9-1-2016

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Accepted version, *Bioresource Technology*, Vol. 215 (September 2016): 186-198. DOI. © 2016 Elsevier Ltd. Used with permission.
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Recovery of Agricultural Nutrients from Biorefineries

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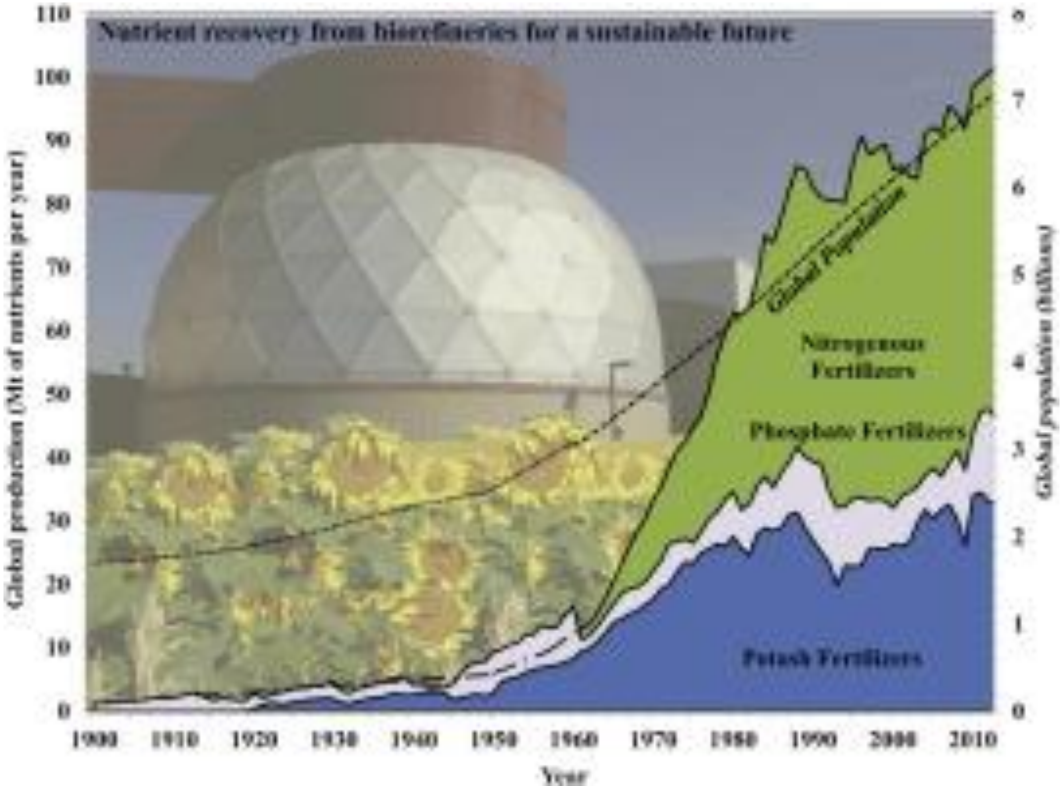
Abstract: This review lays the foundation for why nutrient recovery must be a key consideration in design and operation of biorefineries and comprehensively reviews technologies that can be used to recover an array of nitrogen, phosphorus, and/or potassium-rich products of relevance to

Bioresource Technology, Vol 215 (September 2016): pg. 186-198. DOI.

agricultural applications. Recovery of these products using combinations of physical, chemical, and biological operations will promote sustainability at biorefineries by converting low-value biomass (particularly waste material) into a portfolio of higher-value products. These products can include a natural partnering of traditional biorefinery outputs such as biofuels and chemicals together with nutrient-rich fertilizers. Nutrient recovery not only adds an additional marketable biorefinery product, but also avoids the negative consequences of eutrophication, and helps to close anthropogenic nutrient cycles, thereby providing an alternative to current unsustainable approaches to fertilizer production, which are energy-intensive and reliant on nonrenewable natural resource extraction.

Graphical abstract



Keywords: Nitrogen, Phosphorus, Potassium, Fertilizer, Wastewater

1. Introduction

We live in the age of the Anthropocene, in which today's earth can be characterized as human dominated. This domination is exemplified through alterations to biogeochemical cycles including carbon, nitrogen, phosphorus, and water. The harsh realities of a growing global population in the face of nonrenewable resource constraints, environmental quality concerns, and technological impacts in both economic and social/political realms dictate a shift toward more sustainable development. Biorefineries provide one route toward more sustainable production by valorizing waste and utilizing renewable resources.

Somewhat analogous to a petroleum refinery, a biorefinery is an integrated facility which utilizes extraction/conversion processes to produce various fuels, platform chemicals, and energy (Naik et al., 2010). Unlike conventional petroleum refineries, however, biorefineries use renewable biomass as a feedstock to produce these carbon-based products, thereby providing a sustainable option for fulfilling future product demands. Nutrients are an additional, albeit oft-omitted, biorefinery product attracting increased attention, and must also be considered as part of an integrated biorefinery and environmental management approach (Anex et al., 2007 and Tonini et al., 2013).

This review begins by establishing the importance of nutrient recovery as an integral aspect of biorefinery design and operation. The relative nutrient value of different feedstocks is assessed. Next, an overview of the nutrient-rich products that can be recovered from biorefineries is presented, followed by a comprehensive review of the technologies that can be implemented to recover these products for agricultural application. For brevity, major reviews are cited when feasible, while a more detailed list of relevant references recommended for further reading is included in the Supplementary Material.

2. The compelling case for nutrient recovery

All biological growth relies on the availability of essential elements. For plants, the three primary macronutrients are nitrogen (N), phosphorus (P), and potassium (K) as these elements are needed in relatively large amounts and are most commonly responsible for limiting growth (Leibig's mineral theory circa 1840). During the late 1800s and early 1900s, population growth and rapid urbanization led to the need to supplement crop production with nutrients beyond levels available in natural soil or locally available organic matter (*i.e.*, manure and human excreta) (Cordell et al., 2009 and Galloway and

Cowling, 2002). Increased nutrient demand initiated development of synthetic fertilizers produced using P mined from phosphate rock reserves, K mined from potash reserves, and atmospheric N fixed by the Haber–Bosch process. Harnessing access to these nutrients helped to spawn the Green Revolution, and resulted in rapid intensification of anthropogenic flows of N, P, and K over the last 200 years, leading to major impacts on earth systems.

Rock P regenerates on geologic timescales, analogous to fossil fuels, meaning that P is essentially a nonrenewable resource. At current rates of consumption, P reserves may be exhausted as soon as the next century (Cordell et al., 2009). Since approximately 90% of mined P is used for food-related activity, this looming shortage of raw material imperils food production, and subsequently, the human population (Cordell et al., 2009). Moreover, P reserves are geographically concentrated, with about 83% of the world's resources located in only four countries (Vaccari, 2009). As there is no substitute for P, it is essential to move towards closing the anthropogenic P cycle by recovering P from renewable biomass and reusing it to promote agricultural productivity.

Unlike P, N is a readily renewable resource procured from vast atmospheric reserves for human use via the Haber–Bosch process. Approximately 80–90% of Haber–Bosch-fixed N is used for fertilizer production, and more than half of the food consumed in the world is now grown using N fertilizer produced by this process (Galloway and Cowling, 2002 and Galloway et al., 2008). The remaining N is used for chemical production, e.g., nylon, plastic, explosives, rocket fuels, and animal feed supplements (Galloway and Cowling, 2002 and Galloway et al., 2008). Today, Haber–Bosch is responsible for more N fixation (121 Tg/yr in 2010) than all natural terrestrial processes combined (Galloway and Cowling, 2002). The magnitude of human influences on N flows has substantially altered the global N cycle, which may have serious consequences in water (eutrophication), the lithosphere (soil N saturation and impacts on biodiversity), the atmosphere (greenhouse gases, acid rain, smog), and human systems (resource constraints and economics). Although N is a renewable resource, the Haber–Bosch process is extremely energy intensive, accounting for an estimated 1–2% of the world's total energy consumption (Matassa et al., 2015). Energy-efficient recovery of N from biorefineries would reduce reliance on the Haber–Bosch process, thereby avoiding the associated energy consumption and downstream consequences.

In comparison to N and P, K recovery has received considerably less attention, yet K is also an essential growth nutrient with finite global reserves. Although there are likely several centuries of supply remaining, the more precarious global issue is that 90% of K production is concentrated in only three countries (Ciceri et al., 2015 and Vaccari, 2009). As there are large amounts of K available in certain waste materials, *e.g.*, sugar cane and beet processing, spent grains, yeast, and manure, global demands (approximately 90% of which stem from fertilizer production) could be fully satisfied by recovery and reuse of K from renewable waste biomass (Batstone et al., 2015). K recovery would proactively alleviate future sourcing concerns due to availability, pricing, and geopolitical relations. Likewise, nutrient recovery from waste streams has the potential to largely satisfy P demand in high use efficiency scenarios (*i.e.*, in combination with improved agricultural and food chain efficiency and consumption patterns) as well as approximately 50% of global N demands (Batstone et al., 2015 and Cordell et al., 2009).

Fig. 1 illustrates trends in N, P, and K fertilizer production alongside historic fertilizer prices. As shown, production increased dramatically in the latter half of the 20th century, although prices remained relatively stable until spiking in the last decade. In the future, increased fertilizer demand (and the substantial environmental footprints associated with fertilizer production) is a likely consequence of growing global population and affluence. Economics suggest that as supplies decrease and demand increases, prices will likewise increase. Though future production patterns remain uncertain, the inexact estimation of reserves and timing of peak consumption of essential non-renewable resources is not the critical issue here. Instead, the important take away is that the sustainability of a prosperous global population depends on transition to renewable resource utilization.

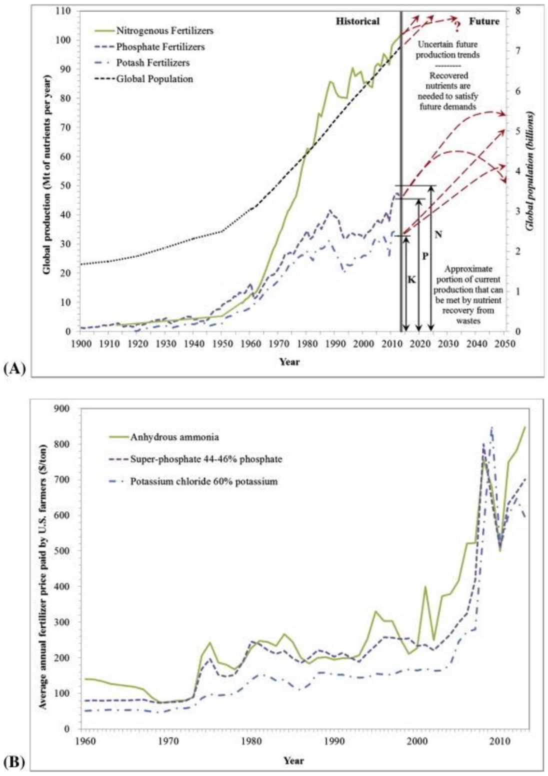


Fig. 1. Fertilizer nutrient trends. (A) Global fertilizer production (million metric tonnes of nutrient/year) alongside world population. Historical trends from 1900 to 2013 are shown. While future projections are uncertain, recovered nutrients must play a major role in supplementing nonrenewable supplies. (B) Average annual prices for representative N, P, and K fertilizers paid by U.S. farmers (1960–2013, $US). Data sources used to create the figure are described in the Supplementary Material.

A simultaneous advantage of recovering nutrients from waste biomass is protection from environmental degradation stemming from eutrophication. Eutrophication results in decreases in the dissolved oxygen content of environmental waters caused by algal overgrowth as a result of excess P and/or N concentrations. According to the U.S. Environmental Protection Agency, eutrophication is the biggest overall source of impairment of U.S. waterbodies (Mayer et al., 2013), and is responsible for more than 400 coastal dead zones around the world (Diaz and Rosenberg, 2008). To address this issue, limitations on nutrient levels in waste discharges have been established around the world. As nutrients must be removed from waste streams prior to discharge to achieve regulatory compliance, biorefineries provide an excellent opportunity to recover nutrients from wastes and recycle it directly back into fertilizer production, thereby short circuiting the lengthy natural-anthropogenic cycle. Characterization of biorefinery feedstocks gives some insight into the fraction and recoverability of these nutrients, *i.e.*, what are the optimal feedstocks for nutrient recovery?

2.1. Where is the N, P, and K?

Biorefinery feedstocks generally consist of biomass containing a high fraction of carbon. For example, bioenergy production typically emphasizes the use of lignocellulosic biomass consisting primarily of the carbon-rich polymers cellulose, hemicellulose, and lignin. However, all biomass also contains nutrients, meaning that N, P, and K are theoretically recoverable from any biomass, including, but not limited to, crop residue, vegetative material, animal waste, and food byproducts (Naik et al., 2010). Inputs to biorefineries are generally in the form of raw biomass, with an average biomass composition of 95% proteins, carbohydrates, lignin and lipids (Octave and Thomas, 2009). Non-structural components such as protein, ash, and organic acids make up only a small fraction of the feedstock, but their presence can be significant in sustainable operation of an industrial-scale biorefinery (Sluiter et al., 2010). For perspective, Table 1 lists the nutrient content of a range of potential biorefinery feedstocks, while Table 2 lists approximate nutrient contents of cellular structures. Waste-based biomass generally has higher N, P, K content relative to lignocellulosic plants, and is thus ideal biorefinery feedstock from the perspective of nutrient recovery.

Table 1. Approximate nutrient content of various potential biorefinery feedstocks.[a]

Category	**Feedstock**	**N**	**P**	**K**	**(unit)**
Waste Biomass	Beef cattle feedlot wastewater	54–113	14–105	465–503	(mg/L)
	Coffee production wastewater	85–173	4–38	20–46	(mg/L)
	Coke plant wastewater	757	0.5		(mg/L)
	Dairy wastewater	185	30		(mg/L)
	Distillery wastewater	2700	680	9600–17,500	(mg/L)
	Domestic wastewater	20–85	4–15	30	(mg/L)
	Empty fruit bunch palm oil waste	0.33	0.03	0.80	%
	Molasses vinasse	1660–4200	225–3040	9600–17,500	(mg/L)
	Palm oil mill effluent	700	450	1710	(mg/L)

Category	Feedstock	N	P	K	(unit)
	Paper mill wastewater	11	0.6		(mg/L)
	Pig manure	2.0–3.0	9.9–12.5	3.5–6.0	%
	Poultry feedlot wastewater	802	50		(mg/L)
	Soybean processing water	1700–2550	125–183		(mg/L)
	Sugar cane stillage	2980	239		(mg/L)
	Sugar cane vinasse	600–4200	100–3800		(mg/L)
	Swine feedlot wastewater	895–3200	66–324	1.4	(mg/L)
	Tannery wastewater	273	21		(mg/L)
	Textile wastewater	90	18	30–50	(mg/L)
	Winery wastewater	110	52	201	(mg/L)
Microbial Biomass	Algae	7–20	1		%
	Microbial biomass	12	2		%
Plants	Cereals (wheat)	0.1			%
	Corn cob	1.38	0.09	0.46	%
	Corn grain	2.15	0.34	0.42	%
	Corn leaves	1.30	0.21	1.48	%
	Corn silage	1.3	0.16	0.9	%
	Corn stem	0.84	0.09	1.23	%
	Giant brown kelp	1.22			%
	Peach leaves		0.14	2.45	%
	Pine	0.1			%
	Rapeseed crop biomass	3.3–5.4			%
	Sugar cane begasse	0.73			%
	Water hyacinth	1.96			%
	Wood	0.07–0.39			%

[a] References provided in the Supplementary Material.

Table 2. Macronutrients in cellular structures.[a]

Nutrient	Nutrient-containing structure	Concentration of element in structure (%)	Descriptions of organisms associated with higher concentrations of structure
P	Free Phosphate	39	
	Polyphosphate	<39	Anoxic polyphosphate accumulating organisms
	DNA/RNA	8	
	ATP	18	
	Phospholipids	5	Organisms with cell walls or gram negative bacteria
	Hydroxylapatite	18	Organisms with bone, cartilage, and enamel
N	Ammonia/ammonium	78–82	
	Nitrate/nitrite	23–30	

Nutrient	Nutrient-containing structure	Concentration of element in structure (%)	Descriptions of organisms associated with higher concentrations of structure
	Amino acids	632	Organisms with high protein content
	DNA/RNA	14	Value represents average in total structure
	Chlorophyll	6–9	Photosynthetic organisms
K	Free potassium ion	100	

[a] References provided in the Supplementary Material.

Approximately 15% of agricultural N input ends up in wastewater, while another 19% is found in animal manure (Matassa et al., 2015), making these wastes an important target for N recovery. Municipal and agricultural wastewater are also major caches of P, as approximately 15% and 40% of mined P ends up in these domains, respectively (Cordell et al., 2009 and Rittmann et al., 2011). In addition to excreta, food commodities also generate municipal solid waste, which accounts for approximately another 5% of mined P (Cordell et al., 2009 and Rittmann et al., 2011). A simplistic analysis of K flows suggests that >90% of agricultural inputs of mined K reside in animal waste, while municipal waste contains <1% (analysis detailed in the Supplementary Material). In addition to high nutrient content, waste biomass feedstock offers a double benefit of transforming a nuisance waste into a beneficial product, prices of which are expected to rise in the future. Although N, P, and K concentrations and availabilities in biorefinery feedstocks vary greatly, Table 1 and Table 2 provide good general values. The biomass processing approach will further determine the potential for recovery of nutrient-rich products.

3. Nutrient-rich recoverable products

Before examining the nutrient recovery technologies, the relevant recoverable products are reviewed, as selection of the desired product dictates process implementation. Although there is some potential for recovery of nutrients via platform or specialty chemical production at biorefineries, levels of N, P, and K are essentially negligible in the top 12 valuable building block chemicals (Werpy et al., 2004), accounting for 1.7%, 0%, and 0% by mass, respectively. These values ignore relative abundance of the products, but this demonstrates that chemical production represents a relatively minor route of nutrient reuse. This, in combination with the fact that approximately 90% of anthropogenic flows of P, K, and N are funneled to agricultural food production, leads to the emphasis in this review being on recovery and reuse of nutrient-rich products for agricultural applications. Recoverable agricultural nutrient products can include complex organic mixtures, *e.g.*, biomass; mixed residuals from thermochemical processes, *e.g.*, char and ash; or separated N, P, K-specific chemicals, *e.g.*, NH_4^+ or K-based struvite. Table 3 lists the nutrient value of these recoverable products alongside commercial fertilizers for comparison.

Table 3. Fertilizer potential (NPK) of recovered nutrient products and commercial fertilizers.[a]

Category	Product	Chemical formula	NPK rating[b]
Mixed nutrient products	Wastewater biosolids	Organic mixture	35-0
	Heat-dried wastewater biosolids (Milorganite)	Organic mixture	6-2-0
	Incinerated sewage sludge ash (ISSA)	Organic mixture	0-6-2
	Wastewater-derived biochar	Organic mixture	6-13-0
	Bone meal	Organic mixture	4-2-0
N, P, K-specific products	Struvite (N)	NH_4MgPO_4	10-52-0
	Struvite (K)	$KMgPO_4$	0-45-30
	Hydroxylapatite	$Ca_5(PO_4)_3$	0-44-0
	Ammonium sulfate	$(NH_4)_2SO_4$	21-0-0
	Ammonium nitrate	NH_4NO_3	35-0-0
	Anhydrous ammonia	NH_3	82-0-0
	Iron(III) phosphate	$FePO_4$	0-47-0
	Calcium nitrate	$Ca(NO_3)_2$	17-0-0
	Urea	$(NH_2)_2CO$	64-0-0
Commercial-grade fertilizers	Ammonium polyphosphate[c]	$[NH_4PO_3]_n$	14-73-0
	Monoammonium phosphate	$NH_4H_2PO_4$	12-62-0
	Diammonium phosphate	$(NH_4)_2HPO_4$	21-54-0
	Potassium nitrate	KNO_3	14-0-47
	Monocalcium phosphate	$Ca(H_2PO_4)_2$	0-61-0
	Potassium sulfate	K_2SO_4	0-0-54
	Potassium chloride	KCl	0-0-63

[a] References provided in the Supplementary Material.
[b] Based on N, P_2O_5 and K_2O rating system.
[c] Small variations expected in NPK based on polymer length.

3.1. Mixed nutrient products

The primary means of nutrient recovery and reuse today is through land application of organic solids such as biosolids, which are the bacterial biomass byproduct from wastewater treatment. Biosolids have long been used as a nutrient source for agriculture, although location-specific restrictions on the basis of pathogens, heavy metals, trace organic contaminants, and/or NPK ratios are important considerations. Once biosolids are applied to agricultural fields, the nutrients are slowly released through natural biodegradation. Similarly, the nutrients locked in large organic biomass structures, particularly single cell biomass which does not have any further use, provides an opportunity to serve as a value-added recoverable product for human food and animal feed. Plant, algae, and microbial-derived biomass may also be directly land applied, but additional research is needed to establish efficacy (*e.g.*, nutrient release rates) (Mehta et al., 2015). Composted organic materials also provide excellent agricultural properties (Hargreaves et al., 2008). Additionally, bone meal produced from animal or slaughterhouse waste is another nutrient-rich byproduct that can be beneficially recycled into agriculture as a slow release P source (Mondini et al., 2008).

Char and ash are increasingly popular soil amendments, offering potential for carbon sequestration, heavy metal immobilization, and improved soil quality (Mehta et al., 2015). These heterogeneous products may contain appreciable amounts of nutrients, depending on feedstock and process operation. Bridle and Pritchard (2004) found that 100% of the P and K in sewage sludge and 55% of N were retained in the solid biochar product following pyrolysis. Biochar has been shown to stimulate plant growth when used as an amendment in soil lacking nutrients (Liu et al., 2014). Biochar may also be used to adsorb N and K prior to land application, as wastewater-saturated biochar can stimulate grass growth (Carey et al., 2015). The viability of char and ash use in agricultural applications depends on nutrient bioavailability and levels of heavy metals co-concentrated in the mixed product.

3.2. N, P, and K chemical products

Although complex mixed nutrient products will continue to play an important role in agriculture (and sustainable resource management scenarios), separate streams of NH_3-N, PO_4-P, and K salts are undeniably desirable as they afford greater flexibility in broader applications and have higher market value (Gerardo et al., 2015). Table 3 summarizes the recoverable N, P, and K chemical products used in agricultural fertilizer applications. Box 1 provides a brief description of the speciation and terminology associated with agriculturally-relevant nutrients.

Box 1. Agriculturally-relevant nutrients. Related references are found in the Supplementary Material.

Phosphorus: Soluble P species may be classified as organic P, orthophosphates, or polyphosphates. Organic P is usually considered nonreactive and nonbioavailable, and must be converted to inorganic forms to enable recovery and/or biological uptake. The orthophosphates, also called reactive P, include species (*e.g.*, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4) that are readily available for biological metabolism without being further broken down. Polyphosphates include complex molecules with two or more P atoms, oxygen, and sometimes hydrogen. These species can be converted to orthophosphates via hydrolysis. For agricultural fertilizer applications, P must be in the orthophosphate form.

Nitrogen: Plants are able to uptake several different forms of N, including ammonium (NH_4^+), nitrate (NO_3^-), and urea ($(NH_2)_2CO$). Unless fresh source-separated urine is used as the biorefinery feedstock, NH_4^+ and its conjugate base, ammonia (NH_3), as well as NO_3^- and its reduced form, nitrite (NO_2^-), will be most commonly encountered. Their relative distribution will depend on the oxygen concentration in the matrix. All of these species are water soluble, although NH_3 may volatilize depending on pH and temperature (K_H = 57 M/atm).

Potassium: The water soluble free ion form, K^+, is needed for plant growth as K is involved in over 60 different enzyme systems in plants and regulates electrochemical and osmotic pressure across cell membranes. Very little free K is available in nature, and most synthetic fertilizers are in the KCl form, although other K salts are also used, as shown in Table 3.

The most commonly recovered N species are NH_3 and NH_4^+, which are most often recovered in solid precipitate forms. The most recoverable form of P in biorefining processes is phosphate, which can be recovered from aqueous streams as solid precipitates. P reuse as struvite and hydroxylapatite is currently favored as these granular products feature qualities comparable to mineral fertilizers (Johnston and Richards, 2004). In addition to its use as fertilizer, hydroxylapatite can be substituted for rock phosphate as a feedstock for fertilizer and chemical production (Cornel and Schaum, 2009). P precipitation is relatively effective; however, speciation of the product is very important in terms of fertilizer reuse. For example, when P is precipitated with iron or aluminum, it exhibits limited bioavailability. The major recovered K-product today is K-struvite, which provides the advantage of simultaneously recovering P. Additionally, K salts can be recovered for use as fertilizers.

Biorefineries offer an opportunity to recover any and all of these nutrient-rich products, and selection of the desired product(s) will determine which recovery technologies should be employed, as reviewed in the following section.

4. Nutrient recovery technologies

Biorefineries are characterized by great diversity in terms of both feedstock inputs and desired product outputs, with both of these choices governing the sequence of physical, chemical, and biological processes needed to recover nutrients. This diversity presents a challenge in that process selection can vary widely; yet, this flexibility also presents an opportunity as some nutrient recovery technologies may already exist in some biorefineries, while other processes may be new additions for nutrient recovery.

As outlined by Mehta et al. (2015), nutrient recovery can be accomplished through various sequences involving any or all of the following steps: (1) capture and concentration of nutrients from dilute streams, (2) release of nutrients from complex structures, and (3) final extraction of nutrient products. In the first step, nutrients in dilute streams may be concentrated since the efficiency of most nutrient recovery processes is proportional to nutrient concentrations, but levels in biomass feedstock are often low. In the second step, complex organics or solids containing nutrients may undergo processing to release soluble inorganic P, K, and (also possibly volatile) N, as these forms are more readily recoverable (Batstone et al., 2015, Mehta et al., 2015 and Rittmann et al., 2011). In the final step, the actual nutrient product, *e.g.*, precipitate, is extracted for reuse. The following sections provide a comprehensive review of nutrient recovery technologies, including processes addressing each of these three steps, which can be integrated into biorefineries to produce valorized mixed nutrient, P, N, and K products for reuse in agricultural applications. Additional details related to operational parameters and performance for nutrient recovery processes can be found in several excellent reviews focused on wastewater treatment, including: Batstone et al., 2015, Mehta et al., 2015 and Morse et al., 1998, and Rittmann et al. (2011).

4.1. Mixed nutrient recovery technologies

4.1.1. Anaerobic digestion to produce biosolids

Anaerobic digestion is a widely-used biological process to convert organic waste to methane (CH_4). By converting solids to gases, the volume of waste is reduced, making it popular for handling both agricultural waste and municipal wastewater residuals. In addition to the value of the CH_4 in the biogas, the heterogeneous, nutrient-rich biosolids product is valuable as a fertilizer, and over half of the wastewater biosolids produced in the U.S. are land applied (NEBRA, 2007). Thus, anaerobic digestion could be one key nutrient recovery process used in biorefineries.

Moreover, anaerobic digestion can release nutrients ahead of extraction technologies as part of an N, P, and K-chemical recovery scenario since it alters nutrient speciation and solubility. Anaerobic digestion could be especially useful for producing a liquid stream that facilitates N and K recovery because neither element readily precipitates or volatilizes in digesters, generally leading to higher effluent concentrations of recoverable N and K in the form of NH_4^+ and K^+, respectively (Marti et al., 2008 and Sanchez et al., 2000). N that is not in a readily available form, such as the organic-bound N found in amino acids, proteins, or urea, is biotransformed into simple carbohydrates and lipids and then into NH_4^+ during anaerobic digestion (Batstone and Jensen, 2011). The breakdown of organic N is impacted by both temperature and pH, with higher temperature and neutral pH favoring conversion of organic N to NH_4^+ (Sanchez et al., 2000).

The fate of P-species during anaerobic digestion is heavily dependent upon the other chemicals present. Inevitably, some P is assimilated into biomass, but P is more economically viable as a precipitate than it is in biosolids (Gerardo et al., 2015 and Latif et al., 2015), especially because the N:P ratio in biosolids can differ from crop requirements, and over application of P can have negative impacts in the environment (Massé et al., 2007). Organic P is converted to inorganic P during digestion, but this inorganic P is not typically present in the effluent as soluble phosphate because it forms chemical precipitates, including Ca-P, Mg-P, and Fe-P solids (Güngör and Karthikeyan, 2008 and Latif et al., 2015). While some of these precipitates have economic value as fertilizers, they are difficult to recover from the biosolids matrix. Thus, to optimize the portfolio of recovered products, a well-designed biorefinery will likely include processes to recover P-specific products ahead of anaerobic digestion or in the nutrient-rich solids dewatering stream. Treatments focused on releasing organic P to facilitate recovery ahead of anaerobic digestion or from the biosolids include lowering pH, microwave thermochemical pretreatment, ultrasonic, or advanced oxidation processes (Jin et al., 2009, Latif et al., 2015, Rittmann et al., 2011 and Wang et al., 2010).

4.1.2. Thermal processing to produce biochar or ash

Pyrolysis and gasification are possible keystone operations for a biorefinery scenario (Gebreslassie et al., 2013 and Naik et al., 2010). Both technologies rely on an oxygen-limited atmosphere and high temperatures to produce three possible phases of materials: gas (py-gas, syngas), liquid (py-oil), and solid (ash, biochar) (Inguanzo et al., 2002). Although both technologies are high temperature (>350 °C) non-oxidative processes, gasification typically refers to a process which uses higher temperature (>700 °C) and longer retention times to obtain complete conversion of organic material to an energy gas (syn-gas), leaving a solid-phase ash (inorganic non-volatile constituents) (Mohan et al., 2014). Pyrolysis is a lower temperature operation which leaves some of the organic fraction in a solid form (*i.e.*, biochar) and may also result in a fraction of gas which condenses to liquid at ambient temperatures.

In the case of gasification, only inorganic components (*i.e.*, ash) are left as a solid form. This may contain metals or other components which do not volatilize at high temperatures. No N will be retained in the solid product, whereas all recoverable P and K will be in the ash since they are not present in appreciable concentrations in volatile compounds (Azuara et al., 2013). The P-rich ash may be used as a soil amendment if it complies with metals-applications standards. Alternatively, using downstream ash processing, as discussed in Section 4.2.2, P and K-specific nutrient products may be separated from the ash for agricultural reuse.

In pyrolysis, the solid biochar product can contain a sizeable fraction of C, N, P, and K (Bridle and Pritchard, 2004 and Carey et al., 2015). The gas contains energy-rich compounds such as CO, H_2, CH_4, and short chain hydrocarbons. The non-condensable gas is typically combusted for energy, before or after refinement (Conesa et al., 2009 and Gebreslassie et al., 2013). Unlike many other biorefinery processes, a portion of recoverable N will be in the gas phase, primarily as NH_3. One study of pyrolysis of biosolids at temperatures above 500 °C found an approximately even distribution of N among the gas, char, and condensable oils phases (Tian et al., 2013). From the gas phase, chemical N products can be extracted by absorption or stripping, as discussed in Section 4.3.2. The condensable liquid fraction, or oil, has many components which can be separated to utilize as platform chemicals, and may also be chemically transformed to create drop-in liquid fuels (Volli and Singh, 2012), but is inconsequential in terms of P and K content and recovery potential. Nitrogenous species found in liquid condensates are in the form of amino, heterocyclic-N, and nitrile compounds (Tian et al., 2013) which are potentially recoverable as N-specific chemicals using downstream processing.

Incineration is an additional thermal process that can be employed using inputs of dry biomass for direct energy production, while the ash produced would be expected to contain the P and K, and may have reuse potential as a soil amendment. For example, incinerated sewage sludge ash (ISSA) may contain 10–25 wt% as P_2O_5 (Donatello and Cheeseman, 2013). However, further processing to separate metals and extract specific nutrients from ISSA is currently a more common approach to nutrient recovery.

4.1.3. Aerobic composting to produce soil amendments

Composting is defined as "the transformation of biodegradable organic material from various sources into humic substances" under aerobic conditions (de Bertoldi et al., 1983). During the composting process, the long-chained organic matter in biomass is oxidized to short-chain products, while a mixture of biogases are released to the atmosphere, including CO_2, NH_3, and a small amount of N_2O or CH_4 (He et al., 2001 and Hellebrand, 1998). Mature composting products are often land applied directly as fertilizer (Bernal et al., 2009).

Since composting products are widely used for agricultural applications, the main nutrient recovery focus is mitigating N losses to the atmosphere (Beck-Friis et al., 2001) while converting polyphosphate to orthophosphate. The extent of gaseous N emissions is affected by composting process design and operational parameters including aeration rate and mode, temperature, water content, C/N ratio, and porosity (Bernal et al., 2009, Jeong and Kim, 2001, Yang et al., 2008 and Yang et al., 2009). In terms of total N losses, gaseous NH_3 emission are generally much larger than N_2O (Beck-Friis et al., 2001 and Jeong and Kim, 2001). However, since N_2O has a 310-fold higher global warming potential than CO_2, it is necessary to reduce atmospheric emissions of both N-containing gases. Limiting denitrification by minimizing anoxic or anaerobic microenvironments is a practical means of reducing N_2O generation, and can be done by increasing the efficiency of oxygen transfer and reducing water content, *e.g.*, adding biochar (Wang et al., 2013). Ammonia emissions depend on the N content in the biomass (NH_3 can represent 25–78% of initial total N), pH, and temperature (Komilis and Ham, 2006 and Leytem et al., 2011). Addition of Mg or other metallic salts and optimization of aeration strategies can reduce emissions of NH_3 (Jeong and Kim, 2001), thereby retaining N in the matured compost, which can serve as a direct source of N for plants.

Most of the P is retained in the composted solids except for that lost in the leachate (Parkinson et al., 2004). Well-adjusted biomass water content and optimized aeration rates can minimize leachate generation, thereby reducing P losses. Dosing of external metallic salts such as Mg can also shift P fractions by converting readily-soluble P to slow-release P, thereby increasing its value as a fertilizer (Jeong and

Kim, 2001 and Yang et al., 2009). During composting, the fraction of water-soluble K also increases (Nishanth and Biswas, 2008). The end result is that composting reduces the solids fraction but retains N, P, and K. Thus, composting increases the nutrient value of the solids, thereby producing a nutrient-rich biomass suitable for nutrient-deficient soils.

4.2. Phosphorus-selective recovery technologies

Value-added chemical P products can be recovered either from solid or liquid phases. The solid phase offers an advantage of smaller working volumes as P is often concentrated into the solid phase from a more dilute aqueous solution. Although the solid-bound P must be released prior to final extraction of the P product, higher starting concentrations are advantageous because recovery processes tend to perform better at higher P levels. Nutrient-extractable solid phases include biomass, biochar, and ash.

4.2.1. Biological P selection for P-extractable solids

Nutrient-extractable biomass can include the biosolids produced during anaerobic digestion, as described in Section 4.1.1, or plant and microorganism biomass. One of the best established approaches to P accumulation in solids is the use of phosphate accumulating organisms (PAOs), which uptake and store greater amounts of P than typical organisms. Enhanced biological P removal (EBPR) selects for PAOs using alternating anaerobic/aerobic conditions, and when applied in wastewater treatment, EBPR sludge can contain up to 5 times more P in comparison to typical activated sludge treatments (Rittmann and McCarty, 2001). Although EBPR was developed to improve P removal from wastewater, once concentrated in the sludge, P chemicals may be recovered following release of the P under anaerobic conditions or further physicochemical processing.

Several other microbes, including purple nonsulfur bacteria, cyanobacteria, and algae, exhibit potential to bioaccumulate potentially extractable nutrients in forms such as proteins or polyphosphate (Mehta et al., 2015). P-rich bacteria tend to settle easily by gravity, but harvesting algal biomass poses greater challenges for full-scale applications (Christenson and Sims, 2011).

Several additional challenges to overcome in scaled-up operations include sufficient nutrient supply to the microbes, gas transfer, and process footprint (Christenson and Sims, 2011). Ongoing algal-based biorefinery research seeks to exploit the potential for co-recovery of biofuel, nutrients, and other high-value byproducts while sequestering carbon and treating wastewaters.

The success of technologies targeting recovery of P-rich chemical products depends on P being present in the inorganic form. Thus, prior to implementation of any P recovery technology, organic P must be released from complex structures via processes such as oxidation or hydrolysis (Rittmann et al., 2011).

4.2.2. Chemical P extraction from solids

Chemical extraction processes using combinations of acid/base addition and/or thermo/chemical/electrical operations can be used to release P from solids such as municipal solid waste, wastewater sludge, or the ash and char produced by thermochemical processes. Wet acid leaching at a pH less than approximately 3 has been applied for recovery of P minerals from ISSA as chemical P products exhibit increased bioavailability in comparison to the ash itself (Donatello and Cheeseman, 2013). One potential disadvantage of acid leaching (or bioleaching using select microorganisms, e.g., *Acidithiobacillus ferrooxidans*) is that metals leach alongside P, which may necessitate further processing if heavy metals are present in the waste matrix (Donatello and Cheeseman, 2013 and Mehta et al., 2015). Thermal processing of ash or char with 5–15% KCl or $MgCl_2$ can remove heavy metals; however, a large proportion of the K is also lost (Donatello and Cheeseman, 2013 and Mehta et al., 2015). A number of technologies have been commercialized targeting nutrient recovery from sludge and ISSA, as summarized by Donatello and Cheeseman, 2013 and Mehta et al., 2015, and Morse et al. (1998), many of which operate at higher temperatures and pressures to aid nutrient extraction.

4.2.3. Physicochemical recovery of soluble P

Once released in the soluble orthophosphate form, a range of physicochemical processes can be applied to further concentrate P and recover chemical P fertilizers. Eventually, however, all paths to P recovery for agricultural applications currently lead to precipitation of solid mineral products, the most common of which are struvite and hydroxylapatite. As precipitation occurs spontaneously at high concentrations, P may have to be concentrated from dilute streams using initial treatments such as adsorption, ion exchange, or electrochemical processing.

Conventional coagulants such as iron effectively adsorb P, but reuse of the resulting products is often constrained by limited agricultural bioavailability (Mayer et al., 2013 and Rittmann et al., 2011). Innovative adsorbents and ion exchangers that selectively and reversibly capture P from complex waste streams are much more effective and relevant to recovery applications. As summarized by Mayer et al. (2013) and Rittmann et al. (2011), polymeric hydrogels, iron-based layered double hydroxides, hydrotalcite, and layered double hydroxides demonstrate promise for P recovery. P-specific anion exchangers, including iron and copper-loaded polymeric resins offer strong potential to selectively and reversibly capture P by exchanging it with other anions such as Cl^-. These materials can concentrate P up to 100 times influent levels, thereby facilitating precipitation of P-rich products (Williams et al., 2015). Other P adsorbents reported in the literature include zirconium, zirconium-loaded orange waste gel, and numerous metal oxide-based byproducts (*e.g.*, fly ash, steel slag, and red mud) (Mayer et al., 2013, Mehta et al., 2015 and Rittmann et al., 2011). The recovery efficiency and bioavailability of the recovered P varies widely among these adsorbents, dependent on the affinity between P and the binding material. By binding nutrient-specific adsorbents to a magnetic carrier such as magnetite, montmorillonite, or zirconium ferrate, high recovery efficiency may be obtained with a small process footprint, but additional research is needed to better define process performance and economics (Mehta et al., 2015 and Rittmann et al., 2011).

Emerging electrochemical technologies such as electrodialysis and capacitive deionization also offer promise for nutrient recovery (Li et al., 2015 and Rittmann et al., 2011). Electrodialysis selectively separates anions such as PO_4^{3-} from cations such as NH_4^+ and K^+ using an applied electric field and ion exchange membranes. While electrodialysis has the potential to recover all of the nutrients, it is currently hampered by high energy consumption (Li et al., 2015). Capacitive deionization uses a charged electrical field to attract ions to the electrodes. Developed for desalination, the potential of this technology for nutrient recovery has yet to be established (Rittmann et al., 2011).

Once concentrated, precipitation of P-rich solid fertilizer products is typically facilitated using additions of Mg^{2+} and $pH \geqslant 8.5$ or Ca^{2+} and $pH \geqslant 10$ to achieve molar ratios and equilibrium conditions suitable for struvite or hydroxylapatite precipitation, respectively.

4.3. Nitrogen-selective recovery technologies

Analysis of the anthropogenic N cycle reveals key processes and targets for N recovery. Approximately 34% of total N entering the agricultural system is ultimately present in animal waste and municipal wastewater (Matassa et al., 2015), making them excellent biorefinery feedstocks to maximize N recovery. Current biological wastewater treatment plants convert NH_3 to NO_3^- through nitrification, with potential conversion to N_2 gas through denitrification, essentially releasing N back to the atmosphere. By recovering NH_3-N instead of converting it to NO_3^- or N_2, substantial energy savings may be realized through reduction of Haber–Bosch energy requirements for N fixation and aeration processes to drive nitrification. In the following section, N recovery using both biological and physiochemical processes is discussed, with an emphasis on wastewater and animal waste as the most fruitful biorefinery feedstocks for N recovery.

4.3.1. Biological N recovery in the form of single cell proteins

Ammonia-N can be recovered from biomass in the form of microbial cells (single cell protein, SCP). The concept of SCP recovery originated from research on algae and lithotrophic bacteria (Vincent, 1969), and reports have shown that the SCP synthesized by methane oxidizing bacteria is suitable for animal feed (D'Mello, 1972 and Matassa et al., 2015). As protein is a key dietary need, SCP has great potential to be used to feed not only animals, but also as food to directly satisfy human dietary needs, thereby augmenting the food production system by bypassing resource-intensive fertilized crop production (Matassa et al., 2015).

Multiple approaches to SCP synthesis can be used to improve N recovery. Anaerobic digestion can serve as the first step for SCP synthesis from biomass or wastewater as it directly releases high concentrations of NH_3 and large volumes of CH_4 (D'Mello, 1972 and Rittmann and McCarty, 2001). NH_3 can satisfy the N needs of the methane oxidizing bacteria used for SCP production, while CH_4 serves as the C source (Bough et al., 1972 and D'Mello, 1972). In addition to methane oxidizing bacteria, algae and fungi can also synthesize SCP using NH_3 from biomass (Cysewski and Wilke, 1976 and Anupama and Ravindra, 2000). The review by Anupama and Ravindra (2000) summarizes many species of fungi and algae (*e.g.*, cyanobacteria) suitable for SCP synthesis. This bioconversion approach lends itself well to implementation in biorefineries as low value organic material can be used to produce multiple value-added products, including biofuels and SCP, as well as treated wastewater.

4.3.2. Physicochemical recovery of N from biomass

As described for P, N recovery technologies can be applied to concentrated N streams released from N-rich solids as well as mainstream liquids. Typical physicochemical approaches for N recovery have been well summarized, including NH_3 stripping and distillation, NH_4^+ precipitation as struvite, ion exchange for NH_4^+ and NO_3^- recovery, and NH_3 adsorption (Anthony, 1971, Capodaglio et al., 2015, Rulkens et al., 1998 and Williams et al., 2015). The form of N present (either NH_3/NH_4^+ or NO_3^-/NO_2^-) and concentration dictate the best strategy for N recovery. Nitrate can only be recovered using anion exchange resins (Samatya et al., 2006), followed by precipitation as an inorganic nitrate salt (as listed in Table 3) for agricultural application. Conversely, multiple NH_3/NH_4^+ recovery technologies are available.

The concentration of NH_3 is one of the most important factors for determining the most suitable means of recovery. When there is a high concentration of NH_3, (*i.e.*, NH_4-N >2000 mg/L), air stripping and distillation are effective for N recovery, although pH (>9.5) and temperature adjustments are needed (>80 °C) (Bonmatí and Flotats, 2003 and Mehta et al., 2015). Capture efficiency of NH_3 during stripping is high (up to 98%), and recovery can be improved through application of a vacuum (El-Bourawi et al., 2007 and Ippersiel et al., 2012). The final N fertilizer product (*i.e.*, NH_3/NH_4^+ salts or concentrated NH_3 solution, as shown in Table 3) is obtained via condensation, absorption, or oxidation of the separated NH_3 (Mehta et al., 2015). Although higher concentrations always favor improved and faster recovery rates, when lower NH_4^+ concentrations are encountered, NH_4^+ may be concentrated, *e.g.*, using clinoptilolite ion exchange media, followed by precipitation as struvite (Williams et al., 2015).

Ammonia can also be recovered from the liquid phase using gas permeable membranes which allow NH_3 to permeate through a hydrophobic membrane, after which it can either be absorbed into an acidic solution or condensed to produce concentrated NH_4^+ liquid. Efficiency is improved by driving the distribution toward NH_3 rather than NH_4^+ using higher temperatures (up to 80 °C) and pH (>9) (Mehta et al., 2015).

For large volumetric flows of wastewater, an emerging strategy using complete anaerobic treatment (*e.g.*, anaerobic membrane bioreactors) can be an effective option in terms of co-recovery of nutrients and energy. Using conventional treatment approaches, the energy used for wastewater treatment is about 3–4% of total electricity generated in the U.S. (USEPA, 2012), and a large amount of this is used for N removal from wastewater. Alternatively, complete anaerobic wastewater treatment does not need aeration, which eliminates the aeration-associated costs. Additionally, NH_4^+ remains in the wastewater (as does PO_4^{3-}), which avoids the release of N back to the atmosphere that occurs during nitrification–denitrification. Subsequent physicochemical treatments can recover the soluble NH_4^+ and PO_4^{3-}. Anaerobic treatment can also facilitate the degradation of proteins, which enables additional N recovery (Grady et al., 1999). Thus, anaerobic treatment is a beneficial pretreatment step for physicochemical N recovery, and ongoing research continues to improve process efficiency and feasibility of implementation (*e.g.*, low temperature operation).

4.4. Potassium-selective recovery technologies

The level of K is particularly high in vinasses from fermentation of molasses or sugar, making this waste an excellent feedstock choice for K recovery (Decloux et al., 2002 and Zhang et al., 2012). To facilitate the final extraction of crystalline K fertilizers (*i.e.*, K-struvite or K salts, as shown in Table 3), K is typically concentrated and/or released using the technologies previously described for P and N recovery. Notably, membrane filtration, electrodialysis, and adsorption/ion exchange show strong potential for effective recovery of K products (Ciceri et al., 2015 and Mehta et al., 2015). Electrodialysis and strong acid cation exchange resins have been used to separate more than 99% K from winery and distillery waste, respectively (Decloux et al., 2002 and Zhang et al., 2012). Moreover, ion exchange resins can be regenerated using sulfuric acid to produce a concentrated K solution, leading directly to precipitation of K_2SO_4 fertilizer (Zhang et al., 2012).

5. Integrated biorefinery technologies to build a nutrient factory

Section 4 provided a comprehensive review of nutrient recovery technologies with potential for integration in a biorefinery. The technologies ranged from well-established with lower-value products (*e.g.*, anaerobic digestion to produce biosolids) to relatively nascent technologies with potential for higher-value products (*e.g.*, electrodialysis followed by precipitation of N, P, and K-chemical fertilizers). Many technologies are inherently specific towards a single nutrient species, while others can co-recover multiple nutrients, sometimes in a less concentrated (or mixed product) form. The primary products of major recovery technologies are summarized in Table 4. Relative assessment of the recoverable portion of each nutrient in the main product is also indicated, as well as additional technologies which can further enhance recovery.

Table 4. Nutrient recovery technology potential and implementation criteria.

Major Technology:	**Anaerobic Digestion[a]**	**Pyrolysis/Gasification[a]**	**Composting[a]**	**Bio-N[b]**	**Bio-P[b]**	**Precipitation[b]**	**Adsorption[b]**	**Ion Exchange[b]**	**Electrochemical Processing[b]**
Implementation									
Ideal Inputs	Wastewater, animal wastes, food byproducts	Dry biomass, crop residue, vegetative material	Vegetative materials, animal wastes, food byproducts	Soluble N wastes; N-rich water such as municipal, animal or food processing wastes	Soluble P wastes; P-rich water such as municipal, animal or food processing wastes	Concentrated N, P, K; concentrate from adsorption or ion exchange	Hydrophobic or ionic N, P, K species in aqueous matrix	Ionic species of N, P, K in aqueous matrix	Soluble wastes, N, P, K-rich water such as municipal, animal or food processing wastes
Technology Maturity[c]	***	**	***	**	***	***	**	**	*
Cost[d]	**	***	*	**	**	**	**	**	***
Recovery Potential									
Primary recovery products	Biosolids	Biochar, ash	Compost	Biomass (Org-N), single cell protein (Org-N)	Biomass	Struvite, hydroxylapatite, ammonium salts, phosphate salts	NH_3, NH_4^+, NO_3^-, K^+, orthophosphates	NH_4^+, NO_3^-, K^+, orthophosphates	NH_4^+, K^+, orthophosphates
Recoverable N fraction[d]	**	**	*	***	*	**	**	***	***
Recoverable P fraction[d]	*	***	**	*	***	***	**	***	***
Recoverable K fraction[d]	**	***	**	*	*	***	**	***	***
Co-processes to increase recovery	Air stripping, precipitation, adsorption, ion exchange, electroc	Ammonia condensation/ adsorption from gas phase, oil refinement, wet acid leaching, thermal processing	NH_3 or N_2O capture from gas; adsorption, precipitation, or ion	Precipitation, adsorption, ion exchange	Precipitation, adsorption, ion exchange	Adsorption, ion exchange, air stripping, electrochemical processing	Precipitation, electrochemical processing	Precipitation	Precipitation

Major Technology:	**Anaerobic Digestion[a]**	**Pyrolysis/Gasification[a]**	**Composting[a]**	**Bio-N[b]**	**Bio-P[b]**	**Precipitation[b]**	**Adsorption[b]**	**Ion Exchange[b]**	**Electrochemical Processing[b]**
	hemical processing		exchange from leachate						

[a]Commonly used primary process in biorefineries.

[b]Technologies targeting nutrient recovery.

[c]Mature, widely implemented = ***; limited use in industry = **; emerging technology = *.

[d]High = ***; intermediate = **; low = *.

Fig. 2 depicts three possible processes representing scenarios designed to recover A) mixed nutrient products, B) chemical N, P, and K precipitates, and C) SCP. As shown, the different process combinations are likely to recover multiple nutrient products. In all scenarios, biological and/or physicochemical processes are used to concentrate the dilute nutrients in the waste biomass feedstock into solid forms, *e.g.*, biomass, biochar, ion exchange media, after which direct agricultural application may follow or further processing to produce liquid or solid chemical fertilizer products. In keeping with the multi-route biorefinery approach to produce an array of value-added products, these technologies are likely to be implemented in various multi-part configurations which optimize recovery of mixed nutrient and N, P, K-specific fertilizer products alongside biofuels, energy, and platform chemicals. This is exemplified by the multi-process biorefinery flow diagram shown in Fig. 3. Although not all processes are shown in the figure, this example arrangement highlights the potential for co-recovery of nutrient products.

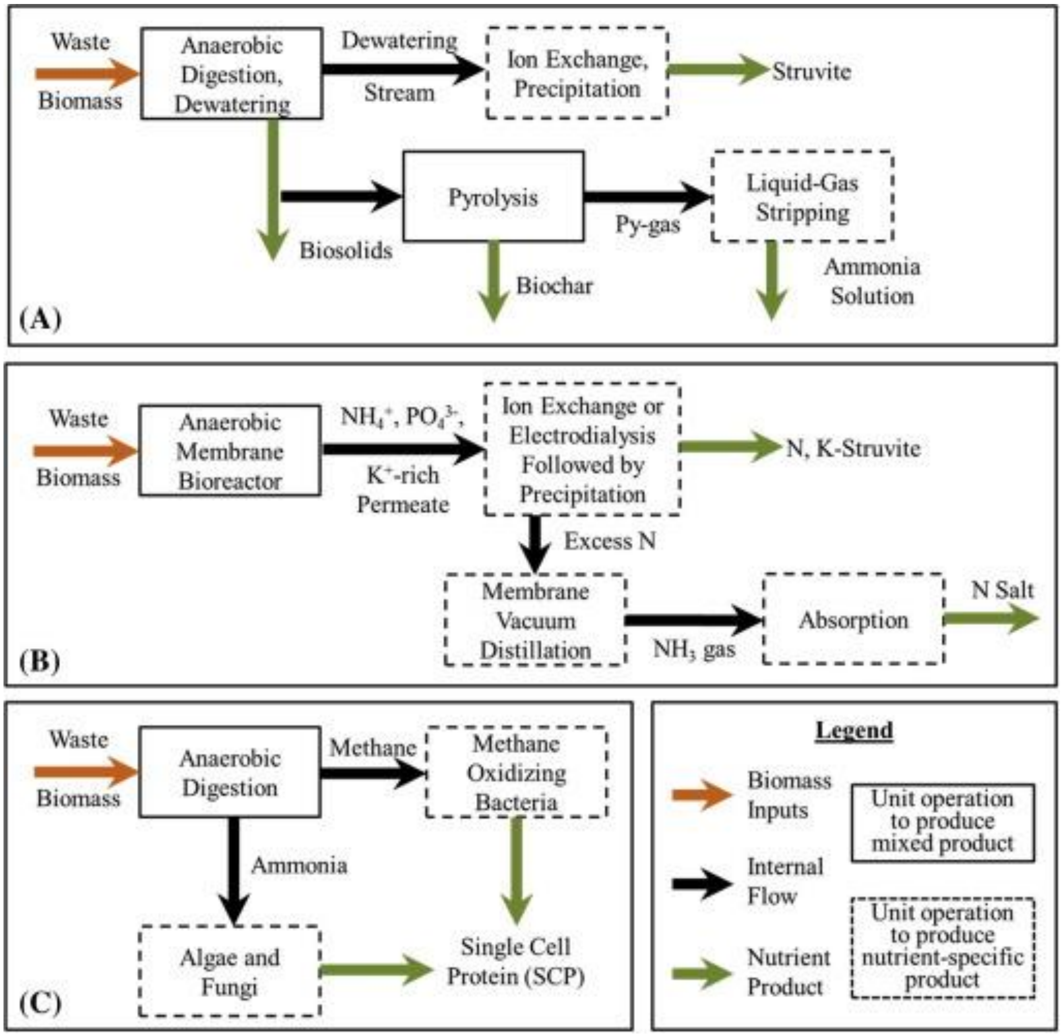


Fig. 2. Example biorefinery processes focused on production of (A) mixed nutrient fertilizer and soil amendment products, (B) N, P, and K-specific fertilizer precipitates, and (C) single cell protein (SCP) for food and feed.

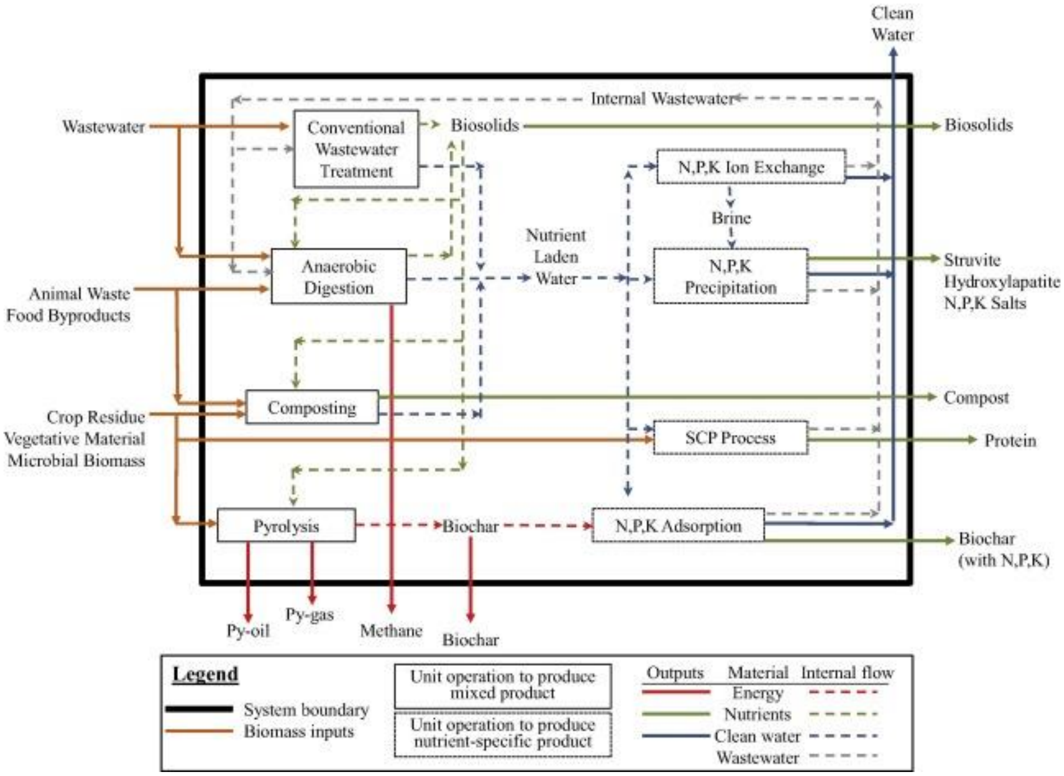


Fig. 3. Material flow diagram depicting an example of how nutrient recovery may fit into an integrated biorefinery.

As innumerable configurations are possible, a life-cycle assessment (LCA) approach could be appropriate to help optimize biorefinery performance. In particular, removal of nutrients can lower eutrophication and acidification potential while offsetting natural resource extraction through reuse of the recovered fertilizer products. Capital and operating costs are also critical considerations in biorefinery process design. Direct cost comparisons among technologies are inherently complex as the processes represent a wide range of technology maturity, ability to integrate with other biorefinery processes, and sensitivity to feedstock and operating conditions. Additionally, the future economic demand for nutrient products is expected to have a major role in implementation of these technologies. For perspective, relative comparisons of cost and technology maturity (which may dictate risks associated with implementing a specific process) are shown in Table 4. Lowering energy inputs, while optimizing product volume and value will prove useful for implementing sustainable biorefinery nutrient recovery scenarios.

6. Conclusions

It is imperative to capitalize on opportunities to recover and reuse agricultural nutrients, and biorefineries provide an excellent, though yet underutilized, approach for doing so. Waste feedstocks offer the greatest opportunity to recover nutrients as part of the biorefinery product portfolio. Depending on the feedstock and desired nutrient product, a number of physical, chemical, and biological technologies can be used to recover mixed nutrient or N, P, K-specific fertilizers. Nutrient recovery technologies may have substantial implications for the sustainability of biorefineries while providing an alternative to current unsustainable approaches to fertilizer production.

Acknowledgements

This work was supported in part by the National Science Foundation's Research Coordination Network (RCN) program. BKM is a member of the Phosphorus Sustainability RCN (the P-RCN).

References

Anex et al., 2007.R.P. Anex, L.R. Lynd, M.S. Laser, A.H. Heggenstaller, M. Liebman. Potential for enhanced nutrient cycling through coupling of agricultural and bioenergy systems. *Crop Sci*., 47 (2007), pp. 1327–1335

Anthony, 1971. W.B. Anthony. Animal waste value – nutrient recovery and utilization. *J. Anim. Sci*., 32 (1971), pp. 799–802

Azuara et al., 2013. M. Azuara, S.R.A. Kersten, A.M.J. Kootstra. Recycling phosphorus by fast pyrolysis of pig manure: concentration and extraction of phosphorus combined with formation of value-added pyrolysis products. *Biomass Bioenergy*, 49 (2013), pp. 171–180

Batstone et al., 2015. D.J. Batstone, T. Hülsen, C.M. Mehta, J. Keller. Platforms for energy and nutrient recovery from domestic wastewater: a review. *Chemosphere*, 140 (2015), pp. 2–11

Batstone and Jensen, 2011. D.J. Batstone, P.D. Jensen. Anerobic processes. P. Wilderer, P. Rogers, S. Uhlenbrook, F. Frimmel, K. Hanaki (Eds.), *Treatise on Water Science*, Academic Press, Oxford, U.K. (2011), pp. 615–640

Beck-Friis et al., 2001. B. Beck-Friis, S. Smars, H. Jonsson, H. Kirchmann. Gaseous emissions of carbon dioxide, ammonia and nitrous oxide from organic household waste in a compost reactor under different temperature regimes. *J. Agric. Eng. Res*., 78 (2001), pp. 423–430

Bernal et al., 2009. M.P. Bernal, J.A. Alburquerque, R. Moral. Composting of animal manures and chemical criteria for compost maturity assessment. A review. *Bioresour. Technol*., 100 (2009), pp. 5444–5453

Bonmatí and Flotats, 2003. A. Bonmatí, X. Flotats. Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion. *Waste Manage*., 23 (2003), pp. 261–272

Bough et al., 1972. W.A. Bough, W.L. Brown, J.D. Porsche, D.M. Doty. Utilization of collagenous by-products from the meat packing industry: production of single-cell protein by the continuous cultivation of *Bacillus megaterium. Appl. Microbiol*., 24 (1972), pp. 226–235

Bridle and Pritchard, 2004. T.R. Bridle, D. Pritchard. Energy and nutrient recovery from sewage sludge via pyrolysis. *Water Sci. Technol*., 50 (2004), pp. 169–175

Capodaglio et al., 2015. A.G. Capodaglio, P. Hlavinek, M. Raboni. Physico-chemical technologies for nitrogen removal from wastewaters: a review. *Rev. Ambient. Agua*, 10 (2015), pp. 481–498

Carey et al., 2015. D.E. Carey, P.J. McNamara, D.H. Zitomer. Biochar from pyrolysis of biosolids for nutrient adsorption and turfgrass cultivation. *Water Environ. Res*., 87 (2015), pp. 2098–2106

Christenson and Sims, 2011. L. Christenson, R. Sims. Production and harvesting of microalgae for wastewater treatment, biofuels, and bioproducts. *Biotechnol. Adv*., 29 (2011), pp. 686–702

Ciceri et al., 2015. D. Ciceri, D.A.C. Manning, A. Allanore. Historical and technical developments of potassium resources. *Sci. Total Environ*., 502 (2015), pp. 590–601

Conesa et al., 2009. J.A. Conesa, R. Font, A. Fullana, I. Martín-Gullón, I. Aracil, A. Gálvez, J. Moltó, M.F. Gómez-Rico. Comparison between emissions from the pyrolysis and combustion of different wastes. *J. Anal. Appl. Pyrolysis*, 84 (2009), pp. 95–102

Cordell et al., 2009. D. Cordell, J.-O. Drangert, S. White. The story of phosphorus: global food security and food for thought. *Global Environ. Change*, 19 (2009), pp. 292–305

Cornel and Schaum, 2009. P. Cornel, C. Schaum. Phosphorus recovery from wastewater: needs, technologies and costs. *Water Sci. Technol*., 59 (2009), pp. 1069–1076

Cysewski and Wilke, 1976. G.R. Cysewski, C.R. Wilke. Utilization of cellulosic materials through enzymatic hydrolysis. I. Fermentation of hydrolysate to ethanol and single-cell protein. *Biotechnol. Bioeng*., 18 (1976), pp. 1297–1313

D'Mello, 1972. J.P.F. D'Mello. A study of the amino acid composition of methane utilizing bacteria. *J. Appl. Bacteriol*., 35 (1972), pp. 145–148

de Bertoldi et al., 1983. M. de Bertoldi, G. Vallini, A. Pera. The biology of composting a review. *Waste Manage. Res*. (1983), pp. 157–176

Decloux et al., 2002. M. Decloux, A. Bories, R. Lewandowski, C. Fargues, A. Mersad, M.L. Lameloise, F. Bonnet, B. Dherbecourt, L.N. Osuna. Interest of electrodialysis to reduce potassium level in vinasses preliminary experiments. *Desalination*, 146 (2002), pp. 393–398

Diaz and Rosenberg, 2008. R.J. Diaz, R. Rosenberg. Spreading dead zones and consequences for marine ecosystems. *Science*, 321 (2008), pp. 926–929

Donatello and Cheeseman, 2013. S. Donatello, C.R. Cheeseman. Recycling and recovery routes for incinerated sewage sludge ash (ISSA): a review. *Waste Manage*., 33 (2013), pp. 2328–2340

El-Bourawi et al., 2007. M.S. El-Bourawi, M. Khayet, R. Ma, Z. Ding, Z. Li, X. Zhang. Application of vacuum membrane distillation for ammonia removal. *J. Membr. Sci.*, 301 (2007), pp. 200–209

Galloway and Cowling, 2002. J.N. Galloway, E.B. Cowling. Reactive nitrogen and the world: 200 years of change. *Ambio*, 31 (2002), pp. 64–71

Galloway et al., 2008. J.N. Galloway, A.R. Townsend, J.W. Erisman, M. Bekunda, Z. Cai, J.R. Freney, L.A. Martinelli, S.P. Seitzinger, M.A. Sutton. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. *Science*, 320 (2008), pp. 889–892

Gebreslassie et al., 2013. B.H. Gebreslassie, M. Slivinsky, B. Wang, F. You. Life cycle optimization for sustainable design and operations of hydrocarbon biorefinery via fast pyrolysis, hydrotreating and hydrocracking. *Comput. Chem. Eng.*, 50 (2013), pp. 71–91

Gerardo et al., 2015. M.L. Gerardo, N.H.M. Aljohani, D.L. Oatley-Radcliffe, R.W. Lovitt. Moving towards sustainable resources: recovery and fractionation of nutrients from dairy manure digestate using membranes. *Water Res*., 80 (2015), pp. 80–89

Grady et al., 1999. C.P.L. Grady, G.T. Daigger, H.C. Lim. *Biological Wastewater Treatment.* (second ed.)Marcel Dekker, New York City, NY (1999)

Güngör and Karthikeyan, 2008. K. Güngör, K.G. Karthikeyan. Phosphorus forms and extractability in dairy manure: a case study for Wisconsin on-farm anaerobic digesters. *Bioresour. Technol*., 99 (2008), pp. 425–436

Hargreaves et al., 2008. J.C. Hargreaves, M.S. Adl, P.R. Warman. A review of the use of composted municipal solid waste in agriculture. *Agric. Ecosyst. Environ.,* 123 (2008), pp. 1–14

He et al., 2001. Y. He, Y. Inamori, M. Mizuochi, H. Kong, N. Iwami, T. Sun. Nitrous oxide emissions from aerated composting of organic waste. *Environ. Sci. Technol.,* 35 (2001), pp. 2347–2351

Hellebrand, 1998. H. Hellebrand. Emission of nitrous oxide and other trace gases during composting of grass and green waste. *J. Agric. Eng. Res*. (1998), pp. 365–375

Inguanzo et al., 2002. M. Inguanzo, A. Domı, J.A. Mene, C.G. Blanco, J.J. Pis. On the pyrolysis of sewage sludge: the influence of pyrolysis conditions on solid, liquid and gas fractions. *J. Anal. Appl. Pyrolysis*, 63 (2002), pp. 209–222

Ippersiel et al., 2012. D. Ippersiel, M. Mondor, F. Lamarche, F. Tremblay, J. Dubreuil, L. Masse. Nitrogen potential recovery and concentration of ammonia from swine manure using electrodialysis coupled with air stripping. *J. Environ. Manage.,* 95 (2012), pp. 165–169

Jeong and Kim, 2001. Y.K. Jeong, J.S. Kim. A new method for conservation of nitrogen in aerobic composting processes. *Bioresour. Technol*., 79 (2001), pp. 129–133

Jin et al., 2009. Y. Jin, Z. Hu, Z. Wen. Enhancing anaerobic digestibility and phosphorus recovery of dairy manure through microwave-based thermochemical pretreatment. *Water Res*., 43 (2009), pp. 3493–3502

Johnston and Richards, 2004. A.E. Johnston, I.R. Richards. Effectiveness of different precipitated phosphates as phosphorus sources for plants. *Phosphorus Res. Bull*., 15 (2004), pp. 52–59

Komilis and Ham, 2006. D.P. Komilis, R.K. Ham. Carbon dioxide and ammonia emissions during composting of mixed paper, yard waste and food waste. *Waste Manage*., 26 (2006), pp. 62–70

Latif et al., 2015. M.A. Latif, C.M. Mehta, D.J. Batstone. Low pH anaerobic digestion of waste activated sludge for enhanced phosphorous release. *Water Res.*, 81 (2015), pp. 288–293

Leytem et al., 2011. A.B. Leytem, R.S. Dungan, D.L. Bjorneberg, A.C. Koehn. Emissions of ammonia, methane, carbon dioxide, and nitrous oxide from dairy cattle housing and manure management systems. *J. Environ. Qual*., 40 (2011), pp. 1383–1394

Li et al., 2015. W.-W. Li, H.-Q. Yu, B.E. Rittmann. Reuse water pollutants. *Nature*, 528 (2015), pp. 29–31

Liu et al., 2014. T. Liu, B. Liu, W. Zhang. Nutrients and heavy metals in biochar produced by sewage sludge pyrolysis: its application in soil amendment. *Pol. J. Environ. Stud*., 23 (2014), pp. 271–275

Marti et al., 2008. N. Marti, A. Bouzas, A. Seco, J. Ferrer. Struvite precipitation assessment in anaerobic digestion processes. *Chem. Eng. J.,* 141 (2008), pp. 67–74

Massé et al., 2007. D.I. Massé, F. Croteau, L. Masse. The fate of crop nutrients during digestion of swine manure in psychrophilic anaerobic sequencing batch reactors. *Bioresour. Technol*., 98 (2007), pp. 2819–2823

Matassa et al., 2015. S. Matassa, D.J. Batstone, T. Hülsen, J. Schnoor, W. Verstraete. Can direct conversion of used nitrogen to new feed and protein help feed the world? *Environ. Sci. Technol*., 49 (2015), pp. 5247–5254

Mayer et al., 2013. B.K. Mayer, D. Gerrity, B.E. Rittmann, D. Reisinger, S. Brandt-Williams. Innovative strategies to achieve low total phosphorus concentrations in high water flows. *Crit. Rev. Environ. Sci. Technol*., 43 (2013), pp. 409–441

Mehta et al., 2015. C.M. Mehta, W.O. Khunjar, V. Nguyen, S. Tait, D.J. Batstone. Technologies to recover nutrients from waste streams: a critical review. *Crit. Rev. Environ. Sci. Technol*., 45 (2015), pp. 385–427

Mohan et al., 2014. D. Mohan, A. Sarswat, Y.S. Ok, C.U. Pittman. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – a critical review. *Bioresour. Technol*., 160 (2014), pp. 191–202

Mondini et al., 2008. C. Mondini, M.L. Cayuela, T. Sinicco, M.A. Sánchez-Monedero, E. Bertolone, L. Bardi. Soil application of meat and bone meal. Short-term effects on mineralization dynamics and soil biochemical and microbiological properties. *Soil Biol. Biochem*., 40 (2008), pp. 462–474

Morse et al., 1998. G. Morse, S. Brett, J. Guy, J. Lester. Review: phosphorus removal and recovery technologies. *Sci. Total Environ*., 212 (1998), pp. 69–81

Naik et al., 2010. S.N. Naik, V.V. Goud, P.K. Rout, A.K. Dalai. Production of first and second generation biofuels: a comprehensive review. *Renewable Sustainable Energy Rev.,* 14 (2010), pp. 578–597

NEBRA, 2007. NEBRA, 2007. *A National Biosolids Regulation, Quality, End Use and Disposal Survey.* Tamworth, NH.

Nishanth and Biswas, 2008. D. Nishanth, D.R. Biswas. Kinetics of phosphorus and potassium release from rock phosphate and waste mica enriched compost and their effect on yield and nutrient uptake by wheat (*Triticum aestivum*). *Bioresour. Technol*., 99 (2008), pp. 3342–3353

Octave and Thomas, 2009. S. Octave, D. Thomas. Biorefinery: toward an industrial metabolism. *Biochimie*, 91 (2009), pp. 659–664

Parkinson et al., 2004. R. Parkinson, P. Gibbs, S. Burchett, T. Misselbrook. Effect of turning regime and seasonal weather conditions on nitrogen and phosphorus losses during aerobic composting of cattle manure. *Bioresour. Technol.,* 91 (2004), pp. 171–178

Anupama and Ravindra, 2000. P. Anupama, P. Ravindra. Value-added food: single cell protein. *Biotechnol. Adv.,* 18 (2000), pp. 459–479

Rittmann et al., 2011. B.E. Rittmann, B. Mayer, P. Westerhoff, M. Edwards. Capturing the lost phosphorus. *Chemosphere*, 84 (2011), pp. 846–853

Rittmann and McCarty, 2001. B.E. Rittmann, P.L. McCarty. *Environmental Biotechnology: Principles and Applications.* McGraw Hill, New York (2001)

Rulkens et al., 1998. W.H. Rulkens, A. Klapwijk, H.C. Willers. Recovery of valuable nitrogen compounds from agricultural liquid wastes: potential possibilities, bottlenecks and future technological challenges. *Environ. Pollut.,* 102 (1998), pp. 727–735

Samatya et al., 2006. S. Samatya, N. Kabay, U. Yuksel, M. Arda, M. Yuksel. Removal of nitrate from aqueous solution by nitrate selective ion exchange resins. *React. Funct. Polym*., 66 (2006), pp. 1206–1214

Sanchez et al., 2000. E. Sanchez, R. Borja, P. Weiland, L. Travieso, A. Martin. Effect of temperature and pH on the kinetics of methane production, organic nitrogen and phosphorus removal in the batch anaerobic digestion process of cattle manure. *Bioprocess Eng*., 22 (2000), pp. 247–252

Sluiter et al., 2010. J.B. Sluiter, R.O. Ruiz, C.J. Scarlata, A.D. Sluiter, D.W. Templeton. Compositional analysis of lignocellulosic feedstocks. 1. Review and description of methods. *J. Agric. Food Chem*., 58 (2010), pp. 9043–9053

Tian et al., 2013. Y. Tian, J. Zhang, W. Zuo, L. Chen, Y. Cui, T. Tan. Nitrogen conversion in relation to NH_3 and HCN during microwave pyrolysis of sewage sludge. *Environ. Sci. Technol*., 47 (2013), pp. 3498–3505

Tonini et al., 2013. D. Tonini, V. Martinez-Sanchez, T.F. Astrup. Material resources, energy, and nutrient recovery from waste: are waste refineries the solution for the future? *Environ. Sci. Technol*., 47 (2013), pp. 8962–8969

USEPA, 2012. USEPA, 2012. *Estimated Animal Agriculture Nitrogen and Phosphorus from Manure*.

Vaccari, 2009. D.A. Vaccari. Phosphorus: a looming crisis. *Sci. Am.,* 300 (2009), pp. 54–59

Vincent, 1969. W.A. Vincent. Algae for food and feed. *Process Biochem*., 4 (1969), pp. 45–47

Volli and Singh, 2012. V. Volli, R.K. Singh. Production of bio-oil from de-oiled cakes by thermal pyrolysis. *Fuel*, 96 (2012), pp. 579–585

Wang et al., 2013. C. Wang, H. Lu, D. Dong, H. Deng, P.J. Strong, H. Wang, W. Wu. Insight into the effects of biochar on manure composting: evidence supporting the relationship between N_2O emission and denitrifying community. *Environ. Sci. Technol*., 47 (2013), pp. 7341–7349

Wang et al., 2010. X. Wang, Z. Qiu, S. Lu, W. Ying. Characteristics of organic, nitrogen and phosphorus species released from ultrasonic treatment of waste activated sludge. *J. Hazard. Mater*., 176 (2010), pp. 35–40

Werpy et al., 2004. T. Werpy, G. Petersen, A. Aden, J. Bozell, J. Holladay, J. White, A. Manheim, D. Eliot, L. Lasure, S. Jones. *Top Value Added Chemicals from Biomass. Volume 1-Results of Screening for Potential Candidates from Sugars and Synthesis Gas* (No. DOE/GO-102004-1992). Department of Energy, Washington, DC (2004)

Williams et al., 2015. A.T. Williams, D.H. Zitomer, B.K. Mayer. Ion exchange-precipitation for nutrient recovery from dilute wastewater. *Environ. Sci. Water Res. Technol.,* 1 (2015), pp. 832–838

Yang et al., 2008. Y. Yang, Y. Wei, J. Liu. Effect of magnesium salt addition on nutrients conservation during swine manure composting. *Huan jing ke xue (Environ. Sci.),* 29 (2008), pp. 2672–2677

Yang et al., 2009. Y. Yang, Y. Wei, J. Liu. Impacts of different aeration modes on nutrients conservation during swine manure composting with magnesium salt addition. *Huan jing ke xue (Environ. Sci.),* 30 (2009), pp. 1238–1243

Zhang et al., 2012. P.J. Zhang, Z.G. Zhao, S.J. Yu, Y.G. Guan, D. Li, X. He. Using strong acid-cation exchange resin to reduce potassium level in molasses vinasses. *Desalination*, 286 (2012), pp. 210–216

Appendix A. Supplementary data

Recovery of Agricultural Nutrients from Biorefineries

Supplementary Material

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The Supplementary Material contains additional information related to the basic assessment of the fate of agricultural flows of potassium (K). Additionally, citations and references for sources used to create all figures and tables shown in the text are presented along with a list of other recommended resources which provide greater detail for interested readers.

Assessment of K flows

Although there are good materials balances published describing the fate of N and P through agricultural systems, there is no analogous report for K. Thus, we performed a crude assessment to determine the percent of mined agricultural inputs of K that winds up in human and animal waste using the following data. The global potash production in 2013 was 34.5 million tonnes K_2O, and 90% of that was assumed to be used for agricultural fertilizer (Jasinski, 2013). Humans excrete a total of 3.5 g/d per person K (Esrey, 2001). Animal waste contains 0.5 – 2.3% K (Smith and Wheeler, 1979), and using the average of these values and the total dry weight production of animal manure from the world's farms in 1997 of 1.7 billion tonnes (Sheffield, n.d.), the K content of animal waste was computed.

Recommended reading

Table S1 identifies all of the sources of information used to create the respective Figures, Tables, and Boxes in the text. In addition to the references included in the text, Table S1 also lists a number of excellent references that are recommended for additional reading.

Table S1. Categorized references recommended for additional reading

Anthropocene influences and global cycles
(Chowdhury et al., 2014; Crutzen, 2002; Erisman et al., 2008; Smil, 2002, 2000; Steen, 1998; Steffen et al., 2007; Vitousek et al., 1997)
Fertilizer production, use, needs, and impacts
(Horn and Sartorius, 2009; Jasinski, 2015; Rosmarin, 2004; Smil, 2004, 2002; Tanabe and Nishibayashi, 2013; Tucker et al., 2010)
General resource recovery
(Guest et al., 2009; Matassa et al., 2015; Peccia and Westerhoff, 2015; Sonesson et al., 2000; Sturm and Lamer, 2011; Wilsenach et al., 2003)
Phosphorus recovery
(Ashley et al., 2011; Biswas et al., 2008; Blaney et al., 2007; Cordell and White, 2011; Cordell et al., 2011; Gaterell et al., 2000; Gifford et al., 2015; Hao et al., 2013; Johnston and Richards, 2003; Le Corre et al., 2009; Mihelcic et al., 2011; Sartorius et al., 2012; Schroder et al., 2009; Sengupta and Pandit, 2011; Shaikh, Ahamad and Dixit, 1992; Tan and Lagerkvist, 2011)
Nitrogen recovery
(Benemann, 1979; Bonmatí and Flotats, 2003; Coullard and Mercier, 1993; Graeser et al., 2008; Vincent, 1971)
Potassium recovery
(Ciceri et al., 2015; Espana-Gamboa et al., 2011; Sheehan and Greenfield, 1980; Yuan et al., 2012)
Biorefineries and biomass
(Cherubini and Ulgiati, 2010; Cook et al., 2002; Fava et al., 2015; Fernando et al., 2006; García et al., 2014; NREL, 2002; Octave and Thomas, 2009; Pleissner and Lin, 2013; Yokoyama, 2008)
Waste treatment
(Lu et al., 2012; McCarty et al., 2011; Tchobanoglous et al., 2003)
Information referenced in Box 1
Phosphorus: (McKelvie, 2005; Tchobanoglous et al., 2003) Nitrogen: (Cao et al., 2010; Mattson et al., 2009) Potassium: (California Fertilizer Foundation, 2009; Ciceri et al., 2015)
Information referenced in Table 1
(Azuara et al., 2013; Christenson and Sims, 2011; Delivand and Gnansounou, 2013; Doblinski et al., 2010; Grady et al., 1999; Hussein, 2013; Juneja et al., 2013; Latshaw and Miller, 1924; Mosse et al., 2011; Olguín, 2012; Rahman et al., 2013; Reimann et al., 2001; Selvamurugan et al., 2010; Shivajirao, 2012; Zhang et al., 2012)
Information referenced in Table 2
Summarized from: (Madigan et al., 2009)
Information referenced in Table 3
Representative organic mixtures: (Bridle and Pritchard, 2004; Tchobanoglous et al., 2003; Zhang et al., 2002)
Information referenced in Figure 1
World population: (US Census Bureau, 2015) Global fertilizer production statistics from the United Nation's Food and Agricultural Organization, FAO (FAO, 2015), were used as-is for available years (1961 and afterward). These datasets specifically note that different methodologies were used for data before and after 2002, which may result in the introduction of discontinuities in the figure due to linking multiple datasets together. For pre-1961 P and K production data, USGS statistics (Kelly and Matos, 2013) were used, while N estimates were made from data presented by

(Mulder, 2003). All units were converted to metric tonnes as nutrients, and an assumption was applied that 90% of world production reported by the USGS was used for fertilizer production. Fertilizer prices paid by U.S. farmers for representative N, P, and K fertilizers were collected from the FAO. For each year 1961 – 2013, the prices reported at different times during the year (n = 1-4) were averaged to report a mean annual price. Additional sources used to create the figure included: (Batstone et al., 2014; Cordell and White, 2011; Cordell et al., 2011).

References

Ashley, K., Cordell, D., Mavinic, D., 2011. A brief history of phosphorus: from the philosopher's stone to nutrient recovery and reuse. Chemosphere 84, 737–46.

Azuara, M., Kersten, S.R.A., Kootstra, A.M.J., 2013. Recycling phosphorus by fast pyrolysis of pig manure: Concentration and extraction of phosphorus combined with formation of value-added pyrolysis products. Biomass and Bioenergy 49, 171–180.

Batstone, D.J., Hülsen, T., Mehta, C.M., Keller, J., 2014. Platforms for energy and nutrient recovery from domestic wastewater: A review. Chemosphere 140, 2–11.

Benemann, J.R., 1979. Production of nitrogen fertilizer with nitrogen-fixing blue - green algae. Enzyme Microb. Technol. 1, 83–90.

Biswas, B.K., Inoue, K., Ghimire, K.N., Harada, H., Ohto, K., Kawakita, H., 2008. Removal and recovery of phosphorus from water by means of adsorption onto orange waste gel loaded with zirconium. Bioresour. Technol. 99, 8685–90.

Blaney, L.M., Cinar, S., SenGupta, A.K., 2007. Hybrid anion exchanger for trace phosphate removal from water and wastewater. Water Res. 41, 1603–1613.

Bonmatí, A., Flotats, X., 2003. Air stripping of ammonia from pig slurry: Characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion. Waste Manag. 23, 261–272.

Bridle, T.R., Pritchard, D., 2004. Energy and nutrient recovery from sewage sludge via pyrolysis. Water Sci. Technol. 50, 169–75.

California Fertilizer Foundation, 2009. Plant nutrients - Potassium. www.cfaitc.org/factsheets/pdf/Potassium.pdf

Cao, J.-P., Li, L.-Y., Morishita, K., Xiao, X.-B., Zhao, X.-Y., Wei, X.-Y., Takarada, T., 2010. Nitrogen transformations during fast pyrolysis of sewage sludge. Fuel 104, 1–6.

Cherubini, F., Ulgiati, S., 2010. Crop residues as raw materials for biorefinery systems - A LCA case study. Appl. Energy 87, 47–57.

Chowdhury, R.B., Moore, G.A., Weatherley, A.J., Arora, M., 2014. A review of recent substance flow analyses of phosphorus to identify priority management areas at different geographical scales. Resour. Conserv. Recycl. 83, 213–228.

Christenson, L., Sims, R., 2011. Production and harvesting of microalgae for wastewater treatment, biofuels, and bioproducts. Biotechnol. Adv. 29, 686–702.

Ciceri, D., Manning, D.A.C., Allanore, A., 2015. Historical and technical developments of potassium resources. Sci. Total Environ. 502, 590–601.

Cook, K.G., Epstein, K., Brown, H., 2002. Biorefineries: National Renewable Energy Laboratory 2002 Research Review, 1st Edition.

Cordell, D., Rosemarin, A., Schröder, J.J., Smit, A.L., 2011. Towards global phosphorus security: a systems framework for phosphorus recovery and reuse options. Chemosphere 84, 747–58.

Cordell, D., White, S., 2011. Peak phosphorus: Clarifying the key issues of a vigorous debate about long-term phosphorus security. Sustainability 3, 2027–2049.

Coullard, D., Mercier, G., 1993. Removal of metals and fate of N and P in the bacterial leaching of aerobically digested sewage sludge. Water Res. 27, 1227–1235.

Crutzen, P.J., 2002. Geology of mankind. Nature 415, 23.

Delivand, M.K., Gnansounou, E., 2013. Life cycle environmental impacts of a prospective palm-based biorefinery in Pará State-Brazil. Bioresour. Technol. 150, 438–446.

Doblinski, A.F., Sampaio, S.C., Silva, V.R., Nóbrega, L.H.P., Gomes, S.D., Bosco, T.C.D., 2010. Nonpoint source pollution by swine farming wastewater in bean crop. Rev. Bras. Eng. Agric. e Ambient. 14 n.1, 87–93.

Erisman, J.W., Sutton, M.A., Galloway, J.N., Klimont, Z., Winiwarter, W., 2008. How a century of ammonia synthesis changed the world. Nat. Geosci. 1, 636–639.

Espana-Gamboa, E., Mijangos-Cortes, J., Barahona-Perez, L., Dominguez-Maldonado, J., Hernandez-Zarate, G., Alzate-Gaviria, L., 2011. Vinasses: Characterization and treatments. Waste Manag. Res. 29, 1235–1250.

Esrey, S.A., 2001. Towards a recycling society: Ecological sanitation - Closing the loop to food security. Water Sci. Technol. 43, 177–187.

FAO, 2015. FAOSTAT. Food Agric. Organ. United Nations, Stat. Div. http://faostat3.fao.org/download/R/RF/E (accessed 12.30.15).

Fava, F., Totaro, G., Diels, L., Reis, M., Duarte, J., Carioca, O.B., Poggi-Varaldo, H.M., Ferreira, B.S., 2015. Biowaste biorefinery in Europe: opportunities and research & development needs. N. Biotechnol. 32, 100–108.

Fernando, S., Adhikari, S., Chandrapal, C., Murali, N., 2006. Biorefineries: Current Status, Challenges, and Future Direction. Energy Fuels 20, 1727–1737.

García, A., González Alriols, M., Labidi, J., 2014. Evaluation of different lignocellulosic raw materials as potential alternative feedstocks in biorefinery processes. Ind. Crops Prod. 53, 102–110.

Gaterell, M.R., Gay, R., Wilson, R.J., Gochin, R.J., Lester, J.N., 2000. An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertiliser markets. Environ. Technol. 21, 1173–1180.

Gifford, M., Liu, J., Rittmann, B.E., Vannela, R., Westerhoff, P., 2015. Phosphorus recovery from microbial biofuel residual using microwave peroxide digestion and anion exchange. Water Res. 70, 130–137.

Grady, C.P.L., Daigger, G.T., Lim, H.C., 1999. Biological Wastewater Treatment, 2nd ed. Marcel Dekker, New York City, NY.

Graeser, S., Postl, W., Bojar, H.-P., Berlepsch, P., Armbruster, T., Raber, T., Ettinger, K., Walter, F., 2008. Struvite-(K), KMgPO4*6H2O, the potassium equivalent of struvite – a new mineral. Eur. J. Mineral. 20, 629–633.

Guest, J.S., Skerlos, S.J., Barnard, J.L., Beck, M.B., Daigger, G.T., Hilger, H., Karvazy, K., Kelly, L., Macpherson, L., Mihelcic, J.R., Pramanik, A., Raskin, L., van Loosdrecht, M.C.M., Yeh, D., Love, N.G., 2009. A new planning and design paradigm to achieve sustainable resource recovery from wastewater. Environ. Sci. Technol. 43, 6126–6130.

Hao, X., Wang, C., van Loosdrecht, M.C.M., Hu, Y., 2013. Looking beyond struvite for P-recovery. Environ. Sci. Technol. 47, 4965–6.

Horn, J.V., Sartorius, C., 2009. Impact of supply and demand on the price development of phosphate (fertilizer), in: Ashley, K., Mavinic, D., Koch, F. (Eds.), International Conference on Nutrient Recovery from Wastewater Streams. IWA Publishing, Vancouver.

Hussein, F.H., 2013. Chemical properties of treated textile dyeing wastewater. Asian J. Chem.

25, 9393–9400.

Jasinski, S.M., 2013. 2013 Minerals Yearbook: Phosphate Rock, U.S. Geological Survey.

Jasinski, S.M., 2015. 2013 Minerals Yearbook: Potash.

Johnston, A.E., Richards, I.R., 2003. Effectiveness of different precipitated phosphates as phosphorus sources for plants. Soil Use Manag. 19, 45–49.

Juneja, A., Ceballos, R., Murthy, G., 2013. Effects of environmental factors and nutrient availability on the biochemical composition of algae for biofuels production: A review. Energies 6, 4607–4638.

Kelly, T.D., Matos, G.R., 2013. Historical statistics for mineral and material commodities in the United States (2013 version): U.S. Geological Survey Data Series 140.

Latshaw, W.L., Miller, E.C., 1924. Elemental composition of the corn plant. J. Agric. Res. 27, 845–861.

Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S. a, 2009. Phosphorus recovery from wastewater by struvite crystallization. Crit. Rev. Environ. Sci. Technol. 39, 433–477.

Lu, Q., He, Z., Stoffela, P.J., 2012. Land application of biosolids in the USA: A review. Appl. Environ. Soil Sci.

Madigan, M.T., Martinko, J.M., Dunlap, P. V., 2009. Biology of Microorganisms, 12th ed. Pearson, San Francisco, CA.

Matassa, S., Boon, N., Verstraete, W., 2015. Resource recovery from used water: The manufacturing abilities of hydrogen-oxidizing bacteria. Water Res. 68, 467–478.

Mattson, N., Leatherwood, R., Peters, C., 2009. Nitrogen: All forms are not equal. Greenh. Manag. Prod. 25, 18–23.

McCarty, P.L., Bae, J., Kim, J., 2011. Domestic wastewater treatment as a net energy producer -

can this be achieved? Environ. Sci. Technol. 45, 7100–6.

McKelvie, I.D., 2005. Separation, preconcentration and speciation of organic phosphorus in environmental samples, in: Turner, B.L., Frossard, E., Baldwin, D.S. (Eds.), Organic Phosphorus in the Environment. CABI Publishing, Wallingford, pp. 1–20.

Mihelcic, J.R., Fry, L.M., Shaw, R., 2011. Global potential of phosphorus recovery from human urine and feces. Chemosphere 84, 832–9.

Mosse, K.P.M., Patti, A.F., Christen, E.W., Cavagnaro, T.R., 2011. Review: Winery wastewater quality and treatment options in Australia. Aust. J. Grape Wine Res. 17, 111–122.

Mulder, A., 2003. The quest for sustainable nitrogen removal technologies. Water Sci. Technol. 48, 67–75.

NREL, 2002. The Biomass Economy, National Renewable Energy Laboratory 2002 Research Review.

Octave, S., Thomas, D., 2009. Biorefinery: Toward an industrial metabolism. Biochimie 91, 659–664.

Olguín, E.J., 2012. Dual purpose microalgae–bacteria-based systems that treat wastewater and produce biodiesel and chemical products within a Biorefinery. Biotechnol. Adv. 30, 1031–1046.

Peccia, J., Westerhoff, P., 2015. We should expect more from our sewage sludge. Environ. Sci. Technol. 49, 8271–8276.

Pleissner, D., Lin, C.S., 2013. Valorisation of food waste in biotechnological processes. Sustain. Chem. Process. 1, 21.

Rahman, S., Scherer, T., Rahman, A., Lang, J., 2013. Water Quality of Runoff From Beef Cattle Feedlots. Fargo, ND.

Reimann, C., Koller, F., Frengstad, B., Kashulina, G., Niskavaara, H., Englmaier, P., 2001. Comparison of the element composition in several plant species and their substrate from a 1 500 000-km(2) area in Northern Europe. Sci. Total Environ. 278, 87–112.

Rosmarin, A., 2004. The precarious geopolitics of phosphorus. Down to Earth Sci. Environ. Fortn. 27–31.

Sartorius, C., Horn, J. Von, Tettenborn, F., 2012. Phosphorus recovery from wastewater—Expert survey on present use and future potential. Water Environ. Res. 84.

Schroder, J.J., Cordell, D., Smit, A.L., Rosemarin, A., 2009. Sustainable Use of Phosphorus.

Selvamurugan, M., Doraisamy, P., Maheswari, M., Nandakumar, N.B., 2010. High rate anaerobic treatment of coffee processing wastewater using upflow anaerobic hybrid reactor 7, 129–136.

Sengupta, S., Pandit, A., 2011. Selective removal of phosphorus from wastewater combined with its recovery as a solid-phase fertilizer. Water Res. 45, 3318–3330.

Shaikh, Ahamad, M.H., Dixit, S.G., 1992. Removal of phosphate from waters by precipitation and high gradient magnetic separation. Water Res. 26, 845–852.

Sheehan, G.J., Greenfield, P.F., 1980. Utilisation, treatment and disposal of distillery wastewater. Water Res. 14, 257–277.

Sheffield, J., n.d. Farm animal manure is an important sustainable renewable energy resource.

Shivajirao, P.A., 2012. Treatment of distillery wastewater using membrane technologies. Int. J. Adv. Eng. Res. Stud. 1, 275–283.

Smil, V., 2000. Phosphorus in the environment: Natural flows and human interferences. Annu. Rev. Energy Environ. 25, 53–88.

Smil, V., 2002. Phosphorus: global transfers, in: Douglas, P.J. (Ed.), Encyclopedia of Global

Environmental Change. John Wiley & Sons, Chichester.

Smil, V., 2004. Enriching the earth: Fritz Haber, Carl Bosch, and the transformation of world food production. MIT Press, Cambridge.

Smith, L.W., Wheeler, W.E., 1979. Nutritional and economic value of animal excreta. J. Anim. Sci. 48, 144–156.

Sonesson, U., Björklund, a., Carlsson, M., Dalemo, M., 2000. Environmental and economic analysis of management systems for biodegradable waste. Resour. Conserv. Recycl. 28, 29–53.

Steen, I., 1998. Management of a nonrenewable resource. Phosphorus and Potassium 25–31.

Steffen, W., Crutzen, J., McNeill, J.R., 2007. The Anthropocene: are humans now overwhelming the great forces of Nature? Ambio 36, 614–621.

Sturm, B.S.M., Lamer, S.L., 2011. An energy evaluation of coupling nutrient removal from wastewater with algal biomass production. Appl. Energy 88, 3499–3506.

Tan, Z., Lagerkvist, A., 2011. Phosphorus recovery from the biomass ash: A review. Renew. Sustain. Energy Rev. 15, 3588–3602.

Tanabe, Y., Nishibayashi, Y., 2013. Developing more sustainable processes for ammonia synthesis. Coord. Chem. Rev. 257, 2551–2564.

Tchobanoglous, G., Burton, F.L., Stensel, H.D., 2003. Wastewater Engineering: Treatment and Reuse; Metcalf & Eddy, 4th Ed. ed. McGraw Hill, New York City, NY.

Tucker, R.W., Mehta, C., McGahan, E., Batstone, D.J., 2010. Fertiliser from waste: Phase 1 GRDC Project UQ00046: Output 1. Canberra.

US Census Bureau, 2015. World Population. http://www.census.gov/population/international/data/worldpop/table_population.php

Vincent, W., 1971. Algae and lithotrophic bacteria as food sources, in: Soc. for Gen. Microbiol. 21st Symp Microbes and Biol Prod. pp. 74–76.

Vitousek, P.M., Mooney, H.A., Lubchenco, J., Melillo, J.M., 1997. Human domination of earth’s ecosystems. Science (80-.). 277, 494–499.

Wilsenach, J.A., Maurer, M., Larsen, T.A., van Loosdrecht, M.C.M., 2003. From waste treatment to integrated resource management. Water Sci. Technol. 48, 1–9.

Yokoyama, S., 2008. Part 2. Biomass resources, in: Yokoyama, S., Matsumura, Y. (Eds.), Asian Biomass Handbook. The Japan Institute for Energy, pp. 12–80.

Yuan, J., Zhao, Y., Li, Q., Ji, Z., Guo, X., 2012. Preparation of potassium ionic sieve membrane and its application on extracting potash from seawater. Sep. Purif. Technol. 99, 55–60.

Zhang, F.S., Yamasaki, S., Nanzyo, M., 2002. Waste ashes for use in agricultural production: I. Liming effect, contents of plant nutrients and chemical characteristics of some metals. Sci. Total Environ. 284, 215–225.

Zhang, P.J., Zhao, Z.G., Yu, S.J., Guan, Y.G., Li, D., He, X., 2012. Using strong acid-cation exchange resin to reduce potassium level in molasses vinasses. Desalination 286, 210–216.