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CELEBRATING THE 350TH ANNIVERSARY OF DISCOVERING PHOSPHORUS—FOR BETTER OR WORSE

Future Phosphorus: Advancing New 2D Phosphorus Allotropes and Growing a Sustainable Bioeconomy

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Abstract

With more than 40 countries currently proposing to boost their national bioeconomies, there is no better time for a clarion call for a "new" bioeconomy, which, at its core, tackles the current disparities and inequalities in phosphorus (P) availability. Existing biofuel production systems have widened P inequalities and contributed to a linear P economy, impairing water quality and accelerating dependence on P fertilizers manufactured from finite nonrenewable phosphate rock reserves. Here, we explore how the emerging bioeconomy in novel, value-added, bio-based products offers opportunities to rethink our stewardship of P. Development of integrated value chains of new bio-based products offers opportunities for codevelopment of "P refineries" to recover P fertilizer products from organic wastes. Advances in material sciences are exploiting unique semiconductor and opto-electrical properties of new "two-dimensional" (2D) P allotropes (2D black phosphorus and blue phosphorus). These novel P materials offer the tantalizing prospect of step-change innovations in renewable energy production and storage, in biomedical applications, and in biomimetic processes, including artificial photosynthesis. They also offer a possible antidote to the P paradox that our agricultural production systems have engineered us into, as well as the potential to expand the future role of P in securing sustainability across both agroecological and technological domains of the bioeconomy. However, a myriad of social, technological, and commercialization hurdles remains to be crossed before such an advanced circular P bioeconomy can be realized. The emerging bioeconomy is just one piece of a much larger puzzle of how to achieve more sustainable and circular horizons in our future use of P.

Core Ideas

- Society's vision for a more circular economy must go beyond the C cycle to include P.
- Some biofuel systems have widened P inequalities and contributed to a linear P economy.
- New bioeconomy in bio-based products offers an opportunity to rethink P stewardship.
- A circular bioeconomy requires efficient P reuse, recovery, and recycling from waste.
- New 2D P allotrope technologies offer a potential antidote to our current P "paradox."

In the years since Hennig Brandt's accidental discovery of phosphorus (P) in 1669, the element is now at the core of our understanding of the challenges and opportunities to sustain the trajectory of prosperity that humankind has forged. The 350th anniversary of the discovery of P (Sharpley et al., 2018) provides an opportunity to use this element as a lens into past and future schemes to sustain humankind. Most recently, the bioeconomy has been hailed as the "next industrial revolution" for today's growing and increasingly affluent global population (Bell et al., 2018; European Commission, 2018; Organisation of Economic Cooperation and Development, 2009, 2018).

It is envisaged that the bioeconomy will provide eco-efficient production of renewable food and energy resources, not only meeting basic needs but also delivering to the consumer healthcare and industrial products demanded by modern society. A major focus of the emerging bioeconomy is conversion of sustainably produced biomass, including crops (food, feed, and energy, lignocellulosic and algae) and organic waste materials (biosolids, manure, stover, food, and municipal organic wastes) into value-added bio-based products: from biofuels to biochemicals to bio-based polymers (Fig. 1). The bioeconomy encompasses a diversity of "agroecological" approaches in the production and use of renewable biomass and "technological" approaches, including the application of knowledge from the life and materials sciences to develop solutions for health and resource-based challenges (Organisation of Economic Cooperation and Development, 2009; Priefer et al., 2017; Zilberman et al., 2013) (Fig. 1).

The surge in interest in the bioeconomy within the last few years, and the corresponding proliferation of national bioeconomy strategies, can be traced back to the Organization of Economic Cooperation and Development's 2009 policy document: "The Bioeconomy to 2030: Designing a Policy Agenda" (Organisation of Economic Cooperation and Development, 2009; Staffas et al., 2013). In 2012, both the United States and Europe adopted their respective bioeconomy strategies, with a broad consensus that the economy needs to gradually transition

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Abbreviations: 2D, two-dimensional; 2D BlackP; two-dimensional black phosphorus; 2D BlueP; two-dimensional blue phosphorus; GHG, greenhouse gas; UV, ultraviolet.

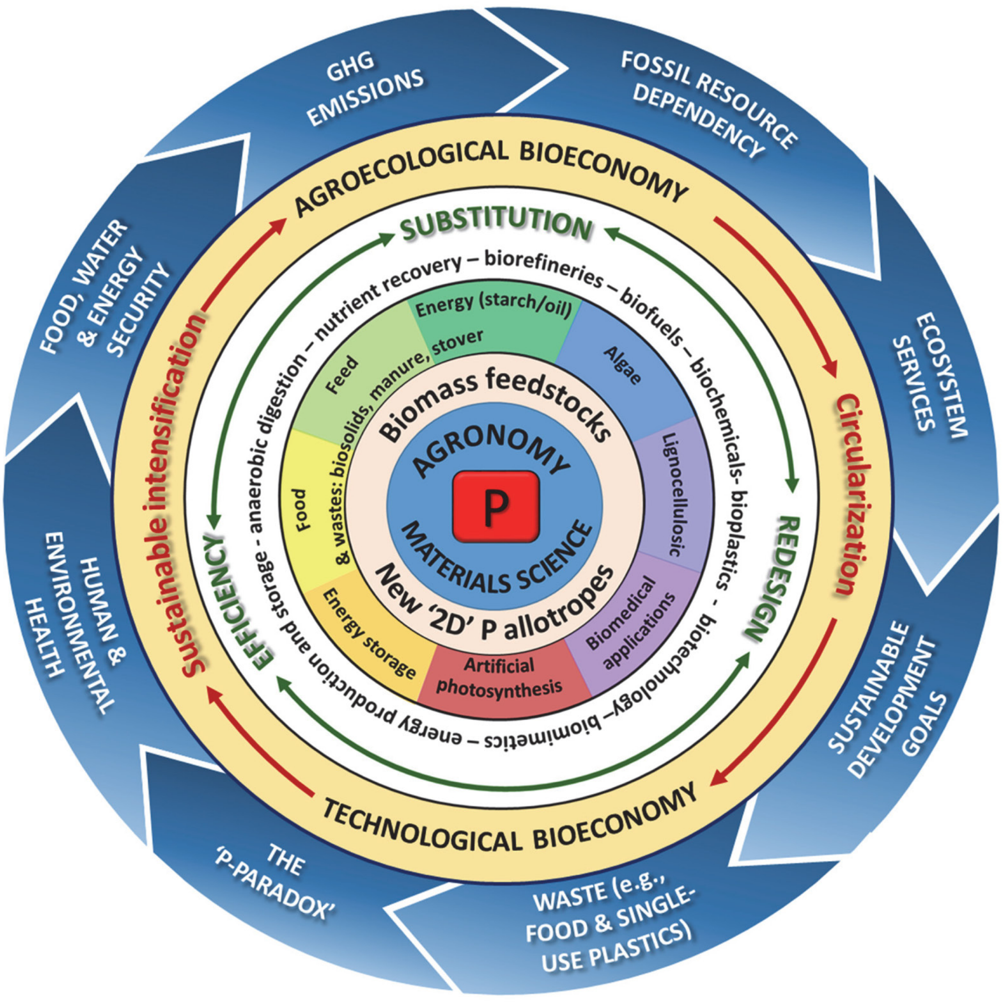

Fig. 1. Vision of P contributions to the emerging bioeconomy: first, as a vital nutrient in the production of biomass crops and feedstocks for a range of bio-based products within the agroecological bioeconomy; and second, through potential future contributions of new two-dimensional (2D) P allotropes to energy and biomedical solutions within the technological bioeconomy. Improvements in P stewardship include the *efficiency* of P use through improved nutrient management; *substitution* of new technologies, such as P recovery and recycling and creation of novel value chains for biobased products; and *redesign* of land management and production systems. Improvements in P stewardship and exploitation of new 2D P technologies are expected to contribute to sustainable intensification and circularization goals, to decoupling production and consumption from resource depletion and environmental degradation, and to a range of "Grand Challenge" sustainability objectives, depicted in blue in the outer sphere of the figure.

from a fossil-based economy to a bio-based economy (European Commission, 2012; White House, 2012).

Envisaged as a means of decoupling consumption from resource depletion and environmental degradation, the bioeconomy aims to address an ambitious range of "grand challenge" sustainability objectives (Fig. 1). These include renewable energy, reducing greenhouse gas (GHG) emissions and mitigating climate change, reducing fossil resource (fuel and rock P) dependence; sustaining and enhancing ecosystem service provision; delivering on UN sustainable development goals; reducing waste (including food and single-use plastics); contributing to both human and environmental health; and improving food, water, and energy security.

While there has been a strategic effort to transform carbon (C) management from linear to circular systems (e.g., Ingrao et al., 2018), there has been relatively little focus on the importance of a circular P economy within the emerging bioeconomy (Withers et al., 2018). Nonetheless, securing and maintaining sustainable P supplies will be vital for growing the renewable biomass feedstocks that provide the foundation of the bioeconomy, particularly given rising concerns about future P security (Cordell et al., 2011). If managed properly (e.g., with suitable technology, public policies, and market incentives), new uses for P in the bioeconomy could play a central role in the valorization of organic wastes (municipal/sewage and industrial, food, and manures), through recovery and recycling of P as a fertilizer, back into the agroecological portion of the bioeconomy (Fig. 1).

We explore here how the emerging bioeconomy, in novel value-added bio-based products, provides an opportunity to augment and rethink our stewardship of P, building on lessons learned from existing biofuel and livestock production systems and the need to address the current "paradox" of P deficits and P surpluses (Jarvie et al., 2015; Sharpley et al., 2018). We highlight how new advances in material sciences are exploiting unique semiconductor and opto-electrical properties of new P allotropes (two-dimensional [2D] black phosphorus and blue phosphorus). These novel P materials, discovered only within the last 5 yr, offer the tantalizing prospect of step-change innovations in renewable energy production and storage, in biomedical applications, and in biomimetic processes, including artificial photosynthesis, thus expanding the importance of P in securing future sustainability across both agroecological and technological domains of the bioeconomy. However, if these novel materials are not recycled or reused properly, they could exacerbate the problems of linear, terminal pathways for P.

Some Existing Biofuel and Livestock Production Systems Have Widened Phosphorus Inequalities and Contributed to a "Linear" Phosphorus Economy

Starch and oil biomass crops—corn (*Zea mays* L.), sugarcane (*Saccharum* spp.), sugarbeet (*Beta vulgaris* L.), soybean [*Glycine max* (L.) Merr.]—grown for biofuels have formed the mainstay of the bioeconomy to date (Fig. 1). These annual monocultures require high external inputs, including P fertilizer, and now compete with food production for land, water, and P use and have diminished ecosystem service provision (Hein and Leemans, 2012; Priefer et al., 2017). Mandates to expand biofuel production in every continent, part of national energy security strategies that also reduce reliance on fossil fuels, have added pressure on P fertilization of biofuel feedstocks. These pressures can increase the risk of P loss to surface waters (affecting water security) and grain prices with competition for food or fuel (affecting food security) (Robertson et al., 2008; Simpson et al., 2008; Tilman et al., 2009).

The drive for bioethanol production in the United States to form a greater share of consumed energy led to an increase in corn acreage over the last 30 yr (Fig. 2), and since 2010, the acreage of corn grown for feed has been similar to that grown for fuel. The rise in acreage of corn has often been at the expense of perennial production systems, that is, lands with low P demand and effective local P cycling. Simpson et al. (2008) investigated these trends in the Chesapeake Bay and Mississippi River basins, where much of the increased acreage came from land in the Conservation Reserve Program (the principal conservation easement program in the United States and a central component of US soil conservation and water quality mitigation strategies), as well as pastures. Assuming fertilizer application rates increased to obtain optimum yields, they estimated a potential annual P load increase of 220% (0.55 million kg P) in the Chesapeake Bay basin and 200% (34 million kg P) in the Mississippi River basin compared with pre-corn land use.

The push toward bioethanol production has also exacerbated inequalities in P availability at regional and national scales. Historical trends in agriculture have favored economically optimized, large-scale food production systems, resulting in a shift from mixed livestock and crop farming (where P was recycled locally) to specialized and intensified systems that rely on large-scale transfers of P from mineral reserves to geographically distinct areas of grain production, animal production, and human consumption (i.e., cities). Areas of P demand for grain production in the Midwest and Mississippi River valley are located hundreds of miles away from the major cities and intensive livestock producing areas where waste P is produced (Jarvie et al., 2015).

Because large transfer distances preclude recycling of P back to areas of grain production, there has been an uncoupling of local P cycles, with reduced efficiency of P reuse and accumulation of P close to areas of production above crop and pasture demand. This uncoupling of the P cycle has resulted in greater losses to the environment around areas of intensive livestock production and urban areas, but it has also accelerated dependency on inorganic P fertilizers, derived from nonrenewable phosphate rock reserves, in areas of grain production (Jarvie et al., 2015), resulting in a linear P economy (Withers et al., 2018). We also face a fundamental P paradox arising from the simultaneous deficiencies and excesses of P across local, regional, and national scales (Leinweber et al., 2018; Sharpley et al., 2018).

Although biofuel digesters are often closer to farmland than to cities, the growth of large-scale, grain-based ethanol production and colocating beef feedlot and dairy-based concentrated animal feeding operations have the potential to create new areas of P imbalances and cycle disconnects. For example, dried distiller's grains, a by-product of ethanol production, are used as a feed ration alternative (mainly for ruminants) due to their availability and low cost. However, the P content of dried distiller's grains (0.8–0.9% P) is about three times that of corn. Based on this, Simpson et al. (2008) determined that <20% dried distiller's grains supplementation in dairy cow diets elevated ration P to 0.5% (0.33–0.36% P is recommended; National Research Council, 2001). Inclusion of dried distiller's grains in rations at rates such as these will increase manure P (Maguire et al., 2004; Wu et al., 2001), which, if land applied, could increase P runoff (Ebeling et al., 2002; Maguire et al., 2007).

Bioethanol production has therefore contributed to an uncoupling of the P cycle in two ways. First, by reversing efforts to perennialize landscapes (which reduces the intensity of management), bioethanol production has created a trend of converting less-productive land, or even Conservation Reserve Program land, into production. Some of this land will be more vulnerable to P loss and, after conversion to corn production, will be subject to much higher P fertilization, at rates consistent with maximizing corn yields, thus increasing risks of P loss. Second,

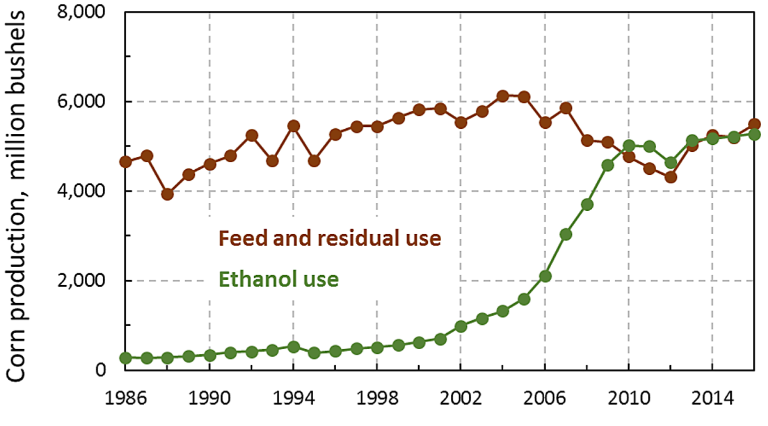

Fig. 2. The production of corn in the United States used for feed and that used for bioethanol production (US Department of Energy, 2019).

by exacerbating the specialization of agriculture and by cojoining two (food and fuel) agricultural systems that both concentrate P in localized areas, the effects of localized P accumulation have become compounded.

In a broader systems analysis of trade-offs between growing corn for fuel or food, Richardson and Kumar (2017) accounted for the energy required to prepare and maintain the landscape for agricultural production for corn and its conversion to biofuel; air and water quality impacts; and corn's societal value, both as food and fuel. They demonstrated that the net social and economic worth of food corn production in the United States was \$1,492 ha^{-1}, versus a \$10 ha^{-1} loss for biofuel corn production. In addition, there is also a wider range of potential "welfare" estimates and impacts that can be considered (e.g., Cui et al., 2011; Janda et al., 2012).

The Emerging Bioeconomy: Biorefineries and Phosphorus Refineries for Production of New Bio-based Products

Biorefineries convert low-value biomass as a renewable feedstock for producing a portfolio of higher-value products, including biofuels, industrial biochemicals, and biomaterials, such as commercially important biopolymers and fibers (Mohan et al., 2016). Analogous to petroleum refineries, biorefineries use biomass conversion processes to produce fuels, power, and chemicals (Fig. 1). Biorefineries are also capable of integrating production processes with remediation, by utilizing waste and nonedible biomass and valorizing waste through treatment, helping to close the P cycle (Carey et al., 2016). Indeed, economies of scale associated with the spatial concentration and specialization of intensive livestock operations can offer cost-effective opportunities for manure processing and production of higher-value recycling products. Anaerobic digestion has been developed for waste stabilization and conversion of a wide range of organic substrates (manure, municipal solid waste, lignocellulosic biomass, and industrial wastewaters to produce energy-rich biogas; Sawatdeenarunat et al., 2016). Anaerobic digestion biorefineries integrate biomass conversion processes with production of a more diverse range of value-added products (in addition to biogas), thus increasing revenues by producing low-volume, high-value bioproducts, as well as supplying energy needs through production of high-volume, lower-value fuels. The product portfolio of biorefining includes biodegradable bio-based polymers: polylactic acid, thermoplastic starch, and microbially-produced polyesters, such as polyhydroxyalkanoates (Mohan et al., 2016).

Polyhydroxyalkanoates combine high functionality (tunable mechanical and physical properties) with lower environmental impact and are promising candidates for sustainable polymer production, potentially substituting polypropylene, polyethylene, and polystyrene, the three main polymers of the global polymer market (Dietrich et al., 2017). Polyhydroxyalkanoates are both compostable and biodegradable, overcoming the recently well documented problems of plastic pollution, where polymer wastes accumulate in the natural environment for up to 2000 years (DiGregorio, 2009). There is also potential for sustainable polyhydroxyalkanoate production from lignocellulosic biomass feedstocks. There have been laboratory successes in the development and use of microbial catalysts that break down cellulose to fermentable sugars and then convert these sugars to bio-based chemicals. Cellulosic biorefineries remain technically challenging and expensive when compared with ethanol mills, and, to date, there are few commercial operations (Philp, 2018). However, improvements in biotechnological processes and synergies with biofuel production and nutrient recovery are likely to increase the predicted share of bio-based polymers.

Lignocellulosic biomass feedstocks have been used in anaerobic digestion biorefineries to generate biomethane, biohydrogen, bioethanol, biobutanol, and a range of chemicals, such as organic acids. Animal manures used as an anaerobic digestion feedstock generate a highly nutrient rich digestate, which can be used for land "fertigation," or for algal farming, facilitating P recovery. Algal lipids can be used for biodiesel production, and the remaining protein-rich solids can be used for animal feed.

Anaerobic digestion also provides a means of valorizing food waste. It is estimated that about one-third of all food for human consumption worldwide is discarded as waste (Food and Agriculture Organization, 2011). The high water, organic matter, and P content of food waste make it an ideal substrate for anaerobic digestion, although the relatively low nitrogen (N) content of food waste (except for meat wastes) means that it is often advantageous to codigest food waste with N-rich substrates (e.g., municipal biosolids or animal manure) to increase anaerobic digestion efficiency. Indeed, the prospect of future "phosphorus refineries" using biowaste streams has also been raised (e.g., Ohtake, 2015; Ohtake and Okano, 2015; Withers et al., 2015) whereby biotechnologies are used to recover P from a range of secondary waste materials for reuse.

Many P-recovery technologies are still in their infancy or remain at the pilot stage, and while others have been already implemented, they face often prohibitive commercialization challenges in competing with cheaper phosphate rock-derived products (Molinos-Senante et al., 2010). As a result, the economics of P-recovery systems range widely (Shu et al., 2005), and a favorable regulatory environment is often needed (Driver et al., 1999; Sartorius et al., 2012). Capitalizing on the potential for biorefineries to integrate bio-based production processes with waste treatment will require transformations in our waste management systems, with investment in areas where there is currently little or no return for producers and with changes in policy and markets needed to support these transformations and innovations. In addition, there are wider trade-offs to consider with P recovery technologies; for example, recovery of P from organic wastes such as manures often results in losses of volatile N compounds, which increases energy requirements to replace lost N via the Haber Bosch process (Mayer et al., 2016).

Increasing Demand for Biomass: The Need for Sustainable Intensification and Improved Phosphorus Stewardship

Growing the bioeconomy will rely on availability of sufficient biomass, of adequate quality, which is sustainably produced. Although biomass is a renewable resource, it is not an unlimited resource, and demands for P fertilizer for growing biomass crops will inevitably intensify pressures on water and P resources at local to global scales (Priefer et al., 2017). Replacing fossil fuels by biomass feedstocks requires life-cycle and sustainability assessments for both biomass production and the transformation of biomass into bio-based products (Aguilar et al., 2018; Hottle et al., 2013). For example, the benefits of reduced GHG emissions from replacing fossil fuel-based feedstocks with crop-based biomass feedstocks come with wider trade-offs arising from the need to expand biomass production, further accelerating P resource depletion. Weiss et al. (2012) estimated that 1 t of bio-based material saves, relative to conventional fossil fuels, 55 (± 34) GJ of primary energy and 3 (± 1) t of CO_2 but may increase eutrophication by 5 (± 7) kg of phosphate equivalents per tonne. Further land use impacts—including potential loss of biodiversity, soil C depletion, soil erosion, deforestation, and GHG emissions from indirect land use change—will also need to be considered in the evaluation of environmental performance of bio-based products.

The major potential for growth in biomass production is often in regions that are geographically distant from markets and demand: international trade in bioenergy is expected to accelerate in the future, especially between Latin America and sub-Saharan Africa as net exporters and North America and Europe as net importers (Lewandowski, 2015). These exporting areas are often regions with low food security and where agricultural production is not often considered sustainable. International trade in biomass also further exacerbates spatial disconnects by transferring P in biomass to Europe and North America, which is not replaced in the soils in the biomass-producing countries and regions, thus contributing to the breakdown of the P cycle, dependence on inorganic fertilizers, and consequent depletion of fossil P reserves.

Meeting increasing demand for biomass will necessitate sustainable intensification of biomass production, simultaneously increasing the productivity, profitability, and performance of biomass production while enhancing environmentally beneficial performance and outcomes—or at least incurring no net environmental cost (Pretty et al., 2018; Zilberman et al., 2018). Improved P stewardship lies at the heart of the sustainable intensification imperative, with three key stages (Hill, 1985; Fig. 1):

- *Efficiency* of resource management: including extension and policy support to help target and rationalize fertilizer and feed P inputs; precision farming; revisiting soil test P recommendations for optimum yield; the "4Rs" of nutrient management (right source, rate, time and place, taking into account local site variations; International Fertilizer Association, 2009); and avoidance of biomass and P losses across the supply chain.
- *Substitution*: replacement of technologies and less efficient components of the agricultural system with, for example, new crop varieties, no-tillage systems, and substituting energy crops with second-generation lignocellulosic biomass.
- *Redesign*: including changes in land management to support agroecological processes that deliver beneficial ecosystem services, such as nutrient cycling, water retention, and soil regeneration (Macintosh et al., 2019); changes from conventional monoculture intensive farming to site-specific and multifunctional agricultural systems; a shift toward mixed farming systems that allow recycling of P and closure of local P cycles; and creation of novel value chains that connect the production of biomass, bio-based chemicals, bioenergy, and recovered nutrients for fertilizers and that are sustainable and competitive against fossil-based products and processes (Carraresi et al., 2018).

Precision agriculture provides opportunities to improve *efficiency* in P use through *substitution* by technologies that offer improved sequestration of soil P by crops. Phosphorus is present in soil in a continuum of labile and nonlabile forms. The labile forms include P dissolved in the soil pore spaces, P adsorbed onto soil particle surfaces, and precipitated P, as well as P incorporated in the soil organic matter. The nonlabile P forms include P in the primary minerals and P coprecipitated with and/or adsorbed onto iron, aluminum and, to a lesser extent, manganese oxyhydroxides. Although soils have a large amount of stored P, most remains in recalcitrant forms that are not available for plants. Therefore, bioavailable P needs to be added to maintain an adequate supply of P to crops, which may have negative environmental impacts as well as other impacts, such as resource depletion and cost. To address this, researchers have investigated ways to mobilize P to more bioavailable forms within soil, as well as to genetically modify plants to be capable of enhanced P uptake from those stable, recalcitrant forms.

While there is evidence of movement from the recalcitrant forms of P to more bioavailable forms with land use management and time (González Jiménez et al., 2019), recent research has found that additions of elements such as silicon (Schaller et al., 2019), arbuscular mycorrhizal fungi (Battini et al., 2017), or phosphate solubilizing bacteria (Adnan et al., 2017) positively affect P mobilization but, in the case of phosphate solubilizing bacteria, may be affected by external factors such as pH and calcium content (Zheng et al., 2019).

As only 20 to 30% of applied fertilizer is taken up by plants (Syers et al., 2008), work has been ongoing to genetically modify plants to increase their efficiency in P utilization. López-Arredondo and Herrera-Estrella (2012) developed transgenic *Arabidopsis* plants, expressing the bacterial phosphite dehydrogenase (*ptxD*) gene, that were capable of the same productivity as control plants grown under the same conditions but which required 30 to 50% less P fertilizer input.

Redesign will include fundamental restructuring of farming systems, such as reintegrating livestock and crop systems, as well as capitalizing on landscape diversity to grow cellulosic crops as biomass feedstock (grasses and woody plants) in less productive areas. Cellulosic agriculture has a lower P demand, has potential for increasing soil C, and is less likely to interfere with food production. The potential to utilize cellulosic and waste biomass has galvanized interest in "multifunctional landscapes" for biomass production, which offer opportunities to simultaneously achieve both productivity and conservation (Williams et al., 2013). Multifunctional landscapes form the basis of the Wisconsin "grass–shed" initiative for bioenergy, whereby perennial grass production is coupled with livestock rearing, the recycling and use of livestock waste to improve biomass production, and the use of both the cellulosic and livestock waste biomass in anaerobic digestion (Williams et al., 2013). Cellulosic materials may also be used in the treatment of groundwater contaminated by agriculture (Healy et al., 2015) and industrial processes (Ahmad et al., 2013) and can potentially lower GHG emissions, particularly if added to stored slurries (Bastami et al., 2016).

Sustainable farming necessitates that inputs of P are eventually balanced by outputs. Phosphorus fertilizer is made from rock phosphate, which is a nonrenewable resource, whereas the outputs, which mainly comprise the anthropogenic mobilization of P, have persisted (Bol et al., 2018). It has been estimated that only 15% of P extracted from nature is consumed by humans, with the remaining 85% lost to the environment along the production, post-harvest, processing, and consumption stages (Suh and Yee, 2011). This is significant, as P is considered to be a critical raw material of high economic importance and potential supply risk (European Commission, 2017). Measures such as precision agriculture can be used to improve the input side, but the output side needs transformation across rural and urban economies. For example, the mean daily P intake by residents of the United States 20 yr and older in 2011–2012 was 1351 mg d^{-1} (Moshfegh et al., 2016), which is higher than the recommended daily allowance of 700 mg d^{-1} for the same age group (Food and Nutrition Board, 1997). Apart from changes to dietary patterns, transformation will be aided by changes in legislation governing the landfilling of waste, the redesign of urban sanitation systems to promote the utilization of waste, and the replacement of mineral fertilizer with fertilizers originating from solid waste.

Phosphorus: The Poster Child for Circularization within the Bioeconomy

The extent to which the attainable potential of sustainably produced biomass could be sufficient to satisfy global bioeconomy demand is frequently disputed, with estimates based on optimal conditions for intensive crop production and high biomass yields (Lewandowski, 2015). Alongside sustainable intensification, it is clear that there will also be a need for sparing and responsible use of biogenic feedstocks, with organic wastes and by-products treated as resources within the bioeconomy, and where biomass is highly valorized, not sent to landfill, a concept known as "circularization."

Circularization retains resources within the economy for as long as possible, reducing waste, and contrasts with traditional linear models of consumption, where products are designed, manufactured, consumed, and then discarded. This involves the creation of "novel value chains" whereby value is added to the products or by-products of biomass processing, with the development of new markets for bio-based products, as well as product certification (Carraresi et al., 2018). Also central to a circular bioeconomy is the concept of "cascading utilization" (Keegan et al., 2013), whereby biomass is first used for production with the highest societal value (highest economic value). For example, high-value specialist biomaterials and chemicals are reused in bulk materials and finally for production of biofuels and power, with loss by burning at the very end of the life cycle (Dietrich et al., 2017; Priefer et al., 2017). Accordingly, the bioeconomy will require profound societal transitions, with changing public attitudes to waste and recycling being an important lever for reducing the demand for biomass.

A core requirement of a circular bioeconomy is a circular P economy, based on efficient reuse, recovery, and recycling of P-rich biowastes (livestock manure, food wastes, industrial and municipal wastewater), thus reducing reliance on fossil phosphate rock resources and helping to close the P cycle (Carraresi et al., 2018). This is already starting to happen through the horizontal integration of agriculture with other industries, stimulating new value-added chains, which connect the production of biomass, chemicals, energy, and recovered nutrients as commercial fertilizers (Carraresi et al., 2018). However, these technologies need to be scalable in producing high-quality P fertilizer products that can be cost-effectively transported back to replenish soil P reserves in areas of crop production, thus addressing the profound inequalities in P surpluses and deficits (Sharpley et al., 2018). At a local scale, better integration of crop and livestock systems, as well as manure trading, can also contribute to a circular P economy.

The circular bioeconomy concept may also address a contradiction that currently exists with legislation, which sets targets for the attainment of water quality and reduced GHG emission targets (e.g., the Water Framework Directive in the EU [Official Journal of the European Communities, 2000] and the Paris Agreement [United Nations Framework Convention on Climate Change, 2015]) while also advocating sustainable intensification of agricultural practices (Food and Agriculture Organization, 2013). The interconnectivity of agricultural production and environmental protection is rarely considered. However, the residues generated in production, post-harvest, and processing stages (which are frequently disposed of) may be used to treat P-rich slurry water in agriculture. These may be used to reduce GHG emissions from storage and land spreading of slurry. They may also improve agronomic yields following land spreading, due to the enhancement of the availability of slurry nutrients.

In recent years, legislation that limits the disposal of waste to landfill (e.g., The Landfill Directive in the EU; European Commission, 2001) has positively affected the circular bioeconomy by forcing the integration of agriculture with the water treatment (Grace et al., 2016) and wastewater treatment sectors (Colón et al., 2017). For example, drinking water treatment residuals from water treatment plants, rich in aluminum or iron and which is currently primarily sent to landfill, may be reused as an adsorbent medium to reduce P in runoff, or as an amendment to reduce GHG from stored slurry. Similarly, treated municipal wastewater sludge (biosolids) is commonly used as a fertilizer.

To achieve a truly circular P economy, however, there needs to be a connection between urban/consumer-based economies and agricultural production. There remains a myriad of economic and social acceptability hurdles yet to be addressed before large-scale recovery and recycling of P in urban wastes for agricultural production are achieved. Concerns about emerging contaminants are currently a major obstacle hindering reuse of sewage biosolids in agriculture (Clarke et al., 2016). Moreover, the costs of recovering nutrients as fertilizer formulations from wastewater streams remain too high to compete effectively with cheap fertilizers derived from mined P rock. There is a clear opportunity to reduce food waste and utilize P-rich food waste as a bioresource, for example, in anaerobic digestion biorefineries, but failure to address these food waste challenges and opportunities also remains a major hindrance to achieving circularization within both the P economy and the wider bioeconomy. Achieving sustainability and circularization will also necessitate an intricate codevelopment of processes and "technical crossover" (Dupont-Inglis and Borg, 2018), bringing convergence and integration between both the agroecological and technological sides of the bioeconomy (Fig. 1); for example by bringing together:

- precision agricultural technologies and agroecological-based beneficial management practices that can contribute to improved P stewardship and sustainable intensification of biomass production; and
- biotechnological advances in metabolic engineering and microbial catalysts that improve microbial fermentation of biomass, increase production capacity for commercial bio-based products, and facilitate scaling up of production facilities in biorefineries and development of bioclusters (Mohan et al., 2016).

There is unlikely to be a one-size-fits-all bioeconomy, but instead a diversity of approaches combining applications of techniques and technologies based on sound ecological principles and which contribute to both agroecological and technological domains of the bioeconomy.

While a sustainable circular P economy is critical to societal and ecological well-being, an equitable apportionment of funding for remedial strategies should involve a myriad of stakeholders and those benefiting from food production (i.e., everyone). Despite mixed success with "green" or environmental excellence labeling to pass some mitigation costs on to the consumer, new strategies should be explored. For example, several companies and nongovernmental organizations (e.g., https://www.landolakessustain.com/ and https://www.tysonsustainability.com/) are collaborating across their supply chains to increase environmental stewardship using sustainability metrics (Shilling, 2016; Tyson Foods, 2017). Driven by fiscal benefits and heightened societal responsibility, such companies are driving change and broadening the sphere of who pays for circular P economy.

Novel Phosphorus Materials Science and the Technological Bioeconomy

Within the last 5 yr, the discovery of a "two-dimensional" black phosphorus allotrope (2D BlackP, also known as phosphorene) has opened up new potential for P to contribute to the technological bioeconomy, through novel solutions to health and energy resource challenges. Discovered in 2014, 2D BlackP is an ultra-thin (single atom-thick or single polyhedral-thick layers) "cousin" of graphene: each P atom is covalently bonded with three adjacent P atoms, forming a bi-layer with a puckered structure. This structural anisotropy contributes to exceptional optical, electrical, thermoelectric and mechanical properties (Akhtar et al., 2017; Hu et al., 2018). Indeed, 2D BlackP has been described as a "rapidly rising star in materials science" and the "new silicon" because, unlike graphene, 2D BlackP has a direct and tunable band gap, a major factor in determining electrical conductivity (Zhu et al., 2017b). In the case of 2D BlackP, this band gap allows broad absorption across the visible, infrared, and ultraviolet (UV) regions of the electromagnetic spectrum, giving it a superior range of optical and semiconductor properties, with a broad range of potential applications in electronic and thermoelectric devices and sensors.

Then, in 2016, 2D blue phosphorus (2D BlueP) was discovered (Zhang et al., 2016). In 2D BlueP, the atoms adopt a honeycomb pattern, and, rather than lying flat, the lattice "buckles," changing the way electrons move. This gives 2D BlueP different electronic properties, including a wider band gap than 2D BlackP; this will allow semiconductors to operate at higher voltages and temperatures (Science Daily, 2018). Clearly, 2D BlueP will offer a wide range of future applications, but here we focus on three potential areas where 2D BlackP is envisaged to contribute to the technological bioeconomy: in biomedical applications, energy storage, and "biomimetic" processes (artificial photosynthesis):

- *Biomedical applications and theranostics.* Although 2D BlackP-based biomedical applications are still in their infancy, the material is already being used in biosensors based on the fluorescent and colorimetric detection of a variety of bioanalytes including DNA and proteins; in field-effect transistor-based immunosensors for detecting antigens and antibodies; and in highly sensitive gas sensors for biomedical applications (Choi et al., 2018). 2D BlackP has also demonstrated potential for drug delivery and anti-tumor therapy, exhibiting a high drug loading capacity, biocompatibility and excellent photothermal and photodynamic properties. In this role, it shows promise in contributing to the new field of "theranostics," which combines targeted therapy with specific targeted diagnostic tests for "personalized medicine." Here, 2D BlackP has potential applications in photoacoustic imaging, as a photosensitizer in photodynamic therapy, and in photo-responsive drug delivery (Choi et al., 2018).
- *Energy storage.* An important prerequisite for any technology harnessing renewable energy (solar, wind, etc.) is an efficient energy storage system (Qiu et al., 2017). 2D BlackP combines mechanical strength, electrochemical performance, and ion-conductivity properties. These properties are vital for high-performance electrochemical energy storage, and 2D BP offers advantages over other 2D layered materials such as graphene in the development of supercapacitors with high power density and cyclability (Qiu et al., 2017).
- *Biomimetic energy production: artificial photosynthesis.* 2D BlackP has the potential to be used as an efficient broad-spectrum (UV-, visible-, and near infrared-activated) photocatalyst for use in artificial photosynthesis and renewable energy conversion (Zhu et al., 2017b). Artificial photosynthesis seeks to solve a fundamental challenge of renewable energy, by directly storing solar energy as a chemical fuel (i.e., what nature does with photosynthesis). One of the cleanest fuels is H_2, which reacts with O_2 to release energy, emitting water as the only product. Hydrogen can be generated by splitting water; however, conventional H_2 production is not sustainable when it requires natural gas or electrical power, as it uses more energy than the H_2 produced can give back. Artificial photosynthesis seeks first to use technological methods to harness solar energy for large-scale clean production of H_2 fuel and, as a second step, to use the harnessed solar energy to reduce CO_2 into CO for onward conversion into useful hydrocarbons. These processes have the potential to remove CO_2 from the atmosphere, as

> plants do, and generate liquid fuels out of CO_2, water, and sunlight, all of which are abundant and practically inexhaustible (Rahman et al., 2018). Materials like TiO_2 semiconductors with a wide band gap have previously been used for "solar to H_2" conversion. However, these materials are inefficient, because TiO_2 only absorbs the UV part of the spectrum, meaning the rest of the solar spectrum is wasted (Science Daily, 2017). In contrast, 2D BlackP can be tuned to absorb light across the UV, visible, and near infrared regions, just by varying the thickness of the sheets, meaning it is able to harvest solar energy with unprecedented efficiency (Zhu et al., 2017a). 2D BlackP, therefore, offers new opportunities for future photocatalytic conversion technology, in realizing H_2 production powered by sunlight (Batmunkh et al., 2018; Zhu et al., 2018) and carbon-neutral hydrocarbon production (Science Daily, 2017).

While 2D BlackP offers great potential in the fields of energy storage, biomedical science, catalysis, artificial photosynthesis, and photochemistry, much work remains to be done in bringing 2D BlackP to large-scale commercial production and application. In particular, there remain challenges in mass production and tuning of the structural properties of the 2D BlackP sheets and nanoflakes, and in optimizing methods of isolating 2D BlackP from exposure to the atmosphere (it is highly reactive to combinations of O_2, water, and light and is vulnerable to degradation), although successes have been achieved using capping and surface passivation technologies, as well as by synthesizing novel 2D BlackP nanostructures that are stable in air and water (Hu et al., 2018).

The commercialization of these novel 2D P materials could undoubtedly increase the importance and awareness of the value of P to society. They also have the potential to expand the role of P from its current contributions to the agroecological bioeconomy, into the technological bioeconomy, through renewable energy production and storage and improved energy efficiency and through biomedical and healthcare solutions. However, these are emerging technologies. It is premature to predict the extent to which commercial applications will be realized, the extent to which these ultrathin 2D P materials will increase global demand for bulk P resources, and their influence on world P prices. But without appropriate life-cycle management of these products and technologies, 2D P materials could also inadvertently contribute to an accelerated linear P pathway of production, consumption and disposal, depending on their future contributions to additional P in circulation and the methods and locations of disposal. Creative management of 2D P materials, throughout their life, would help in the recycling and reuse of P contained within these products and could even stimulate new impetus for recycling P from a wider range of consumer and industrial products and their wastes.

Learning from Present Production Systems and Envisioning the Future of Phosphorus within the Bioeconomy

Today's production systems have become increasingly reliant on large-scale transfers of P from mineral reserves to geographically distinct areas of grain and animal production and human consumption. The large transfer distances, and costs of recycling P from waste streams back to the areas of grain production where P is required, have proved prohibitive. This has created profound inequalities in P availability and inefficiencies in P use. It has accelerated P losses and water quality impairment and created new dependency on inorganic P fertilizers and finite nonrenewable phosphate rock reserves, precipitating a breakdown of the P cycle. By expanding the use of starch and oil crops for biofuels, to date, the bioeconomy has exacerbated this trend, contributing to a pervasive "P paradox" arising from simultaneous deficiencies and excesses of P across local, regional, and national scales.

An emerging bioeconomy based on technological advances in production of new and higher-value bio-based products could provide market stimulus and opportunities for greater circularization, where P-rich organic wastes and by-products could become more highly valorized wastes. As agricultural production of novel biomaterials and bioenergy increases, it will be vital to ensure that we are truly creating a more circular economy that goes beyond the carbon cycle, to include nutrients such as P. The development of integrated value chains of new bio-based products could also allow for codevelopment of "P refineries" to recover P for higher-value fertilizer products—and even for substitution of primary phosphate rock for production of elemental P (Ohtake, 2015).

Recovery of P could also help offset future P demands arising from the anticipated expansion in industrial production of novel 2D P allotropes, which offer a wide range of benefits in consumer, healthcare and energy technologies envisaged as a key benefit of the new global bioeconomy. These technological developments in novel P materials science potentially offer some bright new P horizons, as an antidote to the P paradox into which our agricultural production systems have engineered us. However, numerous technological and commercialization hurdles have to be crossed before such an advanced circular P economy could be realized. But if achievable, this circular approach to P management within the bioeconomy (Fig. 1) could help to break down some of the current barriers for P recovery, recycling, transport, and redistribution and allow us to start to address the fundamental inequalities we currently face in P availability, a root cause of widespread eutrophication of water bodies and a threat to our water, food and P security.

This vision of a circular approach to P management within the bioeconomy would, undoubtedly, require more coherent and integrated policy support that takes a longer-term and strategic view of the wider sustainability and circularization goals of the bioeconomy and addresses current policy shortfalls. For example, existing EU bioeconomy policies have promoted the use of lower-value applications (biofuels, bioenergy) instead of higher-value applications (biochemical, biomaterials), reducing the opportunities for cascading reuse and recycling (Bell et al., 2018). Inevitably, the demands for biomass will impose greater pressures on the agricultural sector and on land, water, and P resources in the quest for growth of agricultural production, with a multitude of potentially conflicting sustainability challenges. In Ireland, for example, the agricultural sector faces the dual challenge of delivering increased output as envisaged under FoodWise 2025 (Department of Agriculture, Food and the Marine, 2015) and delivering this growth in a sustainable manner.

Implementing a circular approach to P management within the bioeconomy will necessitate large-scale investment and a transition to fundamentally different systems of production and consumption, encompassing new technologies and infrastructures and requiring coevolving shifts in agricultural practice and stewardship of water and P. Realizing a sustainable and circular P-centric bioeconomy will also require profound societal transformations in public attitudes to waste and will necessitate recycling and engineering solutions that seamlessly link urban and rural P and bioresource economies, including producers and consumers of food, feed, fiber, and bioresources, as well as users of P fertilizer. The high costs of biorefinery technologies and competition from fossil-based technologies often render risks too high for shareholders and investors. A shift to a circular approach ultimately will require support from the public sector, for example, by funding regional bioclusters to increase regional capacity building; reducing regulatory constraints; and forming public–private partnerships, which will help to reduce the risks for private investment (Kircher et al., 2018; Philp, 2018).

With more than 40 countries currently proposing to boost their national bioeconomies, there is no better time for a clarion call for a "new" bioeconomy that is more circular than the current bioeconomy and that, at its core, tackles the current disparities and inequalities in P availability to secure our future P availability. If we fail to learn from our experiences with the broken P cycle for food, feed, and ethanol production, we risk trading one type of sustainability problem for another. For example, reducing the risk of climate change from using fossil-fuel inputs may increase the risk of insecure food systems and eutrophication of surface water, and recovering P from organic wastes drives off volatile N compounds, which then require additional energy inputs to recover, via the Haber Bosch process.

As we consider our fragmented relationship with P, at the 350th anniversary of its discovery, there remain abundant caveats, challenges, trade-offs and potential pitfalls, which will need to be overcome in our quest to reconnect our broken P cycle. The emerging bioeconomy is just one piece of a much larger puzzle of how to achieve more sustainable and circular horizons in our future use of phosphorus.

Conflict of Interest

The authors declare no conflict of interest.

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