. Redirecting anthropogenic waste P flows from receiving water bodies to high-P-demand agricultural lands will require an interdisciplinary resource management approach.

To illustrate the complexity and necessary contextualization of matching rP generation with its agricultural reuse, we focus on the state of Illinois. Illinois is the largest state contributor of P (13% of total P flux) to the Mississippi watershed (ILEPA, 2014), is an agriculturally dominated landscape (67% of total land area) (USDA Economic Research Service, 2017), and holds two major but distinct point sources of P: Chicago—the largest midwestern metropolitan region with one of the largest wastewater treatment plants (WWTPs) in the United States—and numerous grain milling operations (ILEPA, 2014). The recovery of the 3.9 Gg of point source P that constitutes nearly half of all P losses from Illinois (ILEPA, 2014) has high potential to be reused in geographically proximate agricultural lands with high P crop needs.

Phosphorus in the US Midwest

The definition of the US Midwest used here is the region that encompasses the Upper Mississippi River basin and to a lesser extent the Western Lake Erie basin, including Nebraska, Minnesota, Iowa, Illinois, Wisconsin, South Dakota, Indiana, and Ohio (Green et al., 2018). According to the latest agricultural census (2012), these states accounted for 70% of total maize production in the United States (USDA-NASS, 2014, 2018) and one-third of global maize production in 2017 (FAO, 2017). Soybean [*Glycine max* (L.) Merr.], commonly grown in rotation with maize in alternate years, accounted for over 20 million ha across the Corn Belt in 2018 (USDA-NASS, 2018). The 18 million ha of the Corn Belt (USDA-NASS, 2018) accounts for 56%, or 405 Gg P, of the maize P fertilizer demand in the United States (Metson et al., 2016). The Corn Belt is thus a global hotspot of P fertilization that has resulted in a net positive soil P balance (MacDonald et al., 2011; Potter et al., 2010). Corn Belt P losses serve as primary nutrient source for marine phototrophic growth, the decay of which has led to the development of the hypoxic zone in the Gulf of Mexico (Robertson and Saad, 2013; Robertson et al., 2014). Relative to typical agronomic input rates in the Corn Belt (30–60 kg ha^{-1}), relatively small losses of P (<1 to 7 kg ha^{-1}) can substantially compromise water quality (McDowell et al., 2015; Rowe et al., 2016).

In 2008, the USEPA developed the Gulf Hypoxia Action Plan, which seeks a 45% reduction in riverine total P (as well as N) loads (Mississippi River/Gulf of Mexico Hypoxia Task Force, 2008). In response to the Gulf Hypoxia Action Plan and a resulting directive by the USEPA Region 5 administrator, the contributing states were compelled to develop individual nutrient loss reduction strategies. These strategies vary by state and collectively include (i) a target baseline P load from the 1980s and/or 1990s; (ii) for point sources, total maximum daily loads (TMDLs) and/or total reductions; and, (iii) for nonpoint sources, P loss mitigation portfolios involving on-farm management strategies (e.g., cover cropping, reduced tillage) and off-farm approaches (e.g., riparian buffers) (MPCA, 2008; Wisconsin Department of Natural Resources, 2013; Ohio EPA, 2013; IADA, 2013). In some state strategies, the P loss mitigation targets are source-specific. For example, Iowa's strategy, debuted in 2013, seeks a 16% P load reduction for point sources and a 29% P load reduction for nonpoint sources to achieve the 45% P loss reduction target stipulated by the USEPA and shared with other states such as Minnesota, Wisconsin, and Illinois (MPCA, 2014; Wisconsin Department of Natural Resources, 2013). Progress toward achieving these target reductions varies substantially by state. For example, as of 2014 Minnesota had achieved a 33% reduction, whereas Wisconsin achieved an 11% reduction by 2015 (MPCA, 2014; Wisconsin Department of Natural Resources, 2013). Although various institutional and economic barriers to the capture and reuse of rP exist, as presented below, the potential benefits of establishing a circular P flow in the Midwest warrant consideration to incentivize P loss reduction.

Recovered Phosphorus

Estimating the Potential Magnitude of Recovered Phosphorus Sources in the United States

We constructed a mass balance to quantify the magnitude of P that is transmitted between food (crop and animal protein), bioenergy (maize ethanol and soybean oil), and water systems (point and nonpoint sources of pollution) in the United States (Fig. 1) using published data from the from the USDA, the United Nations Food and Agriculture Organization (FAO), and values reported from the literature. The starting inputs for the US P mass balance include natural vegetation and fertilizers used for crop and animal production. The major outputs from crop production systems include maize milling (ethanol and starch production) and soybean processing, animal feed products, human consumption, and exported grain. Major outputs from animal production systems included animal products for human consumption, manure, and unaccounted losses. These outputs were classified into five major categories: exports, reducible P losses, recovered P, recoverable P that is currently unrecovered, and remaining P losses. Flows directed toward exports included crops, soybean meal, soybean oil, and animal products. Flows directed toward reducible losses included runoff, erosion, and supply chain losses from crop and animal products. The recovered P category included food waste, human waste, crop residues, and reused manure flows. Potentially recoverable P flows included food waste, human waste, crop residues, and excess manure. The manure left on agricultural lands, unaccounted losses from animal production, crop production, fertilizer production, soybean processing, and human population centers were directed toward the remaining P losses category.

A detailed summary of data sources and estimation methods is provided in the Supplemental Material. In brief, census and survey data from the USDA Economic Research Service, USDA National Agriculture Statistics Services (NASS), and the FAO were used to estimate (nonorganic matter) fertilizer inputs for crop production, as well as feed inputs for animal production in 2012 (FAO, 2018; USDA Economic Research Service, 2017, 2018; USDA-NASS 2018). Phosphate rock-derived inputs were estimated using P waste stream generation rates for fertilizer manufacturing (Liu et al., 2008; Smil, 2000; Suh and Yee 2011; USDA Economic Research Service, 2017, 2018). Manure production rates (Mg yr^{-1} $animal^{-1}$) were used to define the mass of manure produced in 2012 (Barker and Zublena, 1995; Crouse et al., 2002; FAO, 2018; Kellogg et al., 2000; Pettygrove et al., 2010; Suh and Yee, 2011; USDA-NASS, 2018). The waste from human population centers was simplified to food waste and human waste. The P content in human waste was calculated using an estimated 2.1 g P $capita^{-1}$ d^{-1}. Phosphorus recovery from human waste was represented as biosolids land application with a land application rate of 60% of biosolids produced (Egle et al., 2016; Iranpour et al., 2004; Lu et al., 2012; Mihelcic and Zimmerman, 2014; Tchobanoglous et al., 2013). Food waste from human population centers was found by balancing the known inputs (crop and animal products) with the known outputs (human waste). Food waste recovery was estimated using composting rates in the United States in 2012, with the rest directed toward potential recovery (Suh and Yee, 2011; USEPA, 2012).

In 2012, phosphate-rock derived fertilizer represented the majority of P (1.71 Gg) applied to crop-producing fields. Approximately 0.54 Gg of P that is transmitted to receiving water bodies as erosive losses could be reduced. The P embodied in crops was exported (0.73 Gg), used for maize ethanol production (0.31 Gg), or directly consumed by livestock animals (0.79 Gg) and humans (0.25 Gg). Secondary sources of P contained in animal and human waste are transmitted to receiving waters, lost within supply chains, or reused. In 2012, roughly 41% of P fertilizer derived from phosphate rock could have been displaced by rP derived from municipal wastewater (5.7%), food waste (4.5%), and manure usage in excess of application standards (30.9%). This potential P recovery from excess animal manure does not include manure left on grazed lands, recovery of which would have doubled rP from animal manure.

As presented in the mass balance, maize and soybean processing facilities should be considered a critical leverage point for P

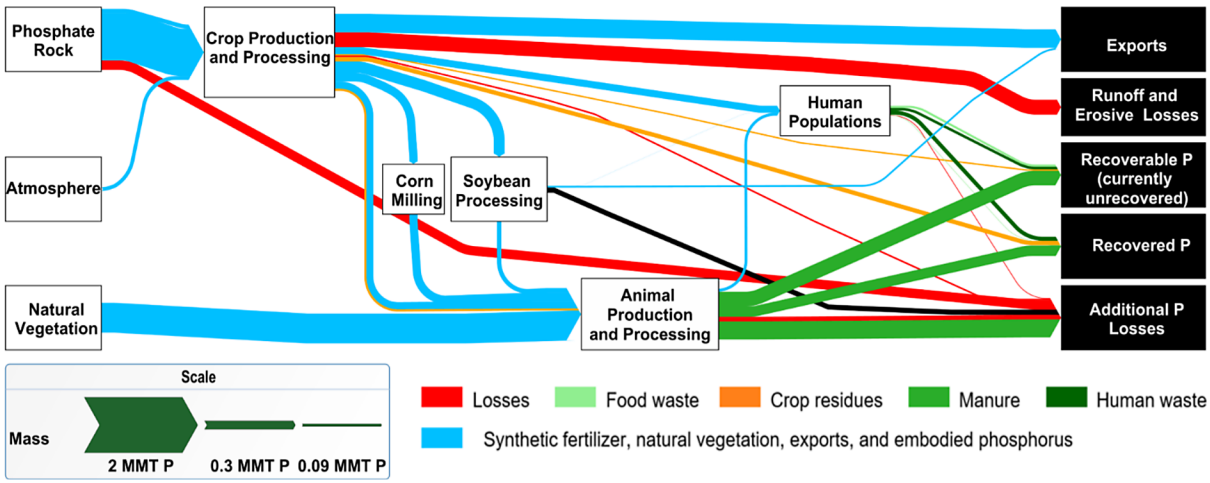

Fig. 1. Sankey diagram illustrating the US P mass balance for 2012. The P flow through the United States in 2012 was estimated using published data from the USDA and the United Nations Food and Agriculture Organization (FAO), as well as values reported from the literature. The waste from human population centers was simplified to food waste and human waste. The P content in human waste was calculated using an estimated 2.1 g P $capita^{-1}$ d^{-1} and a population of approximately 314 million people. MMT = million metric tons, equivalent to teragram (Tg). Further details, including sources used, are provided in the Supplemental Material.

recovery. While P losses directly associated with milling operations are process dependent and were excluded from our mass balance, the magnitude of P contained in maize milling by-products (i.e., maize gluten feed, maize gluten meal, dried distillers grains with solubles) and soybean milling byproducts (i.e., soybean meal) fed to animals is roughly equivalent to the mass of P contained in excess manure (0.54 vs. 0.53 Gg of P). The chemical composition and potential forms of rP from each secondary P source is described in detail in the following sections.

As noted above, midwestern states are responsible for a significant percentage of the maize production in the United States. Approximately 42% of total US maize is crushed and milled, resulting in the production of over approximately 33 Gg of maize milling by-products containing 0.31 Gg of P (Batal et al., 2010; Smith et al., 2017; USDA-NASS, 2014). In 2012, nearly 70% of maize milling byproducts were produced in the Midwest, amounting to 22.8 Gg of by-products containing 0.22 Gg P. In 2012, midwestern states produced nearly two-thirds of the US soybean crop at 48.3 million Mg, which embodied approximately 0.45 Gg of P (Batal et al., 2010; Karr-Lilienthal et al., 2006; USDA-NASS, 2017; Witte, 1995). Since midwestern states are also responsible for a significant portion of US livestock products (49% of cattle, 19% of beef cows, 65% of swine, and 2% of poultry), extracting P from grain milling operations could mitigate downstream P losses associated with manure.

Potential Sources of Recovered Phosphorus

Animal Manure

As expected, the largest potential source of rP in the United States is associated with animal manure. In 2012, approximately 1.6 Gg of P was excreted at animal feeding operations. Animal manure has agricultural benefits as an organic matter and nutrient source for soil enrichment, but it remains an underutilized resource as the transport of manure from where it is generated to cropland can be costly (Gollehon et al., 2001; Ribaudo, 2007). To comply with manure best management practices, a significant percentage of animal feeding operations (33% of hog and 49% dairy production) must transport manure offsite (Ribaudo, 2007). Concentrating manure P would significantly reduce transport costs since manure is mostly water (75–90% by mass) (He et al., 2001). Although concentrating animal feeding operations creates manure management issues, it also presents the opportunity to leverage economies of scale to efficiently recover energy and nutrients from manure. The low solids content of swine and dairy manure favors P recovery through chemical precipitation. Swine and dairy manure both contain high concentrations of cations (K^+, NH_4^+, Mg^{2+}, Ca^{2+}) that can bind PO_4^{3-} to form minerals of low water solubility. High solids content means that additional processing of poultry litter would be required to remove soluble nutrients (Menear and Smith, 1973; Zhang and Westerman, 1997) (Table 1).

Resource recovery from animal waste has primarily focused on using the organic fraction of manure as a renewable energy feedstock. Several governmental programs have been implemented to foster development of on-farm and centralized anaerobic digestion systems to biologically convert manure organic matter into methane-rich biogas, which can be combusted to generate electricity and heat or upgraded to pure methane and blended with compressed natural gas. Despite these efforts, growth of anaerobic digester has been slow: of the 8200 candidate swine and dairy farms in the United States, only 247 farms currently operate digesters (USEPA, USDA, and USDOE, 2014). The number of anaerobic digester installations is limited because the selling price of energy products (electricity and methane) is currently too low to justify widespread digester construction (Lazarus and Rudstrom, 2007). Processes that rely on the presence of inorganic N, such as struvite precipitation, benefit from anaerobic digestion, which effectively converts organic N to ammonium N (Wrigley et al., 1992). For most anaerobic digestion systems, continuous operation with medium- to long-term retention times (≈50 d) is common. At these time scales, increases in soluble P have been reported for stored manures (Kleinman et al., 2005), although this could be counteracted by a higher pH in anaerobic digesters leading to a greater degree of supersaturation and thus precipitation of magnesium and calcium phosphate. Table 1 summarizes reported chemical composition of stored and anaerobically digested animal manures.

Grain Processing Facilities

The national mass balance elucidates grain processing facilities as a central conduit of P between agricultural fields and animal feeding operations (Fig. 1). In 2012, 200 Gg of maize and 43.5 Gg of soybean were processed into food and energy products within the United States (USDA Economic Research Service, 2017). Approximately 40% of domestic maize production was

Table 1. Average composition of potential P recovery streams.†‡

Stream	PO_4^{3-}–P			$NH4^+$-N			Mg^{2+}			Ca^{2+}			K^+			Alkalinity		
	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.
	mg L^{-1}															mg $CaCO_3$ L^{-1}		
Main line§	2.4	NR	NR	14	NR	NR	8.5	4	13	13	8	18	NR	NR	NR	109.5	74	145
AD supernatant	101	18	220	797	220	1,166	59	5	194	71	8	184	80	57	128	1,769	99	3,295
Centrate effluent	168	44	369	749	500	951	51	7	237	68	42	108	56	22	116	2,641	2580	2,702
SSU	324	170	446	4309	1691	10,133	10	0.6	80	44	13	260	1375	770	2290	17,220	8050	26,273
AM	634	21	1376	1649	500	4,700	870	32	2368	2274	98	5408	1856	160	4500	1,475¶	NA	NA
ADAM	124	29	450	1432	272	4,612	92	5	257	227	79	570	1402	350	3111	8,507	4938	11,700

† Full dataset and sources are given in the Supplemental Material.

‡ AD, anaerobic digestate; ADAM, anaerobic digested animal manure; AM, animal manure; NA, not available; NR , not reported; SSU, sewage sludge untreated.

§ "Medium strength" untreated wastewater—Mg^{2+}, Ca^{2+}, K^+ concentrations do not include industrial and commercial contribution.

¶ Single data point.

channeled toward maize starch ethanol production, which accounts for three-quarters of the total US bioenergy market. Ethanol production uses only the starch in the grain; the remaining grain components (protein, fat, fiber) return to the agricultural sector as animal feed in the form of maize gluten meal and dried distillers grains with solubles. Reported P content of maize gluten meal and dried distillers grains with solubles ranges from 0.8 to 1% (dry matter basis), approximately three times the concentration of P in the maize grain (Liu and Han, 2011, Rausch et al., 2005). Reduction of P in maize gluten meal and dried distillers grains with solubles could be accomplished by reducing the soluble P concentration in preceding aqueous streams (thin stillage and light steep water, respectively). Since little water is used in soybean oil production (i.e., dry crushing), P recovery opportunities there are unlikely.

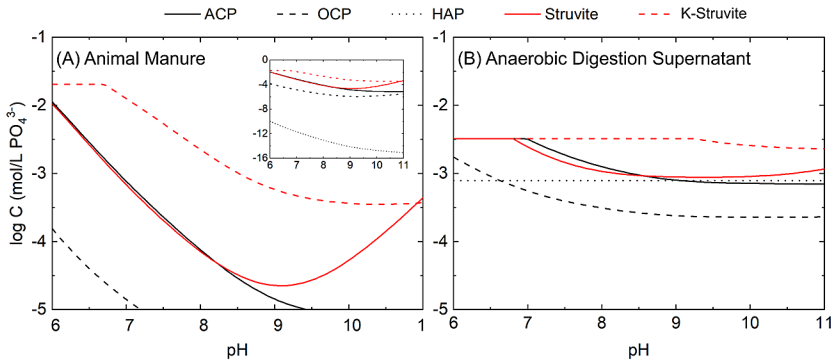

Fig. 2. Total soluble phosphate concentration diagrams based on the solubility of relevant calcium and magnesium solids that can be recovered through chemical precipitation based on mean reported phosphate coprecipitant concentrations in (A) animal manure and (B) the supernatant of anaerobic digesters fed municipal waste activated sludge. Phosphate species include amorphous CaP [ACP; $Ca_3(PO_4)_2$], octacalcium phosphate [OCP; $Ca_8H_2(PO_4)_6{\cdot}5H_2O$], and hydroxyapatite [HAP; $Ca_{10}(PO_4)_6(OH)_2$], struvite ($MgNH_4PO_4{\cdot}6H_2O$), and K-struvite ($KMgPO_4{\cdot}6H_2O$). See Supplemental Material for further details.

Phosphorus in maize processing aqueous streams is often characterized by its distribution between phytate (organic) and PO_4^{3-} (inorganic) forms (Chowdhury et al., 2014; Liu and Han, 2011, Noureddini et al., 2009; Rausch and Belyea, 2006; Rausch et al., 2005). Reported concentrations of P in the light steep of wet milling plants range from 3.3 to 5.2 mg P g^{-1} (dry mass basis) (Noureddini et al., 2009; Rausch et al., 2005), with approximately 20% of P as PO_4^{3-} and the rest as phytate. In the thin stillage streams of dry grind ethanol plants, P contents range from 19.4 to 23.8 mg P g^{-1} (dry mass basis), with a more equal distribution between organic and inorganic P (Alkan-Ozkaynak and Karthikeyan, 2012; Liu and Han, 2011)

Municipal Wastewater

In 2012, 0.24 Gg of P was available for recovery from US municipal WWTPs (Fig. 2). An estimated 0.14 Gg of P was recovered as treated wastewater residuals (biosolids), leaving an additional 0.1 Gg of P still available for recovery (Egle et al., 2016; Egle et al., 2015; Wang et al., 2010; Zhou et al., 2017). While the magnitude of P recovery from WWTPs is less than excess animal manure, large treatment plant capacities in urban centers, regulatory pressures of the USEPA National Pollutant Discharge Elimination System (NPDES), and regulatory guidance on land applied as biosolids in accordance with EPA regulatory requirements (EPA rule 40 CFR Part 503), have combined to create the economies of scale and incentive for P recovery and reuse(USEPA, 2012).

As NPDES permits force plants to reduce the further eutrophication potential of wastewater effluent, the magnitude of P reuse and opportunities for rP production will continue to increase. P removal can be enhanced biologically, by promoting the growth of polyphosphate accumulating organisms within an activated sludge process and by adding metal salts (most commonly iron) to directly precipitate or adsorb soluble P (Tchobanoglous et al., 2013). Both biological and chemical P removal increase the concentration of P in biosolids but have distinct impacts on the water solubility and plant availability of P contained within the organic matrix as well as opportunities for rP production.

Prior to land application as biosolids, waste activated sludge is often treated using anaerobic digestion to reduce sludge volume, recover energy as methane rich biogas, and reduce pathogenicity. Anaerobic digestion is often followed by dewatering in a centrifuge to further enrich the solids content prior to transport offsite (Burton et al., 2013). During digestion, anaerobic microbes ferment complex organic matter, which entails mineralization of N and P. The resulting elevation of soluble NH_4^+ and PO_4^{3-} concentrations and circumneutral pH buffering by inorganic C allows precipitation of PO_4^{3-} solids in the digester and aqueous side-streams. Elevated NH_4^+ and PO_4^{3-} concentrations make anaerobic digestion supernatant a viable stream for P recovery in the form of struvite or calcium phosphates (Cusick et al., 2014; Kazadi Mbamba et al., 2015, 2016; Musvoto et al., 2000). Recovery of P occurs using either anaerobic digestion or centrifuge effluent (Tarragó et al., 2016; Kazadi Mbamba et al., 2016; Jia et al., 2017). Influent wastewater contains concentrations of ions such as Ca^{2+}, Na^+, K^+, and Cl^- that can potentially play a role in the precipitation recovery processes (Burton et al., 2013) (Supplemental Table S2).

Phosphorus Mineralogy of Waste Streams: Chemical Removal from Wastewater

The three major metal salts available for P removal through chemical precipitation are calcium, aluminum and iron (Clark et al., 1997; Jenkins et al., 1971). Calcium addition as lime is less commonly employed due to handling difficulties, high sludge production and optimal removal at pH 11 (Clark et al., 1997). Both iron and aluminum salts have been long considered as coagulants for precipitation of PO_4^{3-} from solution, though iron precipitation is less expensive and is more extensively used for chemical precipitation purposes (Tchobanoglous et al., 2013). Additionally, P can be efficiently mobilized from iron by natural processes in sediments and soils (Korving et al., 2019). The mechanism(s) of P removal with dosed iron is highly complex and is influenced by several factors, notably dissolved oxygen concentration (which impacts oxidation state), the presence of competing ligands, humic acid content, solution pH alkalinity, the type of P present, the use of ferric or ferrous iron salts, and sludge age of the iron (oxide) flocs

(Wilfert et al., 2016). Iron-bound PO_4^{3-} in WWTPs can be either iron phosphate minerals or adsorbed mono- and bidentate complexes (Parsons and Smith, 2008; Hauduc et al., 2015; Luedecke et al., 1989).

The chemical reactions which take place in the wastewater system due to iron salt addition are complex and result in much larger iron demand than that required by the precipitation reactions alone. The removal of P can occur via multiple pathways: (i) adsorption of phosphate onto hydrated ferric oxides, (ii) co-precipitation of phosphate into the iron oxide structures, (iii) precipitation of ferric phosphate, (iv) precipitation of mixed cation phosphates (Wilfert et al., 2016). Iron (III) dosage induces rapid hydrous ferric oxide precipitation (Parsons and Smith, 2008; Hauduc et al., 2015). The precipitation of amorphous hydrous ferric oxide provides a number of surface adsorption sites and surface precipitation of iron phosphates (Hauduc et al., 2015). A variety of iron phosphate minerals can be found in nature but those most relevant to chemical P removal from wastewater include strengite ($FePO_4{\cdot}2H_2O$), $Fe_{2.5}PO_4(OH)_{4.5}$, $Fe_{1.6}H_2PO_4(OH)_{3.8}$ and $Fe_3(PO_4)_2{\cdot}8H_2O$ (Hauduc et al., 2015; Luedecke et al., 1989; Fytianos et al., 1998).

Ferric chloride is most commonly used for P precipitation in activated sludge plants but ferrous salts may also be utilized. Simultaneous dosing of ferrous and ferric salts is a more effective method for P removal than dosing of a single form of iron (Gutierrez et al., 2010). Under anaerobic conditions, the reduction of iron (III) to iron (II) can lead to the release of adsorbed P and/or the formation of precipitate known as vivianite ($Fe_3(PO_4){\cdot}8H_2O$) (Azam and Finneran, 2014; Wang et al., 2018). Since the Fe/P molar ratio of vivianite is significantly higher than the ferric P complexes, ferric P reduction can be used to achieve greater P immobilization as a low solubility mineral. Recent work has confirmed this hypothesis showing that vivianite can be the dominate phase of P at WWTPs that employ iron for chemical P removal and anaerobic digestion (Wilfert et al., 2016, 2018). Researchers have hypothesized that the magnetic properties of vivianite could enable separation from sludge, heightening its potential for P recovery from aqueous waste streams.

Recovering P via precipitation for potential reuse as a fertilizer has historically relied on a small set of magnesium and calcium phosphate mineral phases. Several magnesium phosphate mineral phases have been observed to form in waste solutions, notably struvite ($MgNH_4PO{\cdot}6H_2O$), K-struvite ($KMgPO{\cdot}6H_2O$) dittmarite ($MgNH_4PO_4{\cdot}8H_2O$), newberyite [$Mg(PO_3OH){\cdot}3H_2O$], and the trimagnesium phosphates bobierrite [$Mg_3(PO_4)_2{\cdot}8H_2O$] and cattitte [$Mg_3(PO_4)_2{\cdot}22H_2O$] (Massey et al., 2009; Musvoto et al., 2000). Struvite and its potassium isomorph are the only relevant magnesium phosphate mineral phases that have been observed to form in concentrated waste streams (Table 1). Relevant calcium phosphate species include amorphous calcium phosphate [$Ca_3(PO_4)_2$], dicalcium phosphate dihydrate ($CaHPO{\cdot}2H_2O$), octacalcium phosphate [$Ca_8H_2(PO_4)_6{\cdot}5H_2O$], and hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$]. In most wastewaters including those with substantial Mg^{2+}, hydroxyapatite is the most thermodynamically stable phase due to its low water solubility. However, the spontaneous growth of apatitic minerals without a precursor phase has not been observed outside of organic frameworks with pore sizes sufficiently small to promote direct growth (Kim et al., 2016). This is due to the complex crystal structure of hydroxyapatite, which presents a marked nucleation barrier and correspondingly sluggish nucleation kinetics compared to simpler phases such as amorphous calcium phosphate, the generally accepted precursor phase to all other calcium phosphates (Eliaz and Metoki, 2017). Therefore, based on kinetic rates of formation, the favorability of forming calcium phosphates is primarily associated with the solubility of amorphous calcium phosphate rather than hydroxyapatite.

To illustrate the importance of waste stream composition on rP speciation we present solubility diagrams based on average phosphate, ammonium, potassium, and carbonate concentrations to observe total PO_4^{3-} aqueous concentrations in equilibrium with relevant magnesium and calcium phosphate solid phases (i.e., precipitative removal) as a function of pH for the two streams most commonly considered for P recovery: animal manure and anaerobic digester supernatant (Fig. 2). The equilibrium modeling indicates precipitation could reduce soluble P in both waste streams by increasing pH and that the mineral phrases most stable and likely to precipitate are associated with calcium phosphates. Therefore, if a waste stream is rich in calcium, amorphous calcium phosphate would be expected to co-precipitate with struvite, and in some cases dominate the rP products. This suggests the importance of determining the background concentration of calcium in aqueous waste streams targeted for rP generation. Based on the mean of reported values (Table 1), anaerobic digester animal manure has a high background concentration of Ca^{2+} which will likely result in co-precipitation of struvite and calcium phosphates even with magnesium dosing to promote struvite formation (Fig. 2A). Recovery of a heterogeneous rP product composed of calcium and magnesium phosphate phases could impact its agronomic and/or economic value. Since calcium concentrations are relatively low in anaerobic digester supernatant, supplementing magnesium (generally as $MgCl_2$) and operating at circumneutral pH makes it possible to recover pure struvite. Another important consideration is that of potassium struvite, which favorably combines recovery of P and with another crop macronutrient of K, is unlikely to form in either stream given typical ammonium concentrations (Table 1).

Composition of Recovered Organic Phosphorus

Phytic acid ($C_6H_{18}O_{18}P_6$) is the major P storage unit in grains and accounts for up to 85% of total P in cereals, legumes and oilseeds (Nolan et al., 1987; Oatway et al., 2001; Reddy et al., 1982). Thus, P recovery from grain processing streams will depend on the solubility of phytate salts. Phytic acid has 12 exchangeable protons: six in the strong acid range (pK_a 1.1 to 2.1), three in the weak acid range (one with pK_a 5.7 and two with pK_a 6.8–7.6), and three in the very weak acid range (pK_a > 10) (Costello et al., 1976). Therefore, under circumneutral pH conditions typical of wastewater streams, phytic acid is extensively ionized and can interact strongly with proteins and metal ions (Reddy et al., 1982).

Phytate is also a strong ligand and can form stable complexes with various metal cations such as Ca^{2+}, Mg^{2+}, Zn^{2+}, and $Fe^{2+/3+}$ (Nolan et al., 1987). A number of calcium phytate species can

form in solutions containing Ca^{2+} and phytate (Evans and Pierce, 1981; Grynspan and Cheryan, 1983; Grynspan and Cheryan, 1989; Kornegay, 2000; Veiga et al., 2006). At a molar ratio of $Ca:P_{phytate} > 5$, the main species formed is Ca_5(phytate), though Ca_6(phytate) may also be formed if Ca is present in large excess. Several Ca_n(phytate) complexes may be formed at lower molar $Ca:P_{phytate}$ ratios (n = 1 to 4) (Evans and Pierce, 1981; Grynspan and Cheryan, 1983; Nolan et al., 1987). The mono- and di-calcium species are soluble whereas the tri-calcium or higher complexes are highly insoluble (Nolan et al., 1987). Calcium and phytate are highly soluble at pH <4 and insoluble at pH >6 (Grynspan and Cheryan, 1989; Nolan et al., 1987). Above pH 6, the optimum molar ratio range for Ca precipitation with phytate in synthetic water is reported to be 4 to 6.5 (Grynspan and Cheryan, 1983; Veiga et al., 2006). Reported solubility product values for Ca_5(phytate) complexes are reported to range from 10^{-22} to 10^{-39} (Evans and Pierce, 1981; Veiga et al., 2006) indicating that calcium-driven removal of phytate from light steep and thin stillage waste streams is likely to be an effective P recovery strategy.

Protein–Phytate and Protein–Mineral–Phytate Interactions

Six negatively charged PO_4^{3-} groups make phytate an effective chelator that forms insoluble complexes with cations and proteins (Duodu et al., 2003; Serraino and Thompson, 1984). Ionic bonding between proteins and phytic acid depends on solution pH conditions and availability of bridging divalent cations. At pH values below the isoelectric point of a given mix of proteins, phytic acid binds strongly to the cationic proteins to form binary protein-phytate complexes (Champagne, 1988; Cheryan and Rackis, 1980; Selle et al., 2000; Serraino and Thompson, 1984). At pH values above the protein isoelectric point, net negative charge leads to the formation of insoluble ternary protein-metal-phytate complexes (Champagne, 1988; Cheryan and Rackis, 1980). The negatively charged groups in proteins may be linked to phytate through cations, in particular calcium (Selle et al., 2000). Calcium concentration is expected to affect the extent of ternary complex formation and the excess Ca could lead to formation of Ca_n(phytate) complexes (Champagne, 1988; Selle et al., 2000). Thus, phytate can be recovered via precipitation using components already present in the grain processing stream. A recent combined experimental and modeling study of P recovery from maize wet milling confirmed this hypothesis, showing that more than 90% of soluble P could be removed from light steep water at a molar Ca/P = 1 and solution pH = 9 (Juneja et al., 2019). Model simulations indicated that 90% P removal from light steep would reduce the P content in maize gluten meal to values in line with animal nutritional requirements (Juneja et al., 2019).

Agronomy of Recovered Phosphorus

Availability of Phosphorus in Recovered Phosphorus

The solubility of rP presents a key tension between engineering its recovery and re-using it as a fertilizer because its low water solubility defines both the ability to separate organic and inorganic P from aqueous streams, and the crop-availability and loss risk of rP added to soil. The generally low fraction of water soluble and thus immediately crop-available PO_4^{3-} in rP (Fig. 3) means that theoretical self-sufficiency of the Corn Belt using rP (Metson et al., 2016) is agronomically unfeasible, regardless of additional and well-documented logistic and economic barriers (Sharpley et al., 2016). Broad differences in rP species, such as the majority of P being present in inorganic (struvite) or organic (phytin) forms, entail distinct processes in how rP becomes available for crop uptake– but also loss–following addition to soils as a fertilizer (Fig. 3). Thus, there will likely be rP-specific interactions with crop and soil characteristics of agricultural sinks.

Agronomic Considerations for Recovered Phosphorus Use in the Corn Belt

Research concerning the agronomic use of rP has largely been limited to struvite and crop types that are relatively minor in the United States (e.g., canola [*Brassica napus* L.], ryegrass [*Lolium perenne* L.], wheat [*Triticum aestivum* L.]). However, there is limited research on the hypothesized interactions among rP forms, crop species, and soil properties. Expanding research to include other forms of rP and crops such as maize and soybean that dominate the Midwest (USDA-NASS, 2018) is essential to quantify the potential agricultural sink for rP and to evaluate agronomic optimums for each rP species.

Combining rP with commonly used highly water soluble P fertilizers in a blend may offer greater early-season P availability than using rP alone because a small proportion of crop-available PO_4^{3-} in rP is water soluble, and dissolution (e.g., struvite) or mineralization (e.g., phytin) may not be sufficient to meet crop P demand early in the season (Fig. 3). Limited dissolution and thus availability of P from struvite in early growth stages of wheat (Degryse et al., 2017; Talboys et al., 2016) inflicted a greater

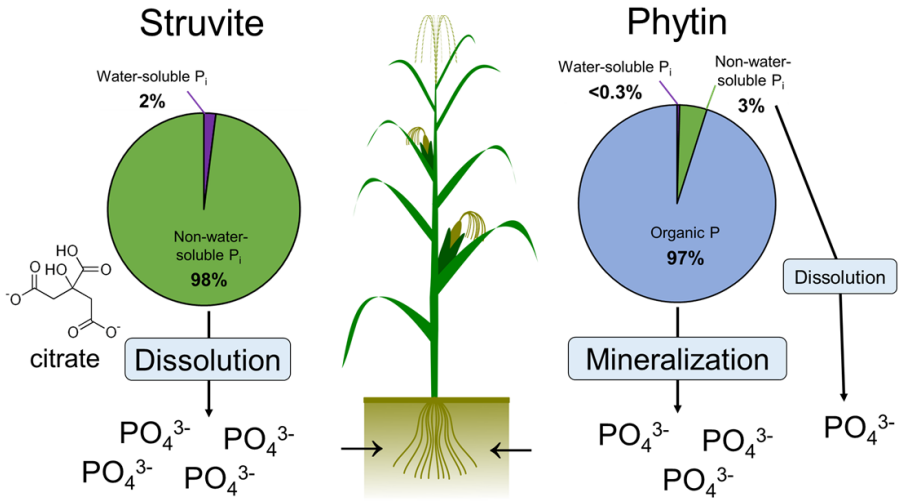

Fig. 3. Comparison of the speciation and mechanisms of crop availability of P in two examples of recovered phosphorus, struvite and phytin. P_i, inorganic P.

yield penalty than a P deficiency experienced in the later stages of growth (Grant et al., 2001).

Crops such as buckwheat (*Fagopyrum esculentum* Moench) and lupine (*Lupinus angustifolius* L.) with high root exudation of organic acids appear able to sufficiently solubilize struvite and consequently can meet the majority of P need from this rP (Hilt et al., 2016; Robles-Aguilar et al., 2019; Talboys et al., 2016). The possibility of similar root exudate-driven dissolution for dominant Midwest crops of maize and soybean is not clear, although these species are thought to produce relatively low concentrations of organic acids (Jones, 1998; Ligaba et al., 2004; Talboys et al., 2016). Soil conditions that promote root secretion of organic anions could indirectly favor struvite dissolution via roots. For example, citrate exudation is strongly induced by aluminum toxicity (Wang et al., 2018) and aluminum toxicity also tends to co-occur with P deficiency and fixation of water-soluble P inputs (i.e., weathered soils) (Fageria and Baligar, 2008; Havlin et al., 2013). Root-mediated mechanisms of P utilization from rP raises the possibility of P input-specific breeding targets to increase P use efficiency (Veneklaas et al., 2012; Withers et al., 2014).

In contrast, crop availability of P in phytin is governed by the activity of extracellular phytases that catalyze organic P mineralization to PO_4^{3-} by hydrolyzing C-O-P bonds (Richardson et al., 2000). Many crop species such as maize are poor exuders of phytase (Hayes et al., 1999), meaning that the majority of phytase activity in soils is likely of microbial origin– and implicating non-crop species in crop response to rP (Menezes-Blackburn et al., 2013; Singh and Satyanarayana, 2011). Lowering the soil C:P ratio by management practices such as the blending of phytin with water soluble P fertilizer could stimulate P mineralization (Marschner, 2007; Zhang et al., 2014).

Increasing evidence suggests that maize and legumes such as soybean can derive a significant portion of their P needs from rP forms applied to soil (Hilt et al., 2016; Thompson, 2013; Vogel et al., 2015). In a greenhouse experiment evaluating early-stage to mid-stage growth of maize and soybean (Fig. 4), substituting up to 50 and 25% of water-soluble P fertilizer with struvite did not significantly hinder maize and soybean growth, respectively (Fig. 4A, C), although significant declines in aboveground biomass occurred at higher proportions of P supplied as struvite. The strong crop species-specific response to struvite and phytin is consistent with crop species differences in root exudate quantity and quality: maize root systems can secrete nearly threefold more exudate C than those of soybean (Gao et al., 2014; Guo et al., 2017). For phytin, no significant difference in aboveground biomass was found for up to 100 and 50% replacement of P as monoammonium phosphate (MAP) for maize and soybean, respectively (Fig. 4B, D), suggesting that in these soils mineralization of organic P in phytin may be less limiting to the availability of this rP than dissolution of P from struvite.

Mitigating Agricultural Phosphorus Loss Risk with Recovered Phosphorus

The highly water soluble P fertilizers such as ammonium phosphates used in midwestern agriculture have contributed to eutrophication and hypoxia in local surface waters and the Gulf of Mexico since use increased in the 1960s (Rockwell et al., 2005;

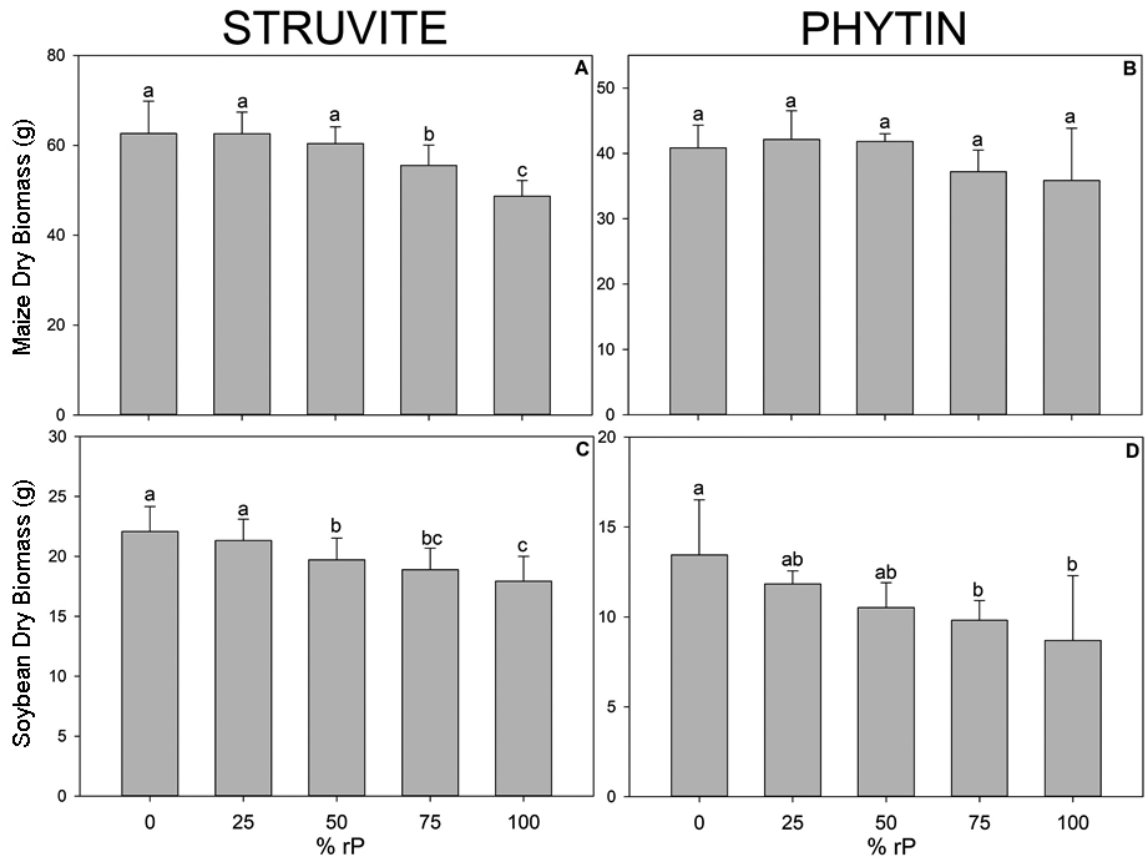

Fig. 4. Aboveground biomass growth of (A–B) maize (V12) and (C–D) soybean (R1) across a gradient of recovered phosphorus (rP) substitution (% of total P) for monoammonium phosphate by struvite or phytin, in a fine, smectitic, mesic Aquic Argiudoll (0–30 cm of A horizon, pH 5.6).

Schindler et al., 2008). Fall and/or surface broadcast application of P in highly water soluble forms increases its susceptibility to off-farm losses as dissolved PO_4^{3-}. Thus, partial substitution of ammonium phosphates with a proportion of a low water solubility rP such as struvite could reduce dissolved losses of applied fertilizer P. Using 0.5-m^2 lysimeters in a loamy sand texture soil, Guertal (2015) identified nearly fourfold lower PO_4^{3-} leaching over 12 wk with struvite (49 g P d^{-1}) compared with MAP (191 g P d^{-1}), and a 66:33 struvite/MAP yielded an intermediate flux of leachate P (100 g P d^{-1}) at a P application rate of 42.6 kg P ha^{-1}. This suggests that even partial substitution of ammonium phosphates by struvite stands to maintain crop productivity while reducing P loss risk. Phytin may also offer potential water quality benefits as it consists of mostly non-water-soluble organic P that must first undergo mineralization to be more susceptible to runoff or subsurface drainage losses as dissolved PO_4^3. Due to their agronomic usefulness and low potential for loss, struvite and phytin could eventually be recommended as the R of "right fertilizer" in the 4Rs of nutrient stewardship (right source of fertilizer at the right rate at the right time in the right place).

Nitrogen Embodied in Recovered Phosphorus

The adoption of the two rP forms, struvite ($MgNH_4PO_4{\cdot}6H_2O$) and calcium phytate ($C_6H_6Ca_6O_{24}P_6$), as P fertilizers requires an understanding of the distinct N release patterns as well as the form and the quantity in which N is present and made available by their use in agriculture (Fig. 5). Although struvite and phytin are both rP, there are innate differences in quantity and quality of co-contained N that determines N crop availability.

Phosphorus availability is likely to be coupled with N availability in struvite but not necessarily for phytin. While struvite has a congruent dissolution of PO_4^{3-} and NH_4^+ ions as an inorganic P source, calcium phytin as the calcium salt of inositol polyphosphate is an organic P source containing coprecipitated N largely in proteinaceous forms (Fontaine et al., 1946; Smith and Rackis, 1957). The dominance of organic forms of phytin N entails uncertainty in the amount of N release via mineralization and is not necessarily related to mineralization of organic P. Thus, N release from phytin is likely to be less predictable than struvite and more influenced by interrelated abiotic (e.g., weather conditions) and biotic factors (e.g., soil microbiological activity).

Ammonium exhibits congruent dissolution with PO_4^{3-} from struvite (Bhuiyan et al., 2008; Bonvin et al., 2015), meaning that the availability of PO_4^{3-} from struvite will be tightly coupled with struvite-derived N. Across soils of varying pH (5.9, 7.0, 8.0), struvite dissolution over 14 d was highest (50%) in the soil with pH 5.9 (Massey et al., 2009). Release of NH_4^+ from struvite following a 90-d incubation period in a neutral (pH 7.4) soil was 95 to 100% (Case and Jensen, 2017). As with the P component of struvite, NH_4^+ from struvite will congruently dissolve in the presence of root-exuded organic acids (e.g., citrate, oxalate, malate). Compared with readily soluble P fertilizers such as MAP, rP forms are likely to have insignificant N losses via leaching (Kataki et al., 2016). For example, only 1.9 and 2.1% of struvite N was lost due to leaching in soil columns (initial pH 6.11–6.17) over 5 wk compared with 7.8 and 6.5% NH_4^+ loss from fused superphosphate (20% P_2O_5) applied at rates of 30 and 40 kg P ha^{-1}, respectively (Rahman et al., 2011). Decoupling

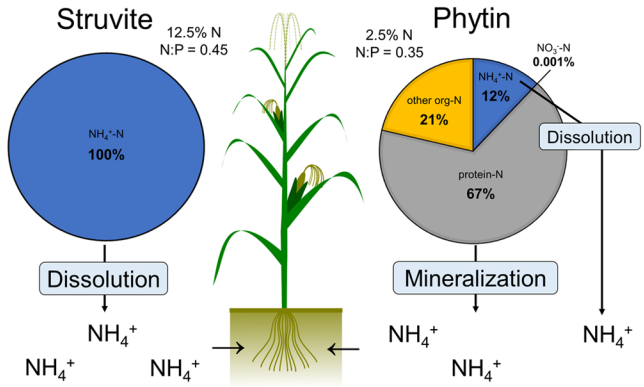

Fig. 5. Comparison of the content, speciation, and mechanisms of crop availability of N in two examples of recovered phosphorus, struvite and phytin.

of P and N in phytin means that phytin contributions to crop N uptake as well as off-farm losses may require explicit evaluation independent of phytin P fate in soils.

At agronomically feasible rates (see section "Mitigating Agricultural Phosphorus Loss Risk with Recovered Phosphorus" above), rP such as struvite provides appreciable, if minor, contributions to the N budget of the intensively managed maize–soybean production systems that dominate the Midwest. For example, a maize–soybean rotation in Illinois with a typical yield of 13.5 Mg maize ha^{-1} and 4.0 Mg soybean ha^{-1} entails removal of 36 and 22 kg P ha^{-1} via maize and soybean grain, respectively. Offsetting this P export of 73 kg P ha^{-1} for a 2-yr maize–soybean rotation using struvite would contribute 35.7 kg N ha^{-1}, equivalent to 23% of the 155 kg N ha^{-1} needed to offset N export via grain harvest (Tenorio et al., 2018). However, a more realistic proportion of 25% of P as struvite would contribute 8.9 kg N ha^{-1}, 6% of total N needs. The presence of background soil NH_4^+ and Mg^{2+} can produce a statistically significant but minor reduction in struvite dissolution (Talboys et al., 2016). Thus, the high N application rates (e.g., 141–171 kg ha^{-1} yr^{-1} in Illinois; Fernández et al., 2012) and the high base saturation of Alfisols and Mollisols (≥35 and ≥50%) common in the Midwest (Soil Survey Staff, 2003) are unlikely to appreciably inhibit NH_4^+ and concurrent PO_4^{3-} solubilization from struvite.

Phytin contains N largely in organic form, the crop availability of which is determined by N mineralization instead of dissolution. The majority of this organic N is in crude protein forms (Fig. 5), the content of which varies based on feedstock and extraction methods. Mediated by the action of protease and other N hydrolytic enzymes secreted by soil microorganisms, mineralization of organic N from phytin will likely depend on multiple factors. Given that the microbial activity that drives N mineralization is strongly sensitive to soil temperature and moisture (Kladivko and Keeney, 1987), weather is likely to influence N availability of applied phytin. As for other organic N inputs such as manure, this can challenge prediction of phytin contribution to crop N demand at the time of application (Carter, 1993; Eghball, 2000; Mengel, 1996).

Economic and Regulatory Aspects of Recovered Phosphorus

Economics of Phosphorus Recovery and Reuse

The overall economics of rP will ultimately determine whether rP generation and usage technologies are adopted and thus the

form(s) of rP produced. Overall economic assessment entails not just the economic costs of recovery and recovered products but, perhaps more important, the policy drivers of P pollution abatement. Phosphorus abatement and recovery are not widespread today because there is no regulatory requirement to do so, and the economic incentives for rP installation are currently limited to potential reductions in operating costs at WWTPs (section "Waste Stream Treatment and Nutrient Recovery Infrastructure" below). Costs of rP fall into two primary categories: the cost of P recovery itself and the cost of using rP products. The engineering cost of recovering P from existing waste streams, the marketing and distribution of rP as a crop fertilizer, and the net cost of using rP products will collectively determine the economic viability of transferring P from waste streams to recipient cropland sinks at various scales. Although beyond the scope of this research, society also incurs damage costs from P losses to surface waters by affecting the economic value of water-based recreational activities and tourism, property values along impaired waters, commercial fishing, and, potentially, human health (see USEPA [2015] for a review of economic costs). Not acting to reduce release into the environment means such damages will continue.

The cost of commercial fertilizer products currently being produced from rP is too high relative to traditional sources of P fertilizer to justify use by producers growing bulk commodities such as maize and soybean such that only higher-valued crops are utilizing rP fertilizer products today. Commercially available struvite today costs over three times more than MAP on a total mass basis, at approximately \$1650 Mg^{-1} for a marketed rP product (Ostara Inc., personal communication, 2019) compared with \$562 Mg^{-1} for MAP (USDA-IL, 2019). This rP fertilizer cost is more than five times greater than MAP on a P content basis at \$13.52 and \$2.48 kg^{-1} P, respectively. If the cost of struvite generation can be reduced, it may become economically rational to use rP instead of conventional P fertilizers such as MAP, although limited crop availability may deter full substitution of water-soluble P fertilizers for rP (see "Agronomy of Recovered Phosphorus," above). This cost comparison is driven not only by the engineering cost of P recovery but also by distribution and marketing of rP, which will require agronomically viable blends based on yield response trials of new fertilizer formulations.

If a market for rP fertilizer products were to become viable, then industrial, agricultural (e.g., concentrated animal feeding operation [CAFO]), and municipal (e.g., WWTP) waste generators could potentially recover a portion of their P abatement costs of installing rP systems through fertilizer sales. The cost of recovery would have to be reduced dramatically in order for CAFOs to be able to cost-effectively recover much smaller amounts of P than are being economically recovered today by WWTPs. The close proximity of CAFOs to farms could dramatically reduce transportation costs to reach land application sites if recovery and fertilizer formulation can be achieved economically on this much smaller scale. An additional source of income relative to current operations for bioprocessing facilities that sell feed products to livestock feeding and finishing operations is possible if the P content in the feed grains can be reduced enough to decrease the amount of land that is required to spread manure. If intensive livestock feeding areas are already land constrained because of high soil P levels, then reduced P content feeds may be economically attractive. The cost of land application of manure can potentially be dramatically reduced given that rP technologies may be capable of reducing P content in feed grains to a level equivalent to what livestock digestion can break down without pass-through to manure (Juneja et al., 2019). Currently, the excess P in maize milling by-products being fed to livestock (maize gluten meal and dried distillers grains with solubles) is excreted in manure and thus is exported to watersheds where crop production and processing may not occur. This highlights the ability of rP to attenuate P loss risk indirectly by reducing P load in agriculturally useful waste stream products after P recovery.

Political and Regulatory Aspects

Phosphorus recovery technologies have not been widely adopted because there is as of yet no uniform incentive to reduce P effluent. In the absence of an effluent limit, disposal of P into waterways is effectively free. New policy instruments such as water quality trading are a policy alternative to traditional command-and-control regulations that specify inflexible technological or performance standards that point sources must satisfy independently (USEPA, 2016). Water quality credit trading programs enable a nonpoint source, in this case a producer, to implement best management practices on-farm that generate an established number of nutrient credits that can be sold to a point source in a given compliance period to satisfy effluent limits on NPDES permits. For example, in Minnesota, the Metropolitan Waste Control Commission and the Minnesota Pollution Control Agency have implemented a P trading program (MPCA, 2014).

Other policy instruments could be pursued. Just as there are regulations requiring a certain amount of renewable fuels to be blended with gasoline under the Renewable Fuel Standard, a similar policy for fertilizer blends requiring a minimum ratio of rP fertilizer to mineral fertilizer could be possible. With respect to reducing the amount of P fertilizer added to fields, US states could adopt regulations similar to some countries in Europe (e.g., Belgium, Denmark, The Netherlands) where there is a maximum limit for P inputs (Amery and Schoumans, 2014). An application restriction of manure on a P basis would hinder the application of manure since crop N demand exceeds P demand. The current regulation in Illinois, for example, requires that soil test P (Bray-1 or Mehlich-3) be no more than 336 kg ha^{-1} for facilities with ≥1000 animal units (Illinois General Assembly, 1996). Phosphorus extracted from manure as rP could enable the resulting low P manure residual to be used as fertilizer, with lower N/P for N-based applications requiring less total land for treatment and utilization of manure. The 4Rs, which provide a framework for nutrient management to apply the right source of fertilizer at the right rate at the right time in the right place, focus on conventional P fertilizers but could be expanded to include rP such as struvite and phytin applied at the right rate, time, and place.

Waste Stream Treatment and Nutrient Recovery Infrastructure

Updating WWTP infrastructure can be done in a way to allow mobilization of nutrients into the cropland sink. Opportunities for rP production will increase significantly as NPDES permits transition toward including numeric criteria for P in discharged

wastewater (USEPA, 2011). In the short term, operational modifications and plant upgrades will center on implementing enhanced biological phosphorus removal (EBPR), in which polyphosphate accumulating organisms sequentially release and uptake PO_4^{3-} to store energy in covalent polyphosphate bonds. Efficient operation of EBPRs will enable WWTPs to reduce P in treated wastewater effluent to ≤1 mg L^{-1} while also incentivizing integration of sidestream rP crystallization reactors based on WWTP specific benefits such as reduced intraplant P cycling, prevention of uncontrolled scaling in digesters and conduit, and operation cost recovery through fertilizer sales. Production of rP can be increased by 60% when an anaerobic detention basin designed to strip P from waste EBPR sludge is used to divert P toward the crystallization reactor rather than allowing struvite formation with the anaerobic digester (Cullen et al., 2013).

Modifications to the established wastewater collection and centralized treatment paradigm will continue to transmit the majority of human-derived P to wastewater treatment biosolids. Since the majority of P is excreted in urine, with reported PO_4^{3-} concentrations ranging from 217 to 637 mg L^{-1} (Table 1) (Etter et al., 2011; Langergraber and Muellegger, 2005; Ronteltap et al., 2007, 2010; Udert and Wächter, 2012), interest in urine-diverting toilets and decentralized nutrient recovery systems has been growing. This is particularly true in less-developed countries as an alternative to centralized wastewater collection and treatment infrastructure (Cordell et al., 2009; Langergraber and Muellegger, 2005). Urine separation may also be feasible for densely populated cities in developed countries. A recent life-cycle assessment, for example, showed that decentralized collection and recovery could reduce the cost and greenhouse gas emissions of nutrient removal in the Bay Area of California, indicating that urine collection should be further investigated for urban centers in developed countries (Kavvada et al., 2017).

Illinois: A Case Study in Multidisciplinary Approaches to Realize Recovered Phosphorus Opportunities

In the 350 years since the discovery of P in 1669, the midwestern P cycle has undergone drastic changes commencing with European American settlement and agriculture in the 19th century. Like much of the Midwest, the landscape of Illinois has been fundamentally altered by agricultural activity over the past two centuries. Today, Illinois is one of the most agriculturally dominated landscapes in the world and in human history, with two-thirds of all land area under intensive row crop agriculture, second in the United States only to Iowa (75%) (USDA Economic Research Service, 2017). Inherent to this intensive agricultural land use are anthropogenically engorged P stocks and fluxes through soils, crops, and surface waters.

The landscape of Illinois formed over thousands of years of glacial activity during the Pleistocene Epoch (Killey, 2007). Following the Wisconsian glaciation, prairie grass dominated the postglaciation landscape starting in 8300 BP (King, 1981). Of the 8.9 million ha of the presettlement prairie, less than 0.01% (≈900 ha) was estimated to remain by the end of the 20th century (White, 1978). As prairie was converted to row crop production, P inputs increased to replenish P removed via crop harvest. The need to amend agricultural soils with P sources such as phosphate rock or manure was identified in the early work of Cyril Hopkins at the University of Illinois (Hopkins, 1910; Hopkins et al., 1911). As Hopkins accurately estimated at the beginning of the 20th century, approximately 75% of the P taken up by maize is exported from the agricultural system as grain (Bender et al., 2013; Hopkins et al., 1911) and requires replenishment to maintain productivity. Adoption of P fertilizers in the mid–20th century and application rates exceeding export rates have led to positive P balances in Illinois soils (MacDonald et al., 2011), although the degree of P accumulation—and, in particular, severe excess—appears to be decreasing. Reflecting trends in the greater Corn Belt, Illinois agricultural soils saw a 26% decrease in Bray I P concentrations >20 mg kg^{-1}, more than half of which was driven by decreases in soil Bray I >50 mg kg^{-1}, concurrent with an increase of 24% of soils testing at <20 mg kg^{-1} (Johnston et al., 2014; Murrell et al., 2016).

In 2018, Illinois producers planted over 4.3 million ha each of maize and soybean, representing 13.2 and 12.2% of the national area harvested for each crop, respectively (USDA-NASS, 2018), and accounting for 14% of the national maize P demand (Metson et al., 2016). Approximately 166 and 89 Mg P was exported as grain from maize and soybean fields, respectively, in 2018 (USDA-NASS, 2018). An estimated 9 to 29% of P inputs on Illinois croplands was derived from manure, with higher proportions in northern Illinois where livestock production is concentrated (Jacobson et al., 2011; ILEPA, 2014). An equivalent of 17.5% of annual P application is lost to Illinois waterways (USEPA, 2016), amounting to a fertilizer (MAP) value of $2.1 million (USDA Economic Research Service, 2019). This loss also has severe consequences for the Mississippi River and the Gulf of Mexico (Robertson and Saad, 2013).

Nonpoint and point sources each contribute nearly half of total P losses to Illinois surface waters (Fig. 6). Annual crop agriculture is the dominant nonpoint P source (48% of total P losses) due to erosion (80%) and surface runoff (20%) (ILEPA, 2014),

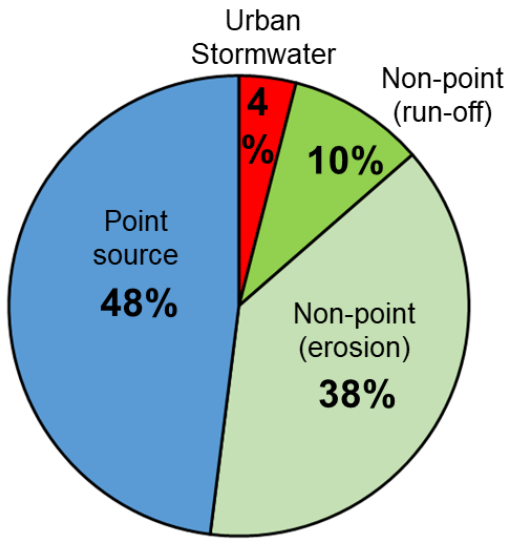

Fig. 6. Distribution of annual P losses estimated for Illinois for the period 1997–2011. Values are derived from the Illinois Nutrient Loss Reduction Strategy (ILNLRS; ILEPA, 2014). Total P losses from Illinois were estimated to be 17.0 Gg annually, with nearly similar contributions (each 48% of total) from nonpoint sources (i.e., agriculture; 8.1 Gg P yr^{-1}) and point sources (8.2 Gg P yr^{-1}).

although the potential contribution of tile drainage to P losses has also been identified (Gentry et al., 2007; Smith et al., 2015). Point sources account for an additional 48% of total P losses in Illinois and include industrial and municipal WWTPs that are required to have NPDES permits that satisfy TMDL limits for the discharge of pollutants. Illinois does not have TMDLs for P, but these are in development (ILEPA, 2014). The major point sources in the state are the WWTP operated by Metropolitan Water Reclamation District of Greater Chicago, which treats municipal effluent from Chicago and surrounding suburbs, and the Sanitary District of Decatur (ILEPA, 2014), which treats a mix of municipal waste and industrial effluent from two grain (maize and soybean) processing plants. Both of these systems generate P waste (e.g., human excrement, cleaning products, grain milling) that could be recovered in forms such as phytin and struvite for use as a fertilizer.

In 2015, the state of Illinois released the Illinois Nutrient Loss Reduction Strategy (ILNLRS). The overall goal of the ILNLRS is to decrease the total P load from Illinois to the Mississippi River by 8.5 million kg yr^{-1} from all sources to reach the 45% target outlined in the Gulf Hypoxia Action Plan (ILEPA, 2014). To reach the proposed total P load reduction goal, the ILNLRS outlines promising best management practices that have shown potential in field studies or other states to reduce N and/or P losses. Currently, ILNLRS-sanctioned best management practices include cover cropping, conventional tillage, the 4Rs of nutrient management, and cropland conversion to the Conservation Reserve Program or perennial crops. In 2015, 129,095 ha of cover crops of cereal rye, oats, and radishes were planted by Illinois producers (ILEPA, 2014), with notable increases in in southern Illinois (Rundquist and Carlson, 2017). Cover crops have complex impacts on net P losses because cover crops can lead to lessened P loss via surface run-off and leaching (Aronsson et al., 2016; Zhang et al., 2017) yet have been found to increase dissolved P losses following freeze–thaw cycles (Øgaard, 2015; Riddle and Bergström, 2013) or post-termination precipitation events (Cober et al., 2018). Conservation tillage can reduce soil erosion and thus associated risk of P loss as particulate P, which is estimated to account for the majority (≥60%) of P losses in Illinois (ILEPA, 2014). However, no-tillage may not necessarily yield net P loss reductions because surface stratification of broadcasted P fertilizer can lead to higher dissolved P losses (Bertol et al., 2007; Sharpley and Smith, 1994). To the extent that it can reduce soil erosion, crop conversion from a continuous maize or maize–soybean rotation to hay or to Conservation Reserve Program land may also offer benefits to P loss mitigation (ILEPA, 2014). Although there is a general lack of data for manure in Illinois (ILEPA, 2014), the state has comparatively low livestock and thus manure usage compared to its neighboring midwestern states (Jacobson et al., 2011). Best practices for manure management, such as avoiding application before anticipated precipitation events, are outlined in the ILNLRS. The first ILNLRS biennial summary report in 2017 focused on outreach to promote producer awareness of the statewide strategy and also explains different cost-sharing programs producers can take part in to implement recommended best management practices. The array of best management practices could be expanded to include initiatives for rP to further target P loss reduction in the state.

The large agricultural P demand and grain P export of Illinois make the state an optimal sink for rP. Illinois is estimated to potentially meet 46% of its maize P needs through rP production from animal manure, human excreta, and food waste (Metson et al., 2016). However, this analysis does not account for P recoverable from grain processing facilities. With Illinois the third-largest producer of maize ethanol in the United States (RFA, 2018), P extraction from thin stillage at dry-grind ethanol plants could significantly increase local rP generation. In 2012, Illinois produced 3 Tg of dried distillers grains with solubles (Smith et al., 2017) containing approximately 26,000 Mg of P. With nearly 3.6-fold the production of dried distillers grains with solubles than potential utilization within the state as animal feed, rP generation from maize ethanol plants would also reduce the overall P footprint of Illinois because elevated P in dried distillers grains with solubles can exacerbate manure nutrient management challenges.

Increasingly stringent regulations on WWTP effluent in the Midwest have created demand for technologies that not only remove P but recover it in an agronomically usable form. A striking example of this is one of the largest WWTPs in the United States, the Stickney Water Reclamation Plant in Chicago, IL. Anticipating stricter nutrient discharge limits that have lowered the effluent discharge limit to 1 mg L^{-1}, the plant implemented a P precipitation system to recover P. The plant partnered with Ostara Inc., a fertilizer company specializing in P removal and recovery through precipitation systems to recover struvite minerals. This technology allows the WWTP to recover P in a form that can be reused for plant growth while also providing a treatment process that greatly reduces annual operating costs, when compared to traditional chemical precipitation with iron or aluminum. The Stickney Water Reclamation Plant is ideal for rP generation due to its size and proximity to cropland with high P demand. It treats on average 2.6 billion L d^{-1} of water and can treat up to 5.5 billion L d^{-1}, a scale that permits this single WWTP to potentially recover up to 9000 Mg of struvite annually, marketed as Crystal Green (Ostara) fertilizer (Lee, 2018). Under its current technology marketing arrangement, Ostara Inc. retains and does not transfer the rP to the waste treatment facility and returns a share of profits from fertilizer sales to the plant. This makes the recovery of P via precipitation beneficial in terms of P removal and recovery while also providing a high-quality P product at a scale that makes the process economically feasible.

Water quality trading programs enable point sources to comply with NPDES nutrient maximums by selling nutrient credits to nonpoint sources. Recovered P offers Illinois a means for water quality trading between point sources and nonpoint by its use as a fertilizer from what would otherwise be considered a point-source P loss. Water quality trading, which is endorsed by the Illinois Pollution Control Board, could create an incentive for point sources to implement processes to capture waste P to be used as rP as it would create revenue and reduce their environmental impact. On the other hand, introducing water quality trading could conceivably disincentivize rP investment by WWTPs depending on the stringency of the P discharge limits and P abatement marginal cost curve by agriculture. Normally, a water quality trading market is based on the economic cost-effectiveness principle that producers are the lowest-cost means of achieving nutrient loss abatement, and thus WWTPs would be able to reduce the cost of

expensive treatment system upgrades by paying agricultural producers that are rP users (not limited by NPDES or TMDL requirements) to reduce nonpoint source nutrient loss to achieve a target improvement in water quality at a lower cost to society than requiring WWTPs to install expensive equipment. However, the incentive for producers to buy and use rP as fertilizer is not any greater under a water quality trading program than it is in its absence if the relative cost of rP inputs still greatly exceeds conventional P inputs (e.g., MAP). The first ILNLRS biennial summary report issued in 2017 explains different cost-sharing programs producers can take part in to implement recommended best management practices.

Forging a regional P economy in Illinois and the greater Midwest on the basis of agricultural reuse of P captured at colocated point sources thus faces a combination of engineering, agronomic, and economic barriers. The engineering challenges are not insurmountable, although lowering the cost of rP technologies should be a central focus of wastewater treatment engineers. Although there is a considerable agronomic knowledge gap on rP, readily translatable approaches in the agricultural sciences exist to address these. In contrast, the economic obstacles to rP reuse for a circular P economy are likely to be substantial. Here, regulatory tools are most likely to be effective, if politically contentious. Given current and projected conventional P versus rP costs, incentivizing utilization of certain rP forms by agricultural sinks is unlikely to be driven by potential agronomic advantages and possible environmental benefits due to reduced P losses are unlikely to be persuasive given that its classification as a nonpoint source does not allow regulatory incentives. Ultimately, the political basis for this chain of incentivization implicates a social dimension to rP for achieving regional circular P economies.

Conclusion

There is high potential to develop a circular P economy in the Corn Belt by extracting P from aqueous waste streams and reusing this rP in agricultural lands as a fertilizer. In addition to urban point sources, grain-processing facilities abundant in this region are a major industrial point source of P, with strong potential for its low-cost recovery. Matching rP sources and sinks necessitates evaluation of rP–cropping system interactions, particularly crop species and soil properties. Depending on waste stream composition and engineering technologies, various rP options can be selected to best suit recipient agricultural sinks. A defining feature of rP is that the low water solubility that enables its recovery limits its crop availability but also off-farm P loss risk. For agronomic reasons alone, low water solubility of rP means that it will likely be limited to a partial substitute for highly water soluble P inputs such as ammonium phosphates. In addition to engineering and agronomic considerations, the economics of rP generation from point sources and rP reuse by agriculture are strongly influenced by regulatory incentives. Sale of rP as fertilizer could be used to abate costs of waste stream P removal, and/or rP could be integrated into water quality trading systems. Identifying ratios of rP and conventional P inputs that maintain crop production and potentially mitigate P losses risk is therefore a strategic next step toward realizing the opportunity of rP in Corn Belt.

Supplemental Material

The Supplemental Material provides a detailed summary of data sources and estimation methods used to construct the US P mass balance for 2012 depicted in Fig. 1.

Conflict of Interest

The authors declare no conflict of interest.

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