Emerging investigator series: Thermodynamic and Energy Analysis of Nitrogen and Phosphorous Recovery from Wastewaters

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WATER IMPACT

To attain a more sustainable circular economy model of nutrient management, N and P present in waste streams need to be recovered for reuse. This study quantitatively shows that recovery from nutrient-rich urine can be realized using separation techniques with technologically-achievable energy efficiencies. The sizable global energy savings provide impetus for broad implementation of nutrient recovery from discarded waste streams.

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Environmental Science: Water Research and Technology

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ABSTRACT

In a circular nutrient economy, nitrogen and phosphorous are removed from waste streams and captured as valuable fertilizer products, to more sustainably reuse the resources in closed-loops and simultaneously protect receiving aquatic environments from harmful N and P emissions. For nutrient reclamation to be competitive with the existing practices of N fixation and P mining, the methods of recovery must achieve at least comparable energy consumption. This study employed the Gibbs free energy of separation to quantify the minimum energy required to recover various N and P fertilizer products from waste streams of fresh and hydrolyzed urine, greywater, domestic wastewater, and secondary treated wastewater effluent. The comparative advantages in theoretical energy intensities for N and P recovery from nutrient-dense waste streams, such as fresh and hydrolyzed urine, were assessed against the other more dilute sources. For examples, compared to reclaiming the nutrients from treated wastewater effluent at centralized wastewater treatment plants, the minimum energy to recover 1.0 M $NH_{3(aq)}$ from source-separated hydrolyzed urine can be ≈40-68% lower, whereas recovering $KH_2PO_{4(s)}$ from diverted fresh urine can, in principle, be ≈13-34% less energy intense. The study also evaluated the efficiencies required by separation techniques for the energy demand of N and P recovery to be lower than the current production approaches of Haber-Bosch process and phosphate rock mining. For instance, the most energetically favorable ammoniacal nitrogen and orthophosphate reclamation schemes, which target hydrolyzed and fresh urine, respectively, require energy efficiencies >7% and >39%. This study highlights that strategic selection of waste stream and fertilizer product can enable the most expedient recovery of nutrients and realize a circular economy model for N and P management.

INTRODUCTION

Nitrogen and phosphorus are essential macronutrients for global food security and principal components of fertilizers. The prevailing Haber-Bosch process to fix atmospheric N_2 into bioavailable ammonia, NH_3, is very energy-intensive (8.9-19.3 kWh/kg-N) and accounts for 1-2% of the world's annual energy consumption.[1-3] Likewise, mining of phosphate rock, the dominant method of P production, requires large amounts of energy (0.80-1.66 kWh/kg-P).[4, 5] Furthermore, phosphate deposits are a finite resource, with reserves predicted to last only 50-100 years and production projected to decline after 2033.[6, 7] On top of the substantial costs of industrial fertilizer production, energy and chemicals are additionally needed to manage the nutrients downstream, after consumption: nitrogen and phosphorus are pollutants and need to be separated from anthropogenic streams in wastewater treatment plants (WWTPs) before discharge to the environment.[8-12] However, most WWTPs in the U.S. are not equipped with advanced tertiary treatments dedicated to nutrients elimination.[13] When N and P are not adequately removed, the nutrients are discharged into aquatic ecosystems and can cause eutrophication, harmful algal blooms, and hypoxic dead zones, which devastate the environment and reduce biodiversity.[14-17] These ecotoxic environments can consequently pose public health threats as conventional drinking water treatment is ineffective in removing algal and cyanobacterial toxins.[18, 19] The biogeochemical flows of both N and P are, hence, flagged as violating the safe operating space for humanity and pose high risks under the planetary boundaries framework.[20]

The significant adulteration of natural ecosystems by nutrients emissions patently highlights the critical shortcomings of the current approach for N and P management and starkly underscores the critical need for more sustainable nutrient management.[21-23] The urgency of the problem was endorsed by the National Academy of Engineers, which identified an improved system for nitrogen management as a grand challenge for the 21st century.[24] There has been considerable efforts to reduce nutrient emissions from WWTPs,[25-32] but majority of the methods remove nutrients from the wastewater (WW) without capture. This approach still contributes to the inefficiencies of the linear nutrient economy model, where nutrients are produced/extracted at immense costs and excess nutrients in wastewater are treated at an additional expense to avoid environmental and public health concerns. The challenges facing current nutrient management practices offer opportunities for synergistic solutions. A circular economy model advocates for the simultaneous removal and recovery of nutrients from waste-sources.[33-36] N and P captured from wastewater can be recycled back into the food chain to close the nutrient loop, easing the demand for nitrogen fixation and phosphorus mining, and simultaneously alleviating potential harms to the environment and public health. The recovery of nutrients from waste streams for reuse is, therefore, a paradigm shift to a more sustainable approach for nutrient management.

The recovery of nutrients from various waste streams of the cycle, including urine,[9, 13, 37-48] greywater,[49] domestic wastewater,[50-54] and WWTP effluent,[55-59] has been investigated in previous studies. A simplified schematic of the wastewater cycle and the principal streams are depicted in Figure 1A. Note that the main form of nitrogen in fresh urine is urea, $CO(NH_2)_2$, which undergoes hydrolysis by naturally present urease enzymes to form ammoniacal nitrogen and bicarbonate, yielding hydrolyzed urine after ≈2-7 d.[60, 61] As the waste streams undergo biological, chemical, and physical transformations along the cycle and combine with other flows, the compositions and aqueous chemistries are significantly altered.[60, 62-68] Similarly, the nutrient content can vary drastically. Figure 1B shows the concentration range of total ammoniacal nitrogen, TAN, and total orthophosphate, TOP, (shaded green and patterned red bars, respectively) for the different waste streams. The TAN and TOP concentrations span over five orders of magnitude, with the general trend, in increasing order of nutrient content, being greywater < secondary (2°) WW effluent < domestic WW < fresh and hydrolyzed urine. Therefore, the various recovery technologies are targeting sources with widely disparate nutrient contents and with N and P in different chemical forms (e.g., nitrogenous compounds include ammonia, nitrate, nitrite, and urea).

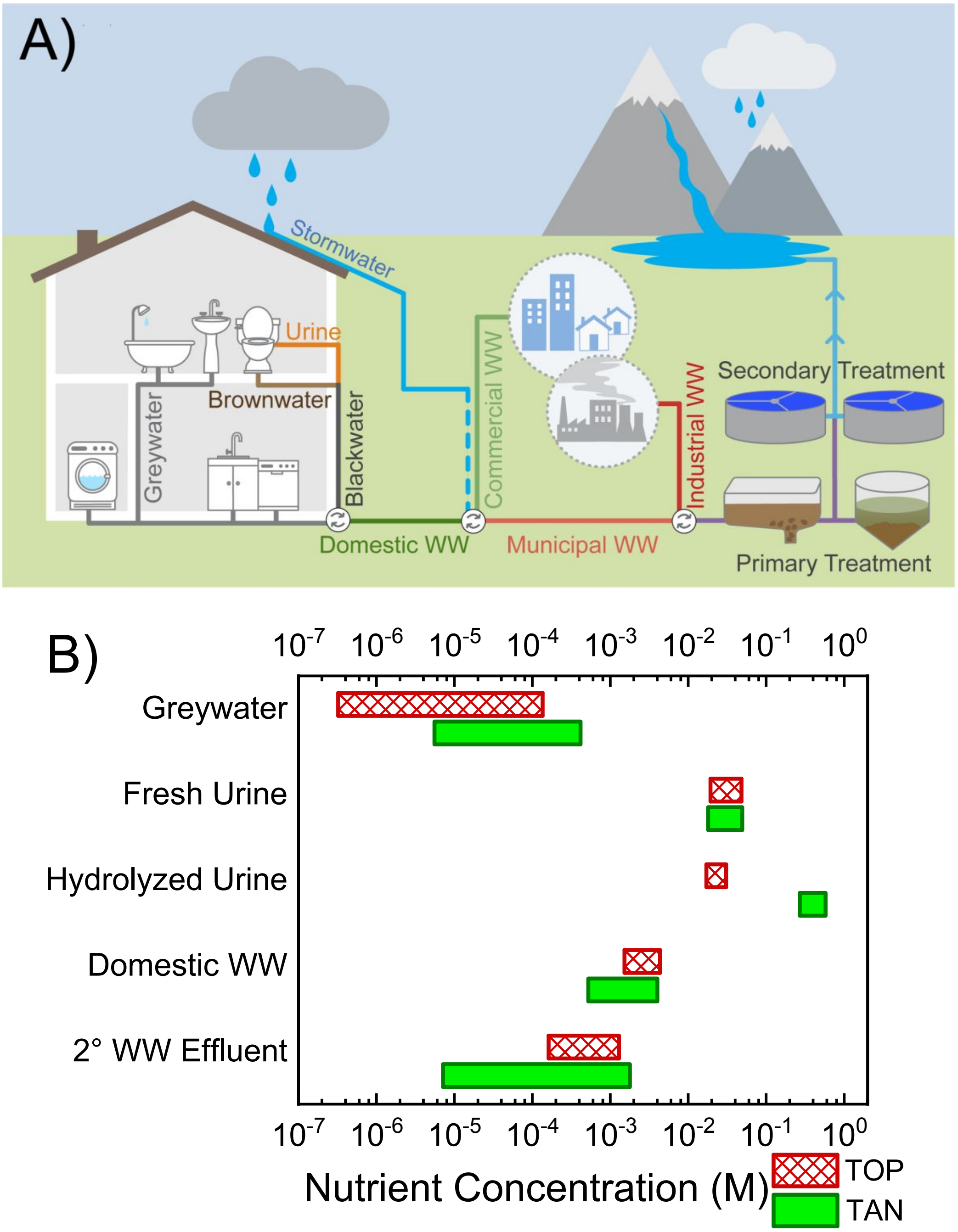

Figure 1. A) Illustrative representation of wastewater sources and streams. The constituents of domestic wastewater (WW) are blackwater, the mixture of brownwater and urine, and greywater. Domestic WW combines with waste streams from commercial and industrial sources, and may be diluted by stormwater runoff in combined sewer systems before treatment at centralized facilities. Treated effluent is eventually discharged to the environment. B) Concentration range of total ammoniacal nitrogen, TAN, and total orthophosphate, TOP, (shaded green and patterned red bars, respectively) for waste streams of greywater, fresh urine, hydrolyzed urine, domestic WW, and secondary (2°) WW effluent.[60, 62-68]

Waste streams that are richer in nutrients should, intuitively, favor recovery efficiency and effectiveness. The advantages of high nutrients content for recovery have been qualitatively discussed in literature,[13, 39, 69] but there are currently no rigorous quantitative analyses to more precisely valuate the benefits. In contrast, energy analyses had been conducted for other environmentally-relevant separations, such as, reverse osmosis desalination, conventional thermal distillation, and membrane distillation,[70-73] to reveal intrinsic limitations and thermodynamic insights of the processes. Applying similar analytical approaches to nutrient recovery can enhance fundamental understanding and shed light on the thermodynamic principles governing the separation, which can in turn inform efforts to capture N and P from the waste streams.

In this study, we conduct a thermodynamic analysis of nutrient recovery from different waste streams. First, governing equations for the theoretical minimum energy required to recover nutrients, determined using the Gibbs free energy of separation, are presented. The minimum energy to recover ammonia and phosphate are quantitatively assessed for different waste streams spanning a range of nutrient content, namely source-separated urine (fresh and hydrolyzed), greywater, domestic WW, and 2° WW effluent. Energy requirements to reclaim products of different nutrient species and concentrations are then examined. The impact of recovery yield on energy demand is evaluated and practical considerations are discussed. The energy to separate and capture other forms of N, specifically, nitrate and urea, is also explored. Next, we analyze the practical efficiency needed from actual processes for nutrient recovery from wastewaters to be competitive with conventional methods of N and P production, i.e., NH_3 fixation by Haber-Bosch and phosphate mining. Finally, implications of ammonia and phosphate separation from wastewaters are discussed and the benefits of nutrient recovery are highlighted.

MINIMUM ENERGY OF NUTRIENT RECOVERY

Gibbs Free Energy of Separation is the Minimum Energy to Recover Nutrients. In the recovery of nutrients from waste streams, the desired nutrient components of N and P are separated from the dilute feed to yield a nutrient-rich product, leaving a wastewater retentate stream less concentrated in N or P. The theoretical minimum energy required to achieve this nutrient recovery, E_{min}, is equal to the Gibbs free energy of separation, ΔG_{sep}, which is the difference between the Gibbs free energy of the product and retentate (resultant streams), and the wastewater (initial feed), as described by eqn (1):

$$E_{\mathrm{min}} = \Delta G_{\mathrm{sep}} = N_{\mathrm{P}} G_{\mathrm{P}} + N_{\mathrm{R}} G_{\mathrm{R}} - N_{\mathrm{F}} G_{\mathrm{F}} \tag{1}$$

where G is the molar Gibbs free energy, N is the total number of moles in each stream, and subscripts P, R, and F, denote the product, retentate, and feed streams, respectively.

The molar Gibbs free energy of a mixed solution is the sum of the partial molar Gibbs free energy of the constituent species:[74, 75]

$$G = \sum x_i G_i^0 + RT\left[\sum x_i \ln\left(\gamma_i x_i\right)\right] \tag{2}$$

where x and γ are mole fraction and activity coefficient of species i, G^0 is Gibbs free energy of formation in the aqueous solution at standard state, R is the gas constant, and T is absolute temperature.

By applying eqns (1) and (2), the Gibbs free energy of separation per mole of nutrient recovered, $\Delta \bar{G}_{\mathrm{sep}}$, can be expressed as:

$$\Delta \bar{G}_{\mathrm{sep}} = \frac{1}{x_{1,\mathrm{P}}} \left\{ \begin{array}{l} \sum x_{i,\mathrm{P}} G_{i,\mathrm{P}} + RT \sum x_{i,\mathrm{P}} \ln\left(\gamma_{i,\mathrm{P}} x_{i,\mathrm{P}}\right) \\ + \dfrac{N_{\mathrm{R}}}{N_{\mathrm{P}}} \left[\sum x_{i,\mathrm{R}} G_{i,\mathrm{R}} + RT \sum x_{i,\mathrm{R}} \ln\left(\gamma_{i,\mathrm{R}} x_{i,\mathrm{R}}\right)\right] \\ - \dfrac{N_{\mathrm{F}}}{N_{\mathrm{P}}} \left[\sum x_{i,\mathrm{F}} G_{i,\mathrm{F}} + RT \sum x_{i,\mathrm{F}} \ln\left(\gamma_{i,\mathrm{F}} x_{i,\mathrm{F}}\right)\right] \end{array} \right\} = \bar{E}_{\mathrm{min}} \tag{3}$$

where subscript 1 denotes the targeted nutrient component, i.e., N or P species. Therefore, with the composition and relative proportion of the feed, product, and retentate streams, the theoretical minimum energy to reclaim a mole of nutrient, $\bar{E}_{\mathrm{min}}$, can be determined using eqn (3). Note that for pure products, i.e., solid minerals or unmixed liquids, the product $\Sigma x \ln \gamma x$ term vanishes and $x_{1,\mathrm{P}}$ can be replaced with $n_{1,\mathrm{P}}$, the number of N or P atoms in the chemical structure of the pure liquid/solid mineral product ($n_{1,\mathrm{P}} = 1$ for all products except for $(NH_4)_2SO_4$, where $n_{1,\mathrm{P}} = 2$). Recovery yield, Y, is defined as the fraction of nutrient available in the initial feed captured in the product stream, and can be described by:

$$Y_{i,\mathrm{P}} = \frac{x_{1,\mathrm{P}} N_{\mathrm{P}}}{x_{1,\mathrm{F}} N_{\mathrm{F}}} \tag{4}$$

Note that, again, for solids and pure liquid products, $x_{1,\mathrm{P}}$ is replaced with $n_{1,\mathrm{P}}$.

Analysis of Minimum Energy for Nutrient Recovery. Detailed methodology to determine the molar minimum energy of nutrient recovery, $\overline{E}_{\mathrm{min}}$, is discussed in the ESI and briefly presented here. Typical ranges of nutrient species mole fraction concentrations and pHs of the greywater, domestic WW, 2° WW effluent, fresh urine, and hydrolyzed urine feed waste streams are based on literature data (Table S1 in the ESI),[60, 62-67] whereas $x_{1,\mathrm{P}}$ and $n_{1,\mathrm{P}}$ are dependent on the concentration and chemical structure of the product, respectively. Typical concentration ranges of other species in the waste streams of the analysis is presented in Table S2 in the ESI.[60, 62-68] For a certain Y (and corresponding $x_{1,\mathrm{P}}$ or $n_{1,\mathrm{P}}$), the retentate composition is determined by mole balance and accounting for speciation due to pH and concentration changes. I.e., the approach incorporates the effects of protonation/deprotonation on x of orthophosphates and ammoniacal nitrogen ($H_3PO_4/H_2PO_4^{-}/HPO_4^{2-}/PO_4^{3-}$ and $NH_4^{+}/NH_{3(aq)}$, respectively). To understand the influence of recovery yield on $\overline{E}_{\mathrm{min}}$, Y of 0.005, 0.2, 0.5, 0.8, and 1.0 are modeled for select wastewater matrices of 2° WW effluent and hydrolyzed urine. Because the complete water chemistry of most wastewater feeds are not fully know (i.e., species composition and buffering capacity), the analysis is able to only consider the capture of an infinitesimally small amount of nutrient, i.e., $Y \rightarrow 0$, such that the feed and retentate compositions are effectively identical. The complete equations utilized to determine the molar Gibbs free energy of separation for all scenarios in the analysis are presented in the ESI, eqns S(5)-S(20).

All calculations model recovery at T = 298 K. Non-ideal behavior in solutions was accounted for using activity coefficients, γ_i, which were determined using the Davies approximation,[37] nonrandom two-liquid method,[76, 77] or experimental data reported in literature,[78] as described in the ESI. G^0 for each species i in aqueous solution can be found in Table S3~~2~~ in the ESI. For pure liquids and solid minerals, the Gibbs free energy of the product is equal to the Gibbs free energy of formation at standard state, $G_{\mathrm{P}} = G_{f,\mathrm{P}}^{0}$ (values are presented in Table S4 of the ESI).

ENERGY REQUIREMENT FOR NUTRIENT RECOVERY

Harvesting Ammonia from More Concentrated Waste Streams Requires Less Energy. The molar minimum energy (i.e., per mole of NH_3 captured) to recover liquid ammonia, $NH_{3(l)}$, from different waste streams of varying TAN concentrations is calculated using eqn S(5) of the ESI and presented in Figure 2. Yields of 1 and 0, representing complete recovery of N in the product and capture of an infinitesimally small amount of N from the feed, respectively, were analyzed (solid and dashed lines). Typical TAN concentration ranges in the various waste streams are shown as floating bars and correspond to the horizontal axis (logarithmic scale). To isolate the impact of [TAN] on $\overline{E}_{\min}$, the analysis for $Y = 1$ assumes the feed waste streams to have pH << pK_a of NH_4^+ (9.24) and inexhaustible buffering capacity, such that the predominant form of TAN in both the feed and retentate is NH_4^+; the influence of $NH_4^+/NH_{3(aq)}$ speciation is considered in the next subsection. We note that the pH of all waste streams examined in this study, except for hydrolyzed urine, are usually well below 9.24 and, hence, TAN is mostly present as ammonium.[60, 62-68]

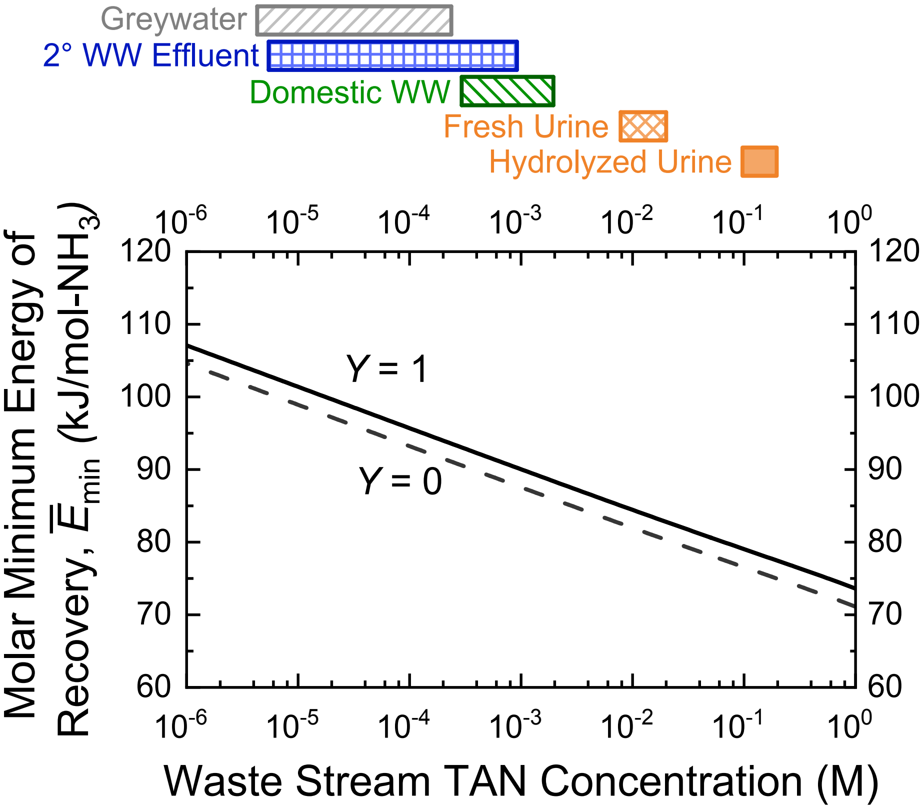

Figure 2. Molar minimum energy, $\overline{E}_{\min}$, to recover nutrient product of pure liquid ammonia as a function of waste stream TAN concentration for recovery yields, Y, of 1 and 0 (solid and dashed lines, respectively). Floating bars, corresponding to the horizontal axis (on logarithmic scale), represent the TAN concentration ranges for waste streams of greywater, secondary wastewater effluent, domestic

wastewater, fresh urine, and hydrolyzed urine. For simplification of analysis, all TAN in the waste streams was assumed to be present as NH_4^+.

As expected, Figure 2 demonstrates that to minimize the theoretical minimum energy to capture $NH_{3(l)}$, it is advantageous to target waste streams with high TAN concentrations. This trend is consistent with thermodynamic assessments of desalination, where $\overline{E}_{\text{min}}$ for water recovery increases with feed salinity.[70, 71] The minimum energy to reclaim $NH_{3(l)}$ essentially decreases linearly with increasing logarithm of TAN concentration in the waste stream, i.e., $\overline{E}_{\text{min}} \approx\propto -\log[\text{TAN}]$, primarily due to the ln$x$ terms of eqn (3). The slight deviation from perfect linearity is attributed to the non-linear dependence of $\gamma_{\text{NH}_4^+}$ on ionic strength (Davies approximation, eqn S(21) in the ESI).[37] In other words, the reduction in $\overline{E}_{\text{min}}$ is not proportional to the increase in [TAN] of the feed stream. Concentrated streams, such as hydrolyzed and fresh urine, have orders of magnitude more TAN than diluted streams of domestic wastewater, secondary wastewater effluent, and greywater; however, $\overline{E}_{\text{min}}$ is not orders of magnitude higher when capturing N from the diluted streams compared to the more concentrated streams. For example, hydrolyzed urine is ≈140-520× more concentrated in TAN than domestic wastewater, but $\overline{E}_{\text{min}}$ for product of $NH_{3(l)}$ at $Y = 0$ is only 1.13-1.22× greater for domestic WW.

Recovery yields of 1 and 0 exhibit similar trends, with $\overline{E}_{\text{min}}$ for $Y = 1$ approximately 3% higher than $Y = 0$ across the TAN concentrations investigated. As Y increases, NH_3 is separated from a progressively more dilute feed stream, thus requiring more energy and the averaged molar energy of separation rises. Again, parallels can be drawn to the increasing specific energy of desalination for larger water recovery yields.[15, 16] However, the magnitude of $\overline{E}_{\text{min}}$ increase for higher nutrient recoveries is drastically smaller than for desalination, where energy requirement almost doubles when Y is raised from 0 to 0.5. Because $\overline{E}_{\text{min}}$ between complete recovery and capturing an infinitesimally minute amount (i.e., $Y = 1$ and 0, respectively) differs only by ≈3%, examination of $\overline{E}_{\text{min}}$ for $Y = 0$ is informative of practical, nonzero recovery yields. Most of the subsequent analyses in this study evaluates $\overline{E}_{\text{min}}$ at $Y = 0$, while the impact of recovery yield on $\overline{E}_{\text{min}}$ will be discussed in depth in a latter section.

Feed Stream pH Affects $\bar{E}_{\mathrm{min}}$ by Influencing Speciation. $\bar{E}_{\mathrm{min}}$ values to recover select ammonia and phosphate products from various waste streams are shown in Figures 3A and B, respectively. The N products of liquid ammonia, $NH_{3(l)}$, aqueous ammonia solutions at 10, 5.0, and 1.0 M, and solid precipitate of ammonium sulfate, $(NH_4)_2SO_{4(s)}$, are common commercial fertilizers.[79-82] Likewise, solid precipitate P products of potassium magnesium phosphate, $KMgPO_4 \cdot 6(H_2O)$, struvite, $NH_4MgPO_4 \cdot 6H_2O$, potassium phosphate, KH_2PO_4, and monoammonium phosphate, $NH_4H_2PO_4$, are also conventional fertilizers available in the market.[82-89] Because each waste stream can be highly heterogeneous in nutrients content, concentrations of product co-species (e.g., SO_4^{2-} is co-species for $(NH_4)_2SO_{4(s)}$ product), and pH, the resultant energy requirement spans a range of values (according to eqn (3)). The top and bottom of the floating bars represent the highest and lowest $\bar{E}_{\mathrm{min}}$, respectively, for each waste stream and product pair. Detailed $\bar{E}_{\mathrm{min}}$ values for all conditions, calculated using eqns S(5)-S(12), can be found in Tables S5 and S6 of the ESI.

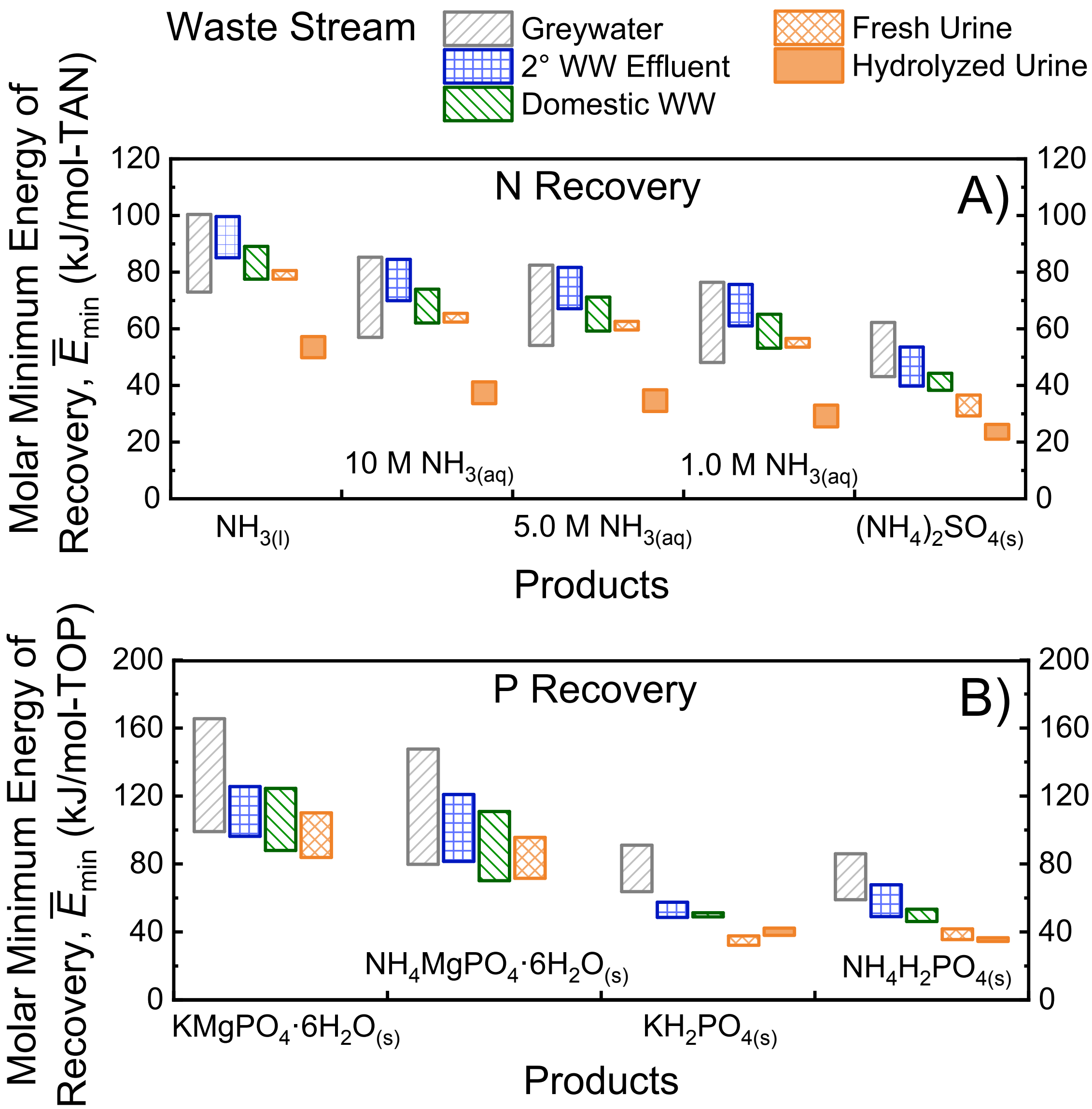

Figure 3. Molar minimum energy, $\overline{E}_{min}$, to recover A) TAN as products of liquid ammonia, $NH_{3(l)}$, 10, 5.0, and 1.0 M aqueous ammonia solutions, and ammonium sulfate solid, $(NH_4)_2SO_{4(s)}$; and B) TOP as mineral products of potassium magnesium phosphate, $KMgPO_4·6(H_2O)$, struvite, $NH_4MgPO_4·6H_2O$, potassium phosphate, KH_2PO_4, and monoammonium phosphate, $NH_4H_2PO_4$. Waste stream sources are greywater, secondary wastewater effluent, domestic wastewater, fresh urine, and hydrolyzed urine. Floating columns indicate the $\overline{E}_{min}$ ranges that correspond to the typical span of nutrient content, product co-species concentrations, and pH reported for the waste streams. The analysis considered recovery yield of 0 for all products, i.e., an infinitesimally minute amount of nutrient is recovered from the waste stream.

As previously discussed, TAN concentration in the waste stream is a primary factor influencing $\overline{E}_{\text{min}}$: minimum energy to capture ammonia products is generally lower when targeting waste streams of higher [TAN], such as hydrolyzed urine, compared to more diluted streams. Additionally, $\overline{E}_{\text{min}}$ is also dependent on the pH of the waste stream. For a certain waste stream [TAN], $\overline{E}_{\text{min}}$ values for the selected products are lower in N recovery scenarios with higher waste stream pH (Table S5). As an illustration, Figure 4 presents $\overline{E}_{\text{min}}$ for products recovered from greywater with [TAN] = 2.11×10^{-4} M (midpoint of concentration range), but at different pH values.

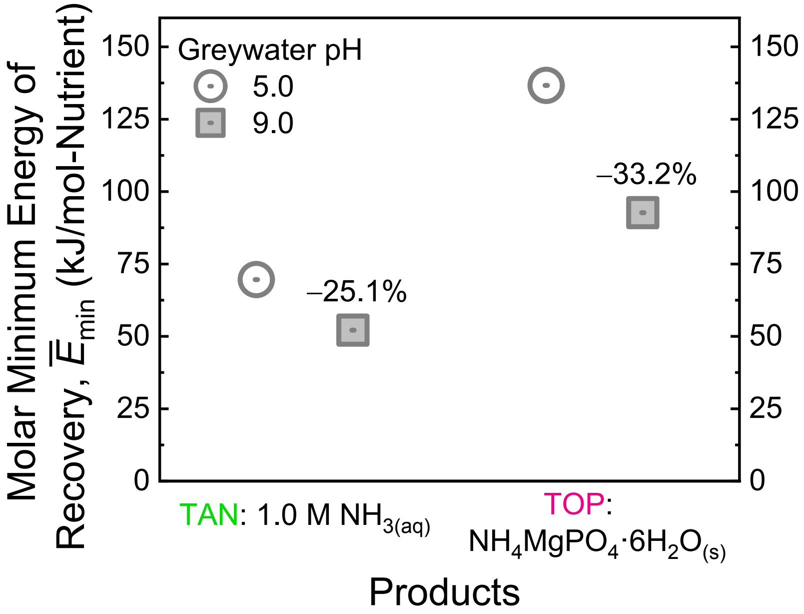

Figure 4. Molar minimum energy, $\overline{E}_{\text{min}}$, to recover TAN product of 1.0 M $NH_{3(aq)}$ and TOP product of struvite, $NH_4MgPO_4\cdot6H_2O_{(s)}$, from greywater at pH of 5.0 and 9.0 (open circle and filled square symbols, respectively). Labels above the symbols indicate the percent decrease in $\overline{E}_{\text{min}}$ from feed pH of 5.0 to 9.0. Mid-range greywater TAN and TOP concentrations of 2.11×10^{-4} M and 6.80×10^{-5} M, respectively, are utilized in this analysis and recovery yield of the product is 0 (i.e., an infinitesimally small quantity of nutrient is recovered from the waste stream).

$\overline{E}_{\text{min}}$ to recover 1.0 M $NH_{3(aq)}$ from greywater at pH of 9.0 is 25.1% less than at pH of 5.0. Because ammonia is a weak base, which can protonate to form ammonium, the fraction of TAN present as $NH_{3(aq)}$ rises with increasing pH (eqn S(1) in the ESI). The standard-state molar Gibbs free energy of formation of $NH_{3(aq)}$ is higher than that of NH_4^+ (−26.6 kJ/mol compared to −79.3 kJ/mol, Table S3) and, thus, the Gibbs free energy of separation is lower for $NH_{3(aq)}$ than NH_4^+, as per eqn (3). Hence, recovery of the N products is thermodynamically more favorable if TAN is present as $NH_{3(aq)}$ in more basic waste streams. The theoretical minimum energy to reclaim N from hydrolyzed urine is significantly lower than other waste streams (Figure 3A) because of the two advantages of higher pH and greater TAN concentration. Hydrolyzed urine pH range is 9-9.2, close to or at the pK_a of 9.24 for ammonium, whereas pH of the other waste streams are mostly ≈5-8.5. Also, [TAN] is 0.270-0.578 M for hydrolyzed urine, at least 67× greater than other N sources aside from fresh urine (still 5.5-32.2× higher). However, the energy benefits for $(NH_4)_2SO_{4(s)}$ recovery from hydrolyzed urine are less pronounced (Figure 3A), because N is captured as NH_4^+. Converting $NH_{3(aq)}$, the predominant TAN species in hydrolyzed urine, to ammonium increases ΔG_{sep} and offsets the beneficial G^0 effect. Overall, waste streams with both high TAN concentration and pH offer the smallest $\bar{E}_{min}$ to overcome for N recovery; of the waste streams examined here, hydrolyzed urine is the most optimal.

Among the N products evaluated, $\bar{E}_{min}$ is generally highest for $NH_{3(l)}$, followed by 10 M $NH_{3(aq)}$, 5.0 M $NH_{3(aq)}$, 1.0 M $NH_{3(aq)}$, and then $(NH_4)_2SO_{4(s)}$ (Figure 3A). For the aqueous ammonia solutions, $\bar{E}_{min}$ decreases with lower product concentration. This is reflected in eqn S(7) and also intuitively understood: a more dilute product stream requires less separation from the feed and, hence, demands less energy. For the pure products of $NH_{3(l)}$ and $(NH_4)_2SO_{4(s)}$, $\bar{E}_{min}$ is largely dependent on the Gibbs free energy of formation of the product, $G^0_{f,P}$ (Table S4 in the ESI), with a lower $G^0_{f,P}$ contributing to a smaller $\bar{E}_{min}$. Because $G^0_{f,(NH_4)_2SO_{4(s)}} << G^0_{f,NH_{3(l)}}$, recovering $(NH_4)_2SO_{4(s)}$ is thermodynamically more favorable than $NH_{3(l)}$.

Rational Selection of Waste Stream Feed and Products Minimizes Energy for Nutrient Recovery. Similar trends are also observed for TOP recovery (Figures 3B and 4). Note that because magnesium precipitates out from urine during hydrolysis,[60, 61, 90] [Mg^{2+}] in hydrolyzed urine is practically negligible and, hence, recovery of Mg-based P products, $NH_4MgPO_4 \cdot 6H_2O_{(s)}$, and $KMgPO_4 \cdot 6H_2O_{(s)}$, were not analyzed. Higher concentrations of TOP and product co-species (TAN, K^+, and Mg^{2+}) in the waste stream lowered $\bar{E}_{min}$. TOP concentrations in the waste stream follow the trend: greywater < secondary wastewater effluent < domestic wastewater < hydrolyzed urine < fresh urine, resulting in $\bar{E}_{min}$ values largely following the reverse trend, i.e., P recovery from fresh urine generally has the lowest $\overline{E}_{\min}$. However, one deviation is the separation of $NH_4H_2PO_{4(s)}$ from hydrolyzed urine. This is due to the low concentration of the product co-species, NH_4^+, significantly contributing to $\overline{E}_{\min}$. Although fresh urine is richer in TOP (1.13-1.57×), [TAN] is only 0.067-0.085 that of hydrolyzed urine.

Despite fresh urine having significantly higher [TOP], the molar minimum energies of recovery for struvite, $NH_4MgPO_4{\cdot}6H_2O_{(s)}$, and potassium magnesium phosphate (KMP), $KMgPO_4{\cdot}6H_2O_{(s)}$, are comparable with the lower $\overline{E}_{\min}$ range for the more dilute streams of domestic WW, 2° WW effluent, and greywater. This is because P is present in struvite and KMP as PO_4^{3-}, the least protonated form of phosphate, and a greater portion of TOP in the feed exists as PO_4^{3-} at higher pHs. The pH range for fresh urine (6-7.5) is lower than domestic wastewater and secondary-treated wastewater effluent (6.5-8.5 and 6.8-7.7, respectively) and is considerably below the high-end of greywater (pH = 9). In the recovery of struvite and KMP from fresh urine, the deprotonation of $H_2PO_4^-$ (predominant species below pH of 7.2) to PO_4^{3-} increases ΔG_{sep}, and partially nullifies the benefits of the high [TOP]. Therefore, $\overline{E}_{\min}$ is not substantially lower than other waste streams at higher pH (Table S6). The impact of pH on $\overline{E}_{\min}$ is further illustrated by Figure 4, which shows $\overline{E}_{\min}$ of struvite recovery from greywater at pH = 5.0 and 9.0. $\overline{E}_{\min}$ at pH = 9.0 is markedly depressed (−33.2%) relative to pH of 5.0. As the dominant forms of phosphate at pH = 5.0 and 9.0 are $H_2PO_4^-$ and HPO_4^{2-}, respectively, less energy is required for the conversion to PO_4^{3-} with the more basic feed stream. This trend is observed for struvite and KMP across the different waste streams (Table S6) and also corroborated by experimental observations that the two minerals precipitate more readily in higher pH solutions.[91] In contrast, the effect of pH on $\overline{E}_{\min}$ is negligible for KH_2PO_4 and $NH_4H_2PO_4$, where P is present as $H_2PO_4^-$ (Table S6).

The most thermodynamically favorable products for P recovery are $KH_2PO_{4(s)}$ and $NH_4H_2PO_{4(s)}$, followed by $NH_4MgPO_4{\cdot}6H_2O_{(s)}$ and $KMgPO_4{\cdot}6H_2O_{(s)}$, with $\overline{E}_{\min}$ primarily affected by the phosphate identity ($H_2PO_4^-$ or PO_4^{3-}) and feed concentrations of product co-species (specifically Mg^{2+}). The acid dissociation constants of phosphoric acid are 2.2, 7.2, and 12.4. For the waste streams investigated here, the typical pH ranges between 5 and 9.2. Hence, the predominant phosphate species are $H_2PO_4^-$ or HPO_4^{2-}. Because the conversion of the predominant phosphate species to $H_2PO_4^-$ (no reaction or protonation of one H^+) needed to form $KH_2PO_{4(s)}$ and $NH_4H_2PO_{4(s)}$ requires less energy than the conversion to PO_4^{3-} (deprotonation of one or two H^+), $\overline{E}_{\mathrm{min}}$ is larger for struvite and KMP. Furthermore, the formation of struvite and KMP require Mg^{2+} in additional to NH_4^+ and K^+, respectively. The separation of Mg^{2+} from waste streams with low $[Mg^{2+}]$ adds to the energy cost, hence, contributing to the greater $\overline{E}_{\mathrm{min}}$ for $NH_4MgPO_4{\cdot}6H_2O_{(s)}$ and $KMgPO_4{\cdot}6H_2O_{(s)}$.

For nutrient recovery from waste streams, it is advantageous to minimize energy requirements, thus a low $\overline{E}_{\mathrm{min}}$ is desirable. The main factors influencing the molar minimum energy for nutrient recovery are: nutrient concentrations in the feed, waste stream pH, and co-species in the product. To minimize $\overline{E}_{\mathrm{min}}$, waste streams and products can be strategically targeted. Hydrolyzed urine and fresh urine, which contain the highest concentrations of TAN and TOP, respectively, are almost always the most optimal streams for TAN and TOP recovery. However, depending on the product, certain waste streams may be better suited because of the more favorable pH and co-species concentration. Therefore, the selection of product should be informed by the pH, availability of nutrients, and co-species in the specific waste stream.

Impact of Nutrient Recovery Yields on Minimum Energy of Recovery. Previous analysis modeled $\overline{E}_{\mathrm{min}}$ for capturing various products from different waste streams at $Y = 0$. However, actual nutrient recovery will have nonzero recovery yields. Figure 5 shows $\overline{E}_{\mathrm{min}}$ of select ammonia products of 1.0 M NH_3 aqueous solution and $NH_{3(l)}$ (open and filled symbols, respectively) from two waste streams of secondary wastewater effluent and hydrolyzed urine (blue square and orange circle symbols, respectively) as a function of NH_3 recovery yield. As discussed previously, at $Y = 0$, i.e., infinitesimally small NH_3 recovery, the pH and TAN speciation in the feed and retentate are essentially equal. However, at higher recovery yields, the pH and TAN speciation in the retentate stream differ significantly from the feed stream. Therefore, to calculate $\overline{E}_{\mathrm{min}}$ for $Y > 0$, the speciation of TAN (i.e., fraction of TAN as $NH_{3(aq)}$ and NH_4^+, denoted by $\alpha_{\mathrm{NH_3}}$ and $\alpha_{\mathrm{NH_4^+}}$, respectively) in both the feed and retentate stream must be considered in conjunction with the TAN material balance (i.e., $x_{\mathrm{TAN,F}}N_{\mathrm{F}} + x_{\mathrm{TAN,RXN}}N_{\mathrm{RXN}} = x_{\mathrm{TAN,P}}N_{\mathrm{P}} + x_{\mathrm{TAN,R}}N_{\mathrm{R}}$).

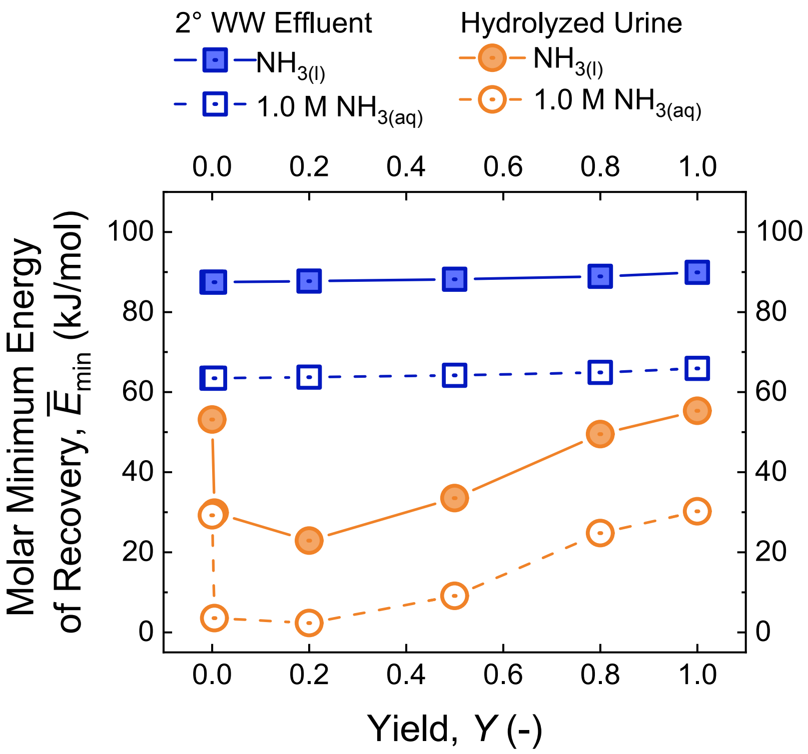

Figure 5. Molar minimum energy, $\bar{E}_{\text{min}}$, to recover NH_3 as products of liquid ammonia, $NH_{3(l)}$, or 1.0 M $NH_{3(aq)}$ aqueous solution (filled and open symbols, respectively) from secondary wastewater effluent and hydrolyzed urine (blue square and orange circle symbols, respectively) as a function of recovery yield, Y (0, 0.005, 0.2, 0.5, 0.8, and 1). The mid-range TAN and pH of 2° WW effluent and hydrolyzed urine were utilized for this analysis.

For scenarios with secondary wastewater effluent (blue square symbols), the feed stream pH << pK_a, which results in nearly complete predominance of NH_4^+ over $NH_{3(aq)}$ (i.e., $\alpha_{NH_4^+} \approx 1$ and $\alpha_{NH_3} \approx 0$). Because removing basic NH_3 leaves the remaining solution more acidic, pH of the retentate stream is always lower than the feed stream pH. Therefore, TAN speciation in the feed and retentate streams for 2° WW effluent are essentially equal, with $\alpha_{NH_4^+,R} \approx \alpha_{NH_4^+,F} \approx 1$ and $\alpha_{NH_3,R} \approx \alpha_{NH_3,F} \approx 0$. Increasing Y results in a slight increase in $\bar{E}_{\text{min}}$ for both $NH_{3(l)}$ and 1.0 M $NH_{3(aq)}$ recovery. This trend is consistent with Figure 2, which also simulated waste streams with NH_4^+ as the predominant form of TAN. Importantly, $\bar{E}_{\text{min}}$ only marginally increases (< 4%) between $Y = 0$ and 1. Thus, actual nutrient recovery applications can take advantage of this by striving for higher yields without significantly raising the theoretical energy requirement.

For hydrolyzed urine (orange circle symbols in Figure 5), the feed pH is near the pK_a of ammonium, such that $\alpha_{NH_3} \neq 0$. Thus at $Y > 0$, TAN speciation in the feed and retentate streams differ significantly, i.e., $\alpha_{NH_3,R} \neq \alpha_{NH_3,F}$ and $\alpha_{NH_4^+,R} \neq \alpha_{NH_4^+,F}$. An in-depth discussion of methodology to account for this differing speciation can be found in the ESI. In contrast to 2° WW effluent, the trends for $\overline{E}_{min}$ of $NH_{3(l)}$ and 1.0 M $NH_{3(aq)}$ recovery from hydrolyzed urine are not monotonic, but instead exhibit L-shaped rebounds with initial sharp decreases and followed by gradual increases. This signifies that reclaiming the first molecule of NH_3 from hydrolyzed urine requires, in theory, more energy than the next molecules until a certain amount of ammonia is recovered and, thereafter, capturing every additional NH_3 molecule requires more energy than the last. In contrast to secondary wastewater effluent, $\overline{E}_{min}$ of hydrolyzed urine changes significantly as a function of recovery yield. The distinction between $\overline{E}_{min}$ trends of the two waste streams is due to the disparate speciation of TAN in the retentates. For 2° WW effluent scenarios, $\alpha_{NH_4^+,R}$ and $\alpha_{NH_3,R}$ are effectively independent of Y and, therefore, the concentration of both NH_4^+ and $NH_{3(aq)}$ in the retentate consistently decrease with higher yields. However, for hydrolyzed urine scenarios, pH of the retentate significantly declines at higher yields and, thus, $\alpha_{NH_4^+,R}$ increases and $\alpha_{NH_3,R}$ decreases (see ESI Tables S8 and S9 for pH and speciation in the feed and retentate at different Y, for products of $NH_{3(l)}$ and 1.0 M $NH_{3(aq)}$, respectively). Because the magnitude of the Gibbs free energy of formation for NH_4^+ is much greater than $NH_{3(aq)}$ (−79.3 and −26.6 kJ/mol, respectively), NH_4^+ is the thermodynamically preferred form of TAN in solution. This results in competing factors affecting $\overline{E}_{min}$: TAN in the retentate decreases with increasing yield, which drives $\overline{E}_{min}$ to increase, but this is countered by the reduction in $\overline{E}_{min}$ as the fraction of TAN present as NH_4^+ in the retentate increases with increasing yield. At low Y, the latter factor is more dominant, thus explaining the initial dip in $\overline{E}_{min}$. With greater Y, retentate pH drops and NH_4^+ becomes increasingly predominant over $NH_{3(aq)}$. Beyond a certain point, the former factor dominates and $\overline{E}_{min}$ increases. Further quantitative analysis and a more detailed discussion can be found in the ESI.

Nitrate and Urea are Other Forms of Nitrogen Suitable for Recovery. In addition to ammoniacal products of $NH_{3(l)}$, $NH_{3(aq)}$, and $NH_4SO_{4(s)}$, N can be recovered in other forms, such as nitrate, NO_3^-, and urea, $CO(NH_2)_2$.[80, 82] Nitrate is present in greywater, domestic wastewater, and secondary wastewater effluent (but is only present in negligible amounts in fresh or hydrolyzed urine), whereas urea is excreted in fresh urine (upon storage, the compound hydrolyzes into TAN and bicarbonate and, thus, urea is not present in significant quantities in the other waste streams). Figure 6 shows the range of molar minimum energies to reclaim aqueous and solid products containing NO_3^- from 2° WW effluent, as well as aqueous and solid urea from fresh urine. Based on complied literature data, nitrate concentration in secondary wastewater effluent spans from 0.0714-1.42 mM and urea concentration range in fresh urine is 126-265 mM (252-530 mM-N).[60, 62-68] To calculate $\overline{E}_{\text{min}}$ for 1.0 M $KNO_{3(aq)}$, 1.0 M $NH_4NO_{3(aq)}$, $KNO_{3(s)}$, and $NH_4NO_{3(s)}$ recovery from 2° WW effluent, eqns S(13), S(14), S(15), and S(16) were used, respectively; to calculate $\overline{E}_{\text{min}}$ to recover 1.0 M $CO(NH_2)_{2(aq)}$ and $CO(NH_2)_{2(s)}$ from fresh urine, eqns S(17) and S(18) were utilized, respectively. Note that, for every mole of product, $CO(NH_2)_2$ and NH_4NO_3 contain 2 moles of N, whereas KNO_3 has only 1 mole of N.

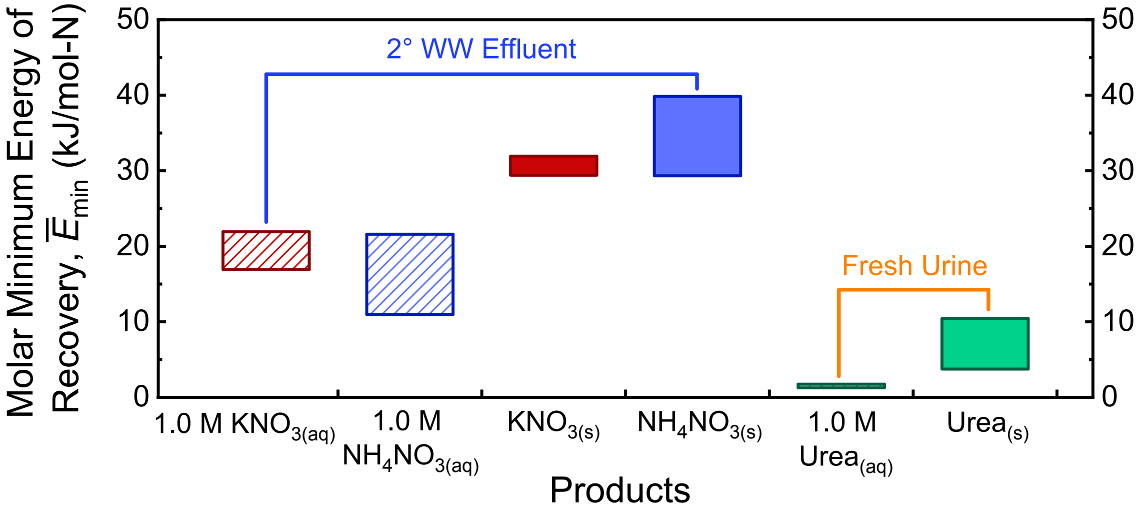

Figure 6. Molar minimum energy, $\overline{E}_{min}$, to recover different N products from waste streams of secondary wastewater effluent and fresh urine. Products recovered from 2° WW effluent are 1.0 M $KNO_{3(aq)}$, 1.0 M $NH_4NO_{3(aq)}$, $KNO_{3(s)}$, and $NH_4NO_{3(s)}$, whereas products reclaimed from fresh urine are 1.0 M aqueous urea solution, $CO(NH_2)_{2(aq)}$, and solid urea, $CO(NH_2)_{2(s)}$. Patterned and shaded columns denote aqueous and solid products, respectively. Floating columns indicate the $\overline{E}_{min}$ ranges that correspond to the typical span of nutrient content, product co-species concentrations, and pH reported for the waste streams. The recovery yield is 0 for all products, i.e., an infinitesimally minute amount of nutrient is recovered from the waste stream.

The recovery of urea products from fresh urine is less energy demanding than the recovery of nitrate products from secondary wastewater effluent. This is attributed to urea being over 100-fold more concentrated in fresh urine than nitrate and the product co-species (NH_4^+ and K^+) are in 2° WW effluent. As discussed previously, $\overline{E}_{min}$ is lower when capturing products from a more concentrated waste stream. For the aqueous products, $\overline{E}_{min}$ is lowest for $CO(NH_2)_{2(aq)}$ followed by $NH_4NO_{3(aq)}$, then $KNO_{3(aq)}$. For solid products, $NH_4NO_{3(s)}$ recovery from secondary wastewater effluent has the highest $\overline{E}_{min}$. This is because the Gibbs free energy required to form solid NH_4NO_3 from the initial species of aqueous NH_4^+ and NO_3^- in the feed is greater than for $CO(NH_2)_{2(s)}$ and $KNO_{3(s)}$ (Table S10 in the ESI). Generally, the recovery of 1.0 M aqueous products are thermodynamically more favorable than pure solids. This can be intuitively understood: producing solids requires the separation of all the water from the minerals, whereas less water needs to be removed to yield aqueous solutions. Furthermore, ordering free ions in aqueous solution into a solid crystal lattice incurs an additional entropic energy penalty, which further raises $\overline{E}_{\min}$. However, there can be exceptions to the rule. Specific scenarios of pH-dependent speciation in the feed and Gibbs free energy of formation of the solid product can yield opposite trends. An example of such a deviation is the higher $\overline{E}_{\min}$ for the recovery of 1.0 M $NH_{3(aq)}$ than for $NH_4SO_{4(s)}$ (Figure 3).

The $\overline{E}_{\min}$ values to reclaim aqueous nitrate products, 1.0 M $KNO_{3(aq)}$ and 1.0 M $NH_4NO_{3(aq)}$, from 2° WW effluent are less than 1.0 M $NH_{3(aq)}$ recovery from hydrolyzed urine, which is the lowest $\overline{E}_{\min}$ for aqueous TAN recovery in Figure 3. $\overline{E}_{\min}$ values to recover solid nitrate products, $KNO_{3(s)}$ and $NH_4NO_{3(s)}$, from 2° WW effluent are also comparable to or lower than recovery of TAN product $(NH_4)_2SO_{4(s)}$ from all waste streams other than fresh and hydrolyzed urine. These comparisons suggest that, in principle, recovering nitrate from 2° WW effluent may be an equally or more favorable alternative to TAN recovery. However, the Gibbs free energy to reduce nitrate to the bio-preferred form of N—ammonia, NH_3—is 591 kJ/mol.[3] The additional energy requirement to reduce the oxidation state of N from +5 to −3 (8 electrons) is an order of magnitude higher than $\overline{E}_{\min}$ for TAN recovery. The better suitability of NH_3 as a fertilizer and the huge energy cost to convert nitrate to ammonia, thus, indicate that targeting TAN over NO_3^- would be more prudent for nutrient recovery. $\overline{E}_{\min}$ values to capture urea as aqueous and solid products from fresh urine are significantly lower than the different TAN product and waste stream pairing examined here. Specific pros and cons of different nitrogen fertilizers aside,[92-94] the theoretically less energy-intensive path provides impetus to pursue the realization of urea recovery from fresh urine.

Presence of Other Species in Wastewater Matrix Marginally Increases Energy Demand for Nutrient Recovery. Analyses presented earlier consider the feed streams as simplified solutions containing only species required for the product (i.e., nutrients and co-species), in addition to H_2O, OH^-, and H^+. However, actual waste streams are complex water matrices with many other solutes, including different ions and neutral compounds. Na^+ and Cl^- are two prominent ionic species universally present in all the examined waste streams (e.g., NaCl concentrations in secondary wastewater effluent and hydrolyzed urine are 1.41-17.4 and 64.9-119 mM, respectively). To quantify the influence of species passive, such as NaCl, to the nutrient recoveries $\overline{E}_{\min}$ values are evaluated for the capture of NaCl-free $NH_{3(l)}$ and 1.0 M $NH_{3(aq)}$ from secondary wastewater effluent and hydrolyzed urine using eqns S(6) and S(7) (with 0 mM NaCl) and eqns S(19) and S(20) (with 9.40 and 88.9 mM NaCl in the feeds, respectively). Because the recovered products do not contain the passive species NaCl, the difference in $\overline{E}_{\text{min}}$ signifies the additional energy to separate the nutrients from Na^+ and Cl^- present in the waste streams. In this analysis, mid-range TAN content, NaCl concentration, and pH of the waste streams were utilized. Detailed results are presented in Table S11 in the ESI.

The inclusion of passive species in the determination of $\overline{E}_{\text{min}}$ results in only miniscule added energy requirements of 0.10-1.89% across the investigated scenarios. When NaCl in the waste stream is considered, $\overline{E}_{\text{min}}$ is marginally higher due to the additional energy to separate TAN from Na^+ and Cl^-, in addition to H_2O. However, because NaCl is present at substantially lower concentrations compared to H_2O at ≈55 mol/L (i.e., the waste streams are >99% water, even for the most saline feeds), this increase is minimal. Therefore, the ubiquitous presence of passive species in the waste streams has a negligible impact on the theoretical energy to recover N and P nutrients. Nonetheless, the purity of the product and the presence of undesired species, such as Na^+, are important metrics for the resultant fertilizers.

Energy Intensity of N and P Recovery from Waste Streams can be Competitive with Conventional Nutrient Production. The energy demand discussed so far is the theoretical minimum, but in practical nutrient recovery processes, the actual energy required to capture N and P will be higher than $\overline{E}_{\text{min}}$ due to inevitable inefficiencies of the recovery techniques. This analysis examines the practical molar energy of recovery, $\overline{E}_{\text{prac}}$, defined as the energy required to recover a mole of nutrient using a putative practical process with an assumed efficiency of η, i.e., $\overline{E}_{\text{prac}} = \overline{E}_{\text{min}}/\eta$. Figures 7A and B present $\overline{E}_{\text{prac}}$ as a function of η for harvesting TAN and TOP products, respectively, from different waste streams. For each nutrient, two products $\overline{E}_{\text{min}}$ were selected to illustrate a range of energy demand, namely pure liquid ammonia and 1.0 M aqueous ammonia solution for N and solid precipitates of potassium magnesium phosphate and potassium phosphate for P. For the waste streams, a centralized source of secondary wastewater effluent and a decentralized source of either hydrolyzed urine or diverted fresh urine for N and P, respectively, were selected for quantitative comparisons. Mid-range $\overline{E}_{\text{min}}$ values from

Figure 3 were used and recovery yield $Y \rightarrow 0$, i.e., an infinitesimally small amount of nutrient is reclaimed from the waste stream. The ranges of energy costs for conventional linear economy approaches to nutrient production, i.e., Haber-Bosch for N-fixation[1-3] and mining and beneficiation for phosphate,[5, 8] are also depicted as shaded green regions.

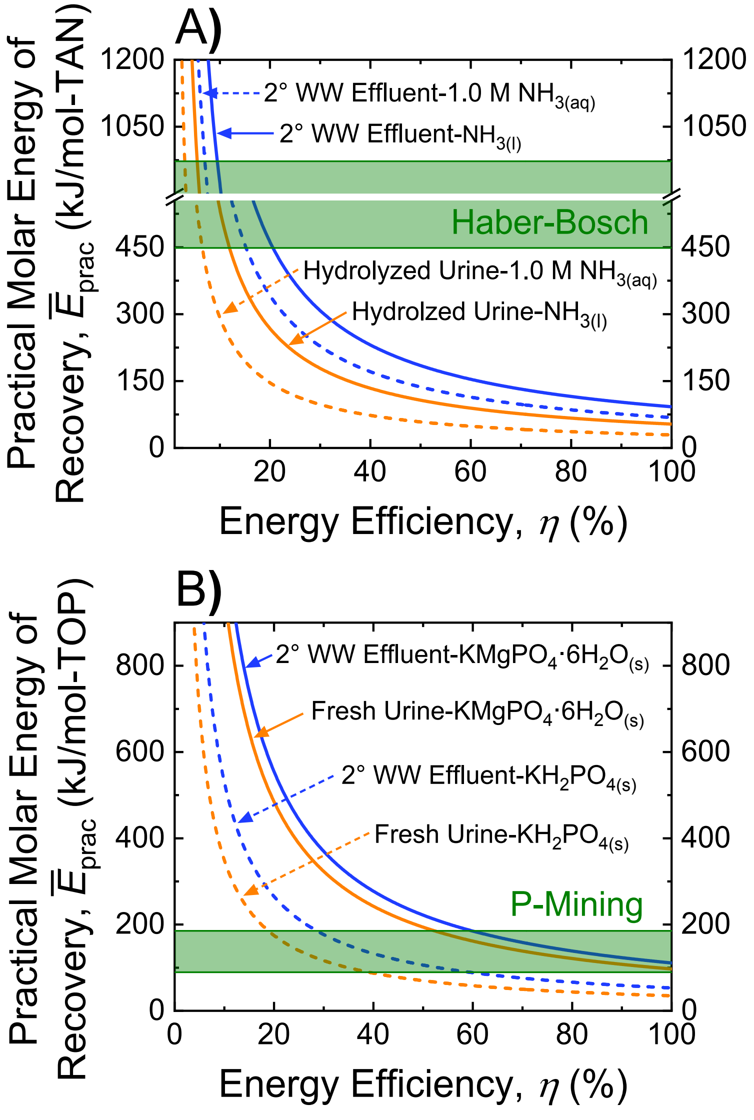

Figure 7. Practical molar energy, $\bar{E}_{\mathrm{prac}}$ as a function of efficiency, η, for an actual process to recover A) TAN from hydrolyzed urine and secondary wastewater effluent as 1.0 M $NH_{3(aq)}$ and $NH_{3(l)}$ and B) TOP from fresh urine and secondary wastewater effluent as $KMgPO4\cdot 6H2O_{(s)}$ and $KH_2PO4_{4(s)}$. Mid-range $\bar{E}_{\mathrm{min}}$ values were used and $Y \rightarrow 0$, i.e., an infinitesimally small amount of nutrient is recovered from the waste stream, for all scenarios. Note that $\bar{E}_{\mathrm{prac}}$ at η = 100% is equivalent to $\bar{E}_{\mathrm{min}}$. For

comparison, the range of energy costs required for N-fixation by the Haber-Bosch process (448-973 kJ/mol-N)[1-3] and phosphate rock mining and beneficiation (89-185 kJ/mol-P)[5, 8] are shown as shaded green areas in A and B, respectively.

The high energy intensity of nitrogen fixation by the Haber-Bosch process and the relatively low $\overline{E}_{\mathrm{min}}$ signify that TAN recovery from the different waste streams can be competitive across a large range of process efficiencies (lines below green shaded region of Figure 7A). Harvesting TAN as 1.0 M $NH_{3(aq)}$ from hydrolyzed urine requires η as low as ≈7% (dashed orange line, Figure 7A). Even the more energy demanding recovery of $NH_{3(l)}$ from secondary wastewater effluent can be competitive with separation techniques of efficiencies >25% (solid blue line). As comparisons, the energy efficiencies of reverse osmosis desalination and liquid-liquid extraction are around 25% (for 10-fold concentration, approximately equivalent to recovery yield of 0.9).[95] We note that the $\overline{E}_{\mathrm{min}}$ values utilized for this analysis are for $Y \rightarrow 0$. Even for practical recovery yields >> 0, the elevation of $\overline{E}_{\mathrm{min}}$ is only marginal at most, as previously discussed (Figures 2 and 5), and, hence, the increase in required energy efficiencies of the actual processes are expected to be modest.

In contrast, the substantially lower energy cost of conventional P production significantly constrains the energy efficiencies for recovery techniques to be competitive. $KH_2PO_{4(s)}$ recovery from fresh urine and 2° WW effluent need η greater than 39% and 59%, respectively, to have lower energy requirements than current phosphate mining and beneficiation (dashed orange and blue lines, Figure 7B). However, for $KMgPO_4{\cdot}6H_2O_{(s)}$ recovery, the energy requirement can, at best, be comparable with the conventional approach for P production, even with highly efficiency methods of $\eta > 60\%$ (solid orange and blue lines). Therefore, the strategic selection of waste stream and nutrient product are imperative to maximize the chances of success for competitive phosphate recovery.

IMPLICATIONS

A circular economy espouses cyclical material flows.[96] The approach, hence, promotes the recovery of nutrients from discard streams for reuse, to lower industrial N production and P mining from the current unsustainable levels, and concomitantly protect aquatic environments from harmful N and P emissions. To realize viable implementation, the methods for nutrient recovery from waste streams must be competitive with existing practices across key metrics, including energy requirements. This study analyzed the thermodynamics of the separations to identify the minimum energy requirements for various nutrient recovery schemes employing different waste streams as the feed, targeting diverse fertilizer products, and achieving a range of recovery yields. The analysis quantified lower theoretical energy intensities of N and P recovery from nutrient-rich sources, such as diverted fresh and hydrolyzed urine, and indicates that waste stream pH and speciation of components are important factors affecting the separation that need to be considered in the product selection and design of actual nutrient recovery processes. The analytical approach for thermodynamic evaluation presented here can inform the strategic selection of waste stream, fertilizer product, and recovery yield, to enhance the competitiveness of nutrient recovery on the energy-intensity metric. The specific results and/or the general approach for determination of energy requirements presented here can be employed in life-cycle assessments to more comprehensively evaluate the environmental impacts associated with all the stages of nutrient recovery from waste streams.

The study also sheds light on the potential practical energy requirements of actual nutrient recovery using technologies with various efficiencies. Importantly, the separation processes need to operate above certain efficiencies for energy demand of N and P recovery to be lower than the conventional linear economy production methods, i.e., Haber-Bosch for N fixation and phosphate rock mining. For instance, ammoniacal nitrogen recovery from hydrolyzed urine, generally the least energy-intense TAN reclamation among the scenarios investigated here, only requires efficiency >7%. The use of urine as the feed source has additional benefits of reduced pathogen and heavy metal concentrations compared to other waste streams.[69, 97, 98] Further, urine contains approximately 80% and 50% of the N and P in human excretions, respectively.[69, 98] Thus, N and P recovery from urine can enable significant reductions in nutrient loading to WWTPs and, ultimately, aquatic environments. Compared to nitrogen recycling, phosphorous reuse is more challenging. Because concentrations in the waste streams are inherently lower and typical fertilizer products are pure solid minerals, the theoretical minimum energy of phosphate recovery is significantly greater. The relatively smaller energy cost of current P mining practices further compounds to the difficulty of the task, necessitating recovery processes to have higher efficiencies in order to be competitive. Technologies with energy efficiencies >39% are needed even for the least demanding orthophosphate separation and capture from fresh urine. However, with phosphate reserves unceasingly depleting and high-grade ores rapidly exhausted, energy expenditures for mining are expected to surge.[7, 99] Furthermore, nutrient recovery has the additional benefit of environmental protection. Therefore, P recovery from waste streams will likely become increasingly attractive compared to the conventional linear economy approach. Nevertheless, the development of more energy efficient technologies will enhance the accessibility of nutrient recovery from waste streams.

To put in perspective the benefits of a circular economy approach for nutrient management over the existing linear economy model, we performed a first-order estimation of the potential energy savings achievable through supplementing current fertilizer production with nutrient recovery from waste streams. In 2017, the International Fertilizer Association estimated global nutrient demands of 7,930 $\times 10^9$ mol-N and 148 $\times 10^9$ mol-P.[100] Given the respective concentrations of N and P in hydrolyzed and fresh urine, the world population of 7.6 billion in 2017,[101] and 1-2 L/d of urine produced per person, around 748-3,208 $\times 10^9$ mol-N and 54-267 $\times 10^9$ mol-P were excreted in urine annually. Therefore, in principle, 9-40% and 36-180% of the N and P fertilizer markets, respectively, could be supplemented by TAN and TOP reclaimed from urine. The recovery of half of the available TAN in hydrolyzed urine as 1.0 M $NH_{3(aq)}$ using techniques achieving 50% efficiency can notionally reduce the global energy demand for industrial N production by 4.6-20.0%. Similarly, using recovery technologies that are 50% efficient to capture half of the TOP in fresh urine as $KH_2PO_{4(s)}$ can presumably reduce the energy required to produce P fertilizer by 4.0-15.9%. The sizable energy savings and significant environmental benefits of capturing N and P from waste streams, particularly urine, for reuse provide compelling justification for the broad implementation of nutrient recovery.

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REFERENCES

1. J. W. Erisman, M. A. Sutton, J. Galloway, Z. Klimont and W. Winiwarter, How a century of ammonia synthesis changed the world, *Nat. Geosci.* , 2008, **1**, 636-741.

2. D. Fowler, M. Coyle, U. Skiba, M. A. Sutton, J. N. Cape, S. Reis, L. J. Sheppard, A. Jenkins, B. Grizzetti, J. N. Galloway, P. Vitousek, A. Leach, A. F. Bouwman, K. Butterbach-Bahl, F. Dentener, D. Stevenson, M. Amann and M. Voss, The global nitrogen cycle in the Twentyfirst century, *Philos. Trans. R. Soc. B, Biol. Sci.*, 2013, **368**.
3. J. G. Chen, R. M. Crooks, L. C. Seefeldt, K. L. Bren, R. M. Bullock, M. Y. Darensbourg, P. L. Holland, B. Hoffman, M. J. Janik, A. K. Jones, M. G. Kanatzidis, P. King, K. M. Lancaster, S. V. Lymar, P. Pfromm, W. F. Schneider and R. R. Schrock, Beyond fossil fuel-driven nitrogen transformations, *Science*, 2018, **360**.
4. X. D. Gebrehiwet Reta, Zhonghua Li, Bob Su, Xiaonong Hu, Huijuan Bo,Dan Yu,Hao Wan, Ji Liu, Yinghai Li, Gang Xu, Kai Wang, Shijin Xu, Environmental impact of phosphate mining and beneficiation: review, *Int. J. Hydrol. Sci.*, 2018, **2**, 424-431.
5. *ITP Mining: Energy and Environmental Profile of the U.S. Mining Industry* Department of Energy, Office of Energy Efficiency & Renewable Energy, 2002.
6. V. Smil, Phosphorus in the Environment: Natural Flows and Human Interferences, *Annu. Rev. Environ. Resour.*, 2000, **25**, 53-88.
7. J. Elser and E. Bennett, A broken biogeochemical cycle, *Nature*, 2011, **478**, 29-31.
8. D. I. Bleiwas, *Estimates of Electricity Requirements for the Recovery of Mineral Commodities, with Examples Applied to Sub-Saharan Africa*, Report 2011–1253, Reston, VA, 2011.
9. M. Maurer, P. Schwegler and T. A. Larsen, Nutrients in urine: energetic aspects of removal and recovery, *Water Sci. Technol.* , 2003, **48**, 37-46.
10. A. Mulder, The quest for sustainable nitrogen removal technologies, *Water Sci. Technol.* , 2003, **48**, 67-75.
11. B. Wett, Development and implementation of a robust deammonification process, *Water Sci. Technol.*, 2007, **56**, 81-88.
12. T. Schaubroeck, H. De Clippeleir, N. Weissenbacher, J. Dewulf, P. Boeckx, S. E. Vlaeminck and B. Wett, Environmental sustainability of an energy self-sufficient sewage treatment plant: Improvements through DEMON and co-digestion, *Water Res.*, 2015, **74**, 166-179.
13. T. A. Larsen, A. C. Alder, R. I. L. Eggen, M. Maurer and J. Lienert, Source separation: Will we see a paradigm shift in wastewater handling?, *Environ. Sci. Technol.*, 2009, **43**, 6121.
14. A. M. Michalak, E. J. Anderson, D. Beletsky, S. Boland, N. S. Bosch, T. B. Bridgeman, J. D. Chaffin, K. Cho, R. Confesor, I. Daloglu, J. V. DePinto, M. A. Evans, G. L. Fahnenstiel, L. He, J. C. Ho, L. Jenkins, T. H. Johengen, K. C. Kuo, E. LaPorte, X. Liu, M. R. McWilliams, M. R. Moore, D. J. Posselt, R. P. Richards, D. Scavia, A. L. Steiner, E. Verhamme, D. M. Wright and M. A. Zagorski, Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions, *Proc. Natl. Acad. Sci.*, 2013, **110**, 6448-6452.
15. D. J. Conley, H. W. Paerl, R. W. Howarth, D. F. Boesch, S. P. Seitzinger, K. E. Havens, C. Lancelot and G. E. Likens, Ecology - Controlling eutrophication: Nitrogen and phosphorus, *Science*, 2009, **323**, 1014-1015.
16. R. J. Diaz and R. Rosenberg, Spreading dead zones and consequences for marine ecosystems, *Science*, 2008, **321**, 926-929.
17. D. M. Anderson, J. M. Burkholder, W. P. Cochlan, P. M. Glibert, C. J. Gobler, C. A. Heil, R. Kudela, M. L. Parsons, J. E. Rensel, D. W. Townsend, V. L. Trainer and G. A.

Vargo, Harmful algal blooms and eutrophication: Examining linkages from selected coastal regions of the United States, *Harmful Algae*, 2008, **8**, 39-53.
18. B. C. Hitzfeld, S. J. Hoger and D. R. Dietrich, Cyanobacterial toxins: Removal during drinking water treatment, and human risk assessment, *Environ Health Persp*, 2000, **108**, 113-122.
19. B. W. Brooks, J. M. Lazorchak, M. D. A. Howard, M. V. V. Johnson, S. L. Morton, D. A. K. Perkins, E. D. Reavie, G. I. Scott, S. A. Smith and J. A. Steevens, Are Harmful Algal Blooms Becoming the Greatest Inland Water Quality Threat to Public Health and Aquatic Ecosystems?, *Environ. Toxicol. Chem.*, 2016, **35**, 6-13.
20. W. Steffen, K. Richardson, J. Rockstrom, S. E. Cornell, I. Fetzer, E. M. Bennett, R. Biggs, S. R. Carpenter, W. de Vries, C. A. de Wit, C. Folke, D. Gerten, J. Heinke, G. M. Mace, L. M. Persson, V. Ramanathan, B. Reyers and S. Sorlin, Planetary boundaries: Guiding human development on a changing planet, *Science*, 2015, **347**.
21. W. W. Li, H. Q. Yu and B. E. Rittmann, Chemistry: Reuse water pollutants, *Nature*, 2015, **528**, 29-31.
22. W. Verstraete, P. V. de Caveye and V. Diamantis, Maximum use of resources present in domestic "used water", *Bioresour. Technol.*, 2009, **100**, 5537-5545.
23. J. S. Guest, S. J. Skerlos, J. L. Barnard, M. B. Beck, G. T. Daigger, H. Hilger, S. J. Jackson, K. Karvazy, L. Kelly, L. Macpherson, J. R. Mihelcic, A. Pramanik, L. Raskin, M. C. M. Van Loosdrecht, D. Yeh and N. G. Love, A new planning and design paradigm to achieve sustainable resource recovery from wastewater, *Environ. Sci. Technol.*, 2009, DOI: 10.1021/es9010515.
24. NAE Grand Challenges for Engineering, https://www.nae.edu/File.aspx?id=187214, (accessed 02/20/2019, 2019).
25. T. A. Larsen, M. Maurer, K. M. Udert and J. Lienert, Nutrient cycles and resource management: implications for the choice of wastewater treatment technology, *Water Sci. Technol.*, 2007, **56**, 229-237.
26. M. K. Winkler and L. Straka, New directions in biological nitrogen removal and recovery from wastewater, *Curr. Opin. Biotechnol.*, 2019, **57**, 50-55.
27. A. Oehmen, P. C. Lemos, G. Carvalho, Z. Yuan, J. Keller, L. L. Blackall and M. A. Reis, Advances in enhanced biological phosphorus removal: from micro to macro scale, *Water Res.*, 2007, **41**, 2271-2300.
28. S. Yeoman, T. Stephenson, J. N. Lester and R. Perry, The removal of phosphorus during wastewater treatment: a review, *Environ. Pollut.*, 1988, **49**, 183-233.
29. A. L. Smith, L. B. Stadler, N. G. Love, S. J. Skerlos and L. Raskin, Perspectives on anaerobic membrane bioreactor treatment of domestic wastewater: a critical review, *Bioresour. Technol.*, 2012, **122**, 149-159.
30. L. L. Blackall, G. R. Crocetti, A. M. Saunders and P. L. Bond, A review and update of the microbiology of enhanced biological phosphorus removal in wastewater treatment plants, *Antonie Van Leeuwenhoek*, 2002, **81**, 681-691.
31. G. Zhu, Y. Peng, B. Li, J. Guo, Q. Yang and S. Wang, Biological removal of nitrogen from wastewater, *Rev Environ Contam Toxicol*, 2008, **192**, 159-195.
32. P. L. McCarty, What is the Best Biological Process for Nitrogen Removal: When and Why?, *Environ. Sci. Technol.*, 2018, **52**, 3835–3841.
33. K. Webster, *The Circular Economy: a Wealth of Flows*, Ellen MacArthur Foundation, Isle of Wight, 2015.

34. M. B. W. McDonough, *Cradle to Cradle: Remaking the Way We Make Things*, North Point Press, New York, 1 edn., 2002.
35. B. Commoner, *The Closing Circle: Nature, Man, and Technology*, Random House, New York, 1971.
36. W. R. Stahel, The circular economy, *Nature*, 2016, **531**, 435-438.
37. M. Ronteltap, M. Maurer and W. Gujer, Struvite precipitation thermodynamics in source-separated urine, *Water Res.*, 2007, **41**, 977-984.
38. M. Maurer, W. Pronk and T. A. Larsen, Treatment processes for source-separated urine, *Water Res.*, 2006, **40**, 3151-3166.
39. T. Karak and P. Bhattacharyya, Human urine as a source of alternative natural fertilizer in agriculture: A flight of fancy or an achievable reality, *Resour Conserv Recy*, 2011, **55**, 400-408.
40. J. R. Mihelcic, L. M. Fry and R. Shaw, Global potential of phosphorus recovery from human urine and feces, *Chemosphere*, 2011, **84**, 832-839.
41. J. Zhang, Q. She, V. W. C. Chang, C. Y. Tang and R. D. Webster, Mining nutrients (N, K, P) from urban source-separated urine by forward osmosis dewatering, *Environ. Sci. Technol.*, 2014, DOI: 10.1021/es405266d.
42. Q. L. Liu, C. H. Liu, L. Zhao, W. C. Ma, H. L. Liu and J. Ma, Integrated forward osmosis-membrane distillation process for human urine treatment, *Water Res.*, 2016, **91**, 45-54.
43. D. G. Randall and V. Naidoo, Urine: The liquid gold of wastewater, *J. Environ. Chem. Eng.* , 2018, **6**, 2627-2635.
44. W. A. Tarpeh, J. M. Barazesh, T. Y. Cath and K. L. Nelson, Electrochemical Stripping to Recover Nitrogen from Source-Separated Urine, *Environ. Sci. Technol.*, 2018, **52**, 1453-1460.
45. S. N. McCartney, N. Williams, C. Boo, X. Chen and N. Y. Yip, Novel Isothermal Membrane Distillation with Acidic Collector for Selective and Energy-Efficient Recovery of Ammonia from Urine, *ACS Sustain. Chem. Eng.*, 2020, **8**, 7324–7334.
46. N. Jagtap and T. H. Boyer, Integrated Decentralized Treatment for Improved N and K Recovery from Urine, *J. Sustain. Water Built Environ.*, 2020, **6**.
47. K. N. Xu, D. Qu, M. Zheng, X. H. Guo and C. W. Wang, Water Reduction and Nutrient Reconcentration of Hydrolyzed Urine via Direct-Contact Membrane Distillation: Ammonia Loss and Its Control, *J Environ Eng*, 2019, **145**.
48. A. Sendrowski and T. H. Boyer, Phosphate removal from urine using hybrid anion exchange resin, *Desalination*, 2013, **322**, 104-112.
49. H. Kjerstadius, S. Haghighatafshar and A. Davidsson, Potential for nutrient recovery and biogas production from blackwater, food waste and greywater in urban source control systems, *Environ. Technol.*, 2015, **36**, 1707-1720.
50. S. A. El-Shafai, F. A. El-Gohary, F. A. Nasr, N. P. van der Steen and H. J. Gijzen, Nutrient recovery from domestic wastewater using a UASB-duckweed ponds system, *Bioresour. Technol.*, 2007, **98**, 798-807.
51. T. Hulsen, D. J. Batstone and J. Keller, Phototrophic bacteria for nutrient recovery from domestic wastewater, *Water Res.*, 2014, **50**, 18-26.
52. D. J. Batstone, T. Hulsen, C. M. Mehta and J. Keller, Platforms for energy and nutrient recovery from domestic wastewater: A review, *Chemosphere*, 2015, **140**, 2-11.

53. A. J. Ward, K. Arola, E. T. Brewster, C. M. Mehta and D. J. Batstone, Nutrient recovery from wastewater through pilot scale electrodialysis, *Water Res.*, 2018, **135**, 57-65.
54. R. B. Theregowda, A. M. Gonzalez-Mejia, X. Ma and J. Garland, Nutrient Recovery from Municipal Wastewater for Sustainable Food Production Systems: An Alternative to Traditional Fertilizers, *Environ. Eng. Sci.*, 2019, **36**, 833-842.
55. A. K. Umble and L. H. Ketchum, A strategy for coupling municipal wastewater treatment using the sequencing batch reactor with effluent nutrient recovery through aquaculture, *Water Sci. Technol.*, 1997, **35**, 177-184.
56. K. Yetilmezsoy and Z. Sapci-Zengin, Recovery of ammonium nitrogen from the effluent of UASB treating poultry manure wastewater by MAP precipitation as a slow release fertilizer, *J. Hazard. Mater.*, 2009, **166**, 260-269.
57. L. Pastor, D. Mangin, J. Ferrer and A. Seco, Struvite formation from the supernatants of an anaerobic digestion pilot plant, *Bioresour. Technol.*, 2010, **101**, 118-125.
58. R. D. Liu, Y. K. Wang, G. Wu, J. N. Luo and S. G. Wang, Development of a selective electrodialysis for nutrient recovery and desalination during secondary effluent treatment, *Chem. Eng. J.*, 2017, **322**, 224-233.
59. N. A. Booker, A. J. Priestley and I. H. Fraser, Struvite formation in wastewater treatment plants: Opportunities for nutrient recovery, *Environ. Technol.*, 1999, **20**, 777-782.
60. K. M. Udert, T. A. Larsen, M. Biebow and W. Gujer, Urea hydrolysis and precipitation dynamics in a urine-collecting system, *Water Res.*, 2003, **37**, 2571-2582.
61. K. M. Udert, T. A. Larsen and W. Gujer, Estimating the precipitation potential in urine-collecting systems, *Water Res.*, 2003, **37**, 2667-2677.
62. M. C. Almeida, D. Bulter and E. Friedler, At-source domestic wastewater quality, *Urban Water*, 1999, **1**, 49-55.
63. P. Simha and M. Ganesapillai, Ecological Sanitation and nutrient recovery from human urine: How far have we come? A review, *Sustain. Environ. Res*, 2017, **27**, 107-116.
64. *The Use of Reclaimed Water and Sludge in Food Crop Production*, National Academy Press, Washington, D.C., 1996.
65. G. S. Pettygrove, *Irrigation With Reclaimed Municipal Wastewater - A Guidance Manual*, CRC Press, Boca Raton, 1 edn., 1985.
66. E. Friedler, D. Butler and Y. Alfiya, in *Source Separationand Decentralization for Wastewater Management*, eds. T. A. Larsen, K. M. Udert and J. Lienert, IWA Publishing, London, UK, 2013, ch. 17, pp. 241-254.
67. I. Fittschen and H. H. Hahn, Characterization of the municipal wastewaterpart human urine and a preliminary comparison with liquid cattle excretion, *Water Sci. Technol.*, 1998, **38**, 9-16.
68. X. C. Wei, R. C. Viadero and S. Bhojappa, Phosphorus removal by acid mine drainage sludge from secondary effluents of municipal wastewater treatment plants, *Water Res.*, 2008, **42**, 3275-3284.
69. T. A. U. Larsen, K. M.; Lienert, J., *Source separation and decentralization for wastewater management*, Iwa Publishing, 2013.
70. C. Liu, K. Rainwater and L. F. Song, Energy analysis and efficiency assessment of reverse osmosis desalination process, *Desalination*, 2011, **276**, 352-358.
71. K. H. Mistry, R. K. McGovern, G. P. Thiel, E. K. Summers, S. M. Zubair and J. H. Lienhard, Entropy Generation Analysis of Desalination Technologies, *Entropy-Switz*, 2011, **13**, 1829-1864.

72. S. Lin, N. Y. Yip and M. Elimelech, Direct contact membrane distillation with heat recovery: Thermodynamic insights from module scale modeling, *J. Membr. Sci*, 2014, **453**, 498-515.
73. L. M. D Brogioli, NY Yip, Thermodynamic analysis and energy efficiency of thermal desalination processes, *Desalination*, 2018, **428**, 29-39.
74. N. Y. Yip and M. Elimelech, Thermodynamic and energy efficiency analysis of power generation from natural salinity gradients by pressure retarded osmosis, *Environ. Sci. Technol.*, 2012, **46**, 5230-5239.
75. J. M. Smith, H. C. Van Ness and M. M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill, New York, 7th edn., 2005.
76. C. L. Sassen, R. A. C. Vankwartel, H. J. Vanderkooi and J. D. Arons, Vapor-Liquid-Equilibria for the System Ammonia + Water up to the Critical Region, *J. Chem. Eng. Data*, 1990, **35**, 140-144.
77. M. Wang and C. A. I. Ferreira, Absorption heat pump cycles with NH3 - ionic liquid working pairs, *Appl. Energy*, 2017, **204**, 819-830.
78. D. N. Kurhe, D. H. Dagade, J. P. Jadhav, S. P. Govindwar and K. J. Patil, Thermodynamic Studies of Amino Acid-Denaturant Interactions in Aqueous Solutions at 298.15 K, *J Solution Chem*, 2011, **40**, 1596-1617.
79. E. R. Page, Aqueous Ammonia as a Nitrogen-Fertilizer for Summer Cauliflowers, Compared with Ammonium-Nitrate (Broadcast) and Urea (Broadcast and Injected), *J. Agric. Sci.*, 1979, **92**, 251-254.
80. C. J. Smith and P. M. Chalk, Comparison of the Efficiency of Urea, Aqueous Ammonia and Ammonium-Sulfate as Nitrogen Fertilizers, *Plant Soil*, 1980, **55**, 333-337.
81. G. A. Breitenbeck and J. M. Bremner, Effects of Rate and Depth of Fertilizer Application on Emission of Nitrous-Oxide from Soil Fertilized with Anhydrous Ammonia, *Biol. Fertil. Soils*, 1986, **2**, 201-204.
82. T. K. Broschat and K. K. Moore, Release rates of ammonium-nitrogen, nitrate-nitrogen, phosphorus, potassium, magnesium, iron, and manganese from seven controlled-release fertilizers, *Commun. in Soil Sci. Plant Anal.*, 2007, **38**, 843-850.
83. G. L. Mullins and F. J. Sikora, Field-Evaluation of Commercial Monoammonium Phosphate Fertilizers, *Fert Res*, 1990, **22**, 1-6.
84. M. Reuveni, D. Oppenheim and R. Reuveni, Integrated control of powdery mildew on apple trees by foliar sprays of mono-potassium phosphate fertilizer and sterol inhibiting fungicides, *Crop Prot.*, 1998, **17**, 563-568.
85. M. Latifian, J. Liu and B. Mattiasson, Struvite-based fertilizer and its physical and chemical properties, *Environ. Technol.*, 2012, **33**, 2691-2697.
86. Y. Liu, S. Kumar, J. H. Kwag and C. Ra, Magnesium ammonium phosphate formation, recovery and its application as valuable resources: a review, *J Chem Technol Biot*, 2013, **88**, 181-189.
87. M. M. Rahman, M. A. M. Salleh, U. Rashid, A. Ahsan, M. M. Hossain and C. S. Ra, Production of slow release crystal fertilizer from wastewaters through struvite crystallization - A review, *Arab. J. Chem.*, 2014, **7**, 139-155.
88. F. F. Zhang, Q. S. Wang, J. L. Hong, W. Chen, C. C. Qi and L. P. Ye, Life cycle assessment of diammonium- and monoammonium-phosphate fertilizer production in China, *J. Clean. Prod.*, 2017, **141**, 1087-1094.

89. H. Arslanoglu and F. Tumen, Potassium struvite (slow release fertilizer) and activated carbon production: Resource recovery from vinasse and grape marc organic waste using thermal processing, *Process Saf. Environ. Prot.*, 2021, **147**, 1077-1087.
90. K. A. Landry, P. Sun, C. H. Huang and T. H. Boyer, Ion-exchange selectivity of diclofenac, ibuprofen, ketoprofen, and naproxen in ureolyzed human urine, *Water Res.*, 2015, **68**, 510-521.
91. L. Edahwati, S. Sutiyono, D. S. Perwitasari, S. Muryanto, J. Jamari and A. P. Bayuseno, *Effects of the Optimised pH and Molar Ratio on Struvite Precipitation in Aqueous System*, presented in part at the Matec Web Conf, 2016.
92. D. W. Widjajanto, *Environmental advantages and disadvantages of different sources of nitrogen in agricultural systems*, presented in part at the Fertilizers and Environment, Salamanca, Spain, 1995.
93. T. P. Hignett, in *Fertilizer Manual*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1985, pp. 136-145.
94. A. Gnaratnam, M. McCurdy, M. Grafton, P. Jeyakumar, P. Bishop and C. Davies, *Assessment of Nitrogen Fertilizers Under Controlled Environment – A Lysimeter Design*, Fertilizer and Lime Research Centre; Massey University, 2019.
95. E. L. Cussler and B. K. Dutta, On separation efficiency, *AIChE J.*, 2012, **58**, 3825-3831.
96. H. A. Korhonen J., Seppälä J. , Circular economy: the concept and its limitations, *Ecol Econ*, 2018, **143**, 36-47.
97. X. S. Gao, T.; Zheng, Y.; Sun, X.; Huang, S.; Ren, Q.; Zhang, X.; Tian, Y.; Luan, G, *Practical manure handbook. In Chinese*, Agricultural Publishing House, Beijing, 2002.
98. B. V. H. Jönsson, *Adapting the nutrient content of urine and faeces in different countries using FAO and Swedish data*, presented in part at the 2nd International Symposium on ecological sanitation, 2004.
99. K. Ashley, D. Cordell and D. Mavinic, A brief history of phosphorus: From the philosopher's stone to nutrient recovery and reuse, *Chemosphere*, 2011, **84**, 737-746.
100. M. Simonova, A. Gruère, J. de Sousa, V. Couturier, O. Rousseau, S. Marcel-Monnier and S. Beltaief, *Global Medium-Term Outlook for Fertilizers and Raw Materials: 2020-2024*, Market Intelligence and Agricultural Services, Montreal, Canada, 2020.
101. *World Population Prospects- Data Booklet*, P. D. Economic and Social Affairs Report ST/ESA/SER.A/401, 2017.