

CAS INSIGHTS

# SUSTAINABLE AGRICULTURE

Innovation in fertilizer production



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## Introduction

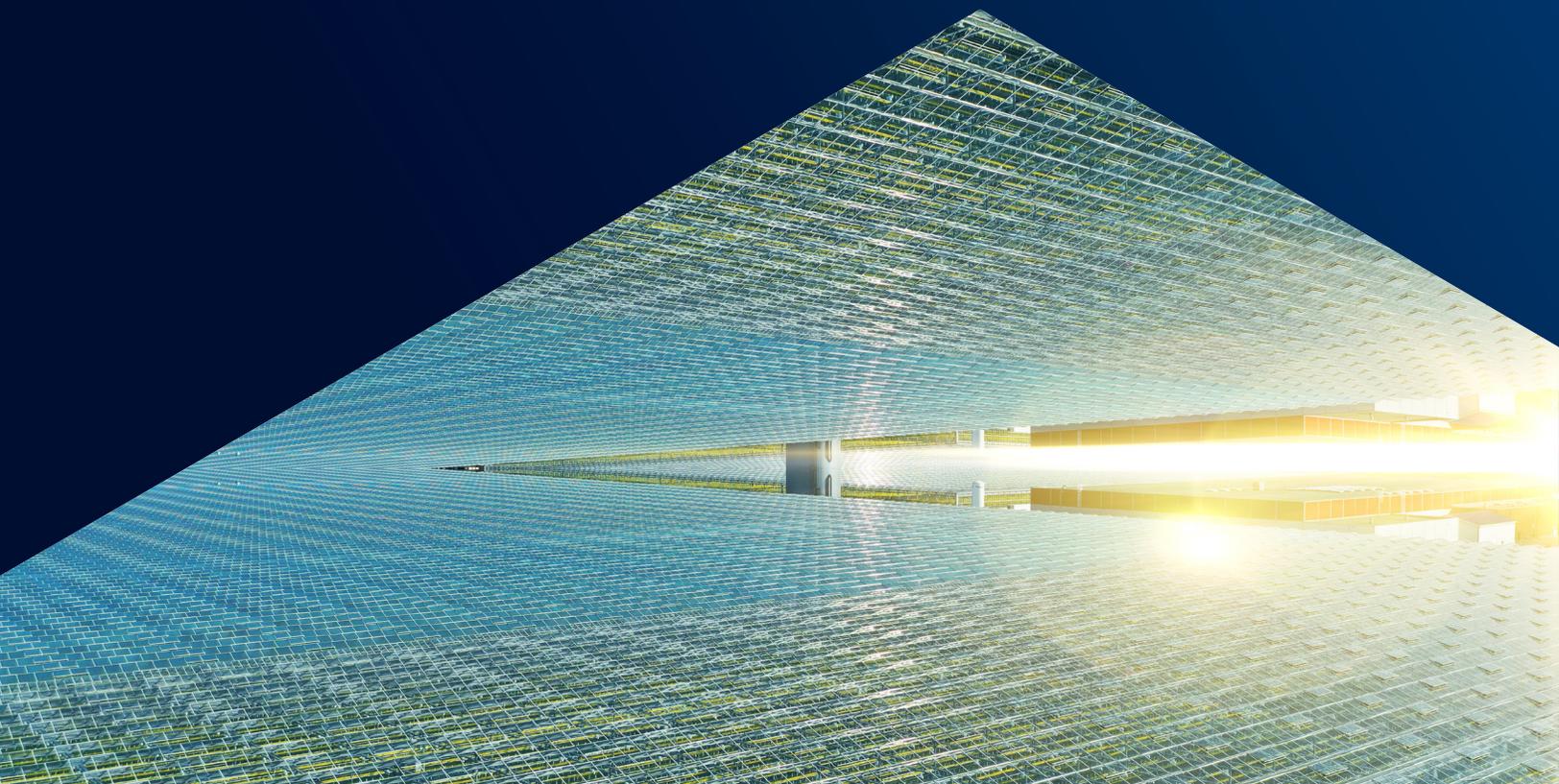
Modern agricultural methods are struggling to meet future food demand imposed by the accelerating growth of the world's population, set to reach 8.5 billion by 2030, and 9.7 billion by 2050.<sup>1</sup> Furthermore, the total global food demand is expected to increase by 35% to 56% between 2010 and 2050.<sup>2</sup>

With mounting pressures come economic consequences. According to reports from The Food and Agriculture Organization of the United Nations and the Intergovernmental Panel on Climate Change Special Report on Climate Change and Land, agricultural emissions are estimated to range between 10.7 and 12.0 gigatonnes of CO<sub>2</sub> equivalent (GtCO<sub>2</sub>e) year.<sup>3</sup>

The most important nutrients for fertilizers are nitrogen, phosphorus, and potassium, while others, such as calcium, magnesium, and sulfur, tend to be less frequently used.<sup>4-7</sup> Synthetic fertilizers use phosphorus mined from phosphate rock, potassium mined from potash ores, and ammonia from atmospheric nitrogen.<sup>8</sup> It has been calculated that 147 million tons of ammonia, 219 million tons of phosphate, and 44 million tons of potassium were produced in 2020.<sup>9-11</sup> Despite these substantial amounts, nearly half of the global population in 2015 (approximately 3.5 billion) were thought to be reliant on food produced by nitrogen fertilizers alone.<sup>12</sup>

Organic fertilizers include manure from various animals, alfalfa meal, blood meal, fish meal, and wood ash, as well as wastewater or sewage.<sup>13</sup> Manure and other agricultural wastes can be bulky and expensive to treat, transport, and dispose. The global organic fertilizer market is expected to reach \$19.88 billion by 2029, at a compound annual growth rate of 11.6% during the forecast period 2022–2029.<sup>14</sup>

China is the world's largest consumer of fertilizers, having consumed more than 45 million metric tons worth of nutrients in 2019.<sup>15</sup> India and the U.S. come in second and third, with consumption recorded at 29.4 and 20.4 million metric tons, respectively.<sup>15</sup> Together, these statistics suggest that fertilizer demand is far outweighing supply. Escalating fertilizer costs further compound the risk of global food security. Following an 80% increase in fertilizer prices in 2021, a further 30% increase has been recorded since the start of 2022, driven by higher production costs, supply disruptions due to conflicts including the Russia–Ukraine war, sanctions, and export restrictions from China.<sup>16</sup>



## The carbon footprint for fertilizer production

While millions of tons of fertilizers are produced and consumed, existing methods for fertilizer production are not sustainable in the long term. **Phosphate** rock is a finite, non-renewable source that may be depleted in the next century, with the majority (70%) being concentrated in Morocco, followed by China (5%), Syria and Algeria (3%), Russia, South Africa, the U.S., Egypt and Jordan (2% each).<sup>17,18</sup> Synthesis of **ammonia** from nitrogen by the Haber-Bosch process (not all of which is converted to fertilizer) is another energy-intensive process estimated to emit 500 tons of CO<sub>2</sub> annually, and is responsible for 1.8% of global total energy emissions.<sup>19</sup> The use of ammonia-based fertilizers in soil can lead to the formation of nitrous oxide, a potent greenhouse gas.<sup>19</sup> Both phosphate rock mining and nitrogen fixation strongly depend on fossil fuels such as oil and natural gas. **Potassium** in the form of potash is derived from soluble salts mined in the upper northern hemisphere, and while its supply is still sufficient, 92% of reserves are concentrated in only four countries: Canada (who owns 53% of global reserves), Russia, Belarus, and Germany.<sup>20</sup>

Most organic fertilizers are bulky and thus impractical and costly to transport over long distances; therefore, production is restricted to local sites, in turn leading to challenges with upscaling production. Pharmaceutical, pathogen, and heavy metal contamination can be found in wastewater and sewage,<sup>21</sup> and require testing and mitigation to avoid transferring contaminants to farmland and crops.<sup>22</sup> There is also significant uncertainty around the true scale of CO<sub>2</sub> emissions associated with the use of organic and synthetic fertilizers.<sup>3,23</sup>

We are reaching a tipping point. Radical transformations must be made to counteract food shortages and combat climate change. The agricultural industry must work towards a system that is sustainable, through efficient use of water, energy and nutrient resources, a reduction of environmental impacts, maintaining economic strength, and minimizing dependence on finite non-renewable resources preserving the ability of both current and future generations to thrive (**Figure 1**).<sup>24</sup>



Figure 1. Circulation of nutrients in sustainable agriculture

# Let's not waste our waste: opportunities for nutrient recovery

The term circular bioeconomy has recently gained popularity as a way of transforming and managing our land, food, health, and industrial systems via the management of biological resources (plants, animals, micro-organisms, and derived biomass, including organic waste), with the goal of achieving sustainable wellbeing in harmony with nature.<sup>25,26</sup>

Traditionally, solid and biosolid wastes have been dumped in landfills or the ocean, or applied to land, while biosolid wastes are also incinerated, which reduces waste volume but still produces ash.<sup>27-29</sup>

Overapplication of manure or treated biosolids to land can result in a build-up of nutrients such as nitrogen and phosphorus, resulting in eutrophication of surface waters, which can be damaging to aquatic ecosystems.<sup>30-32</sup> To address these problems, alternative systems and processes are being developed to provide new uses for waste while reducing contamination, and thus their harm, to human and environmental health.

Sewage sludge generated by wastewater treatment presents significant potential for repurposing waste through various processes, depending on sludge type. Sewage sludge can undergo thermal decomposition to produce biochar, hydrochar, or ashes, which are rich in energy and nutrients for use in fertilizer production.<sup>21,33-35</sup>

Using manure and agricultural wastes in organic fertilizer formulations or deriving chemical nutrients from agricultural wastes and many types of wastewaters could reduce transport and disposal costs while supplementing the available chemical nutrient supply.

Other common methods for nutrient recovery from waste are summarized in **Table 1**.

Potentially sustainable methods include:

- **Eco-friendly technologies:** Composting, vermicomposting, composting with biochar, anaerobic digestion, and pyrolysis using green energy
- **New emerging technologies:** Electrolysis and forward osmosis
- **Smart nano-fertilizers:** A combination of nanotechnology with controlled nutrient release through degradable delivery systems<sup>36</sup>
- **Biorefineries:** A combined production of sustainable energy, biofuels, food, chemicals, and nutrient-rich fertilizers that utilize renewable biomass as a feedstock,<sup>37</sup> which show added environmental benefits following integration with other systems, e.g., a mixed crop-livestock system<sup>38</sup>
- **Struvite:** Struvite ( $MgNH_4PO_4$ ) is a crystalline mineral composed of magnesium, ammonium, and phosphate, and is considered an adequate source of nutrients and a sustainable means for phosphorus recovery from wastewater, but can also be used either in fertilizer formulations or as a slow-release fertilizer<sup>39</sup>

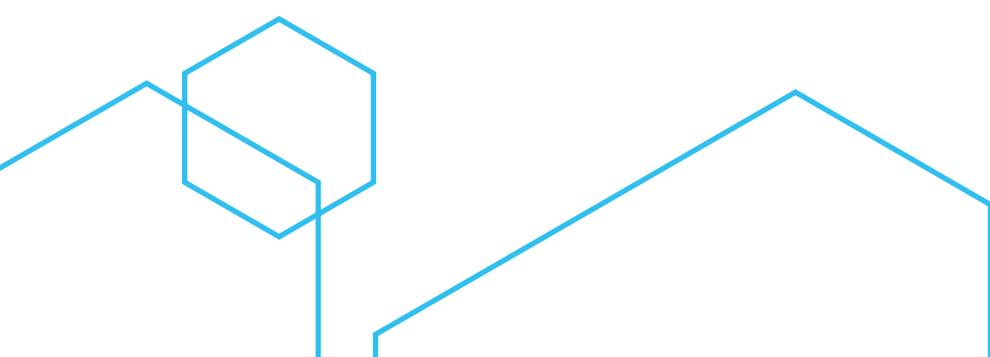
Table 1. Overview of commonly used nutrient recovery processes from waste

Method	Description
<b>Biological</b>	
<b>Anaerobic digestion</b>	<ul style="list-style-type: none"> <li>- The natural process in which micro-organisms break down organic materials in closed spaces where there is no air (or oxygen)<sup>40</sup></li> <li>- Preferred method for treating organic fractions of agricultural, industrial, and municipal solid waste</li> <li>- Methods: Hydrolysis (polymer decomposition), acidogenesis (volatile fatty acid production), acetogenesis (acetic acid production), and methanogenesis (methane production)<sup>40</sup></li> <li>- <b>Products:</b> Digestate (a by-product of biogas production)<sup>40</sup></li> </ul>
<b>Composting</b>	<ul style="list-style-type: none"> <li>- An aerobic, thermophilic, micro-organism-mediated bioconversion of organic matter into humic substances<sup>41</sup></li> <li>- <b>Product:</b> Compost</li> </ul>
<b>Vermicomposting</b>	<ul style="list-style-type: none"> <li>- A bioconversion method that utilizes microbes as well as earthworms for the decomposition of solid organic wastes into useful organic fertilizer</li> <li>- Can be used to convert waste from food, plants, animals, pharmaceuticals, and sewage<sup>42-44</sup></li> <li>- <b>Product:</b> Vermicompost</li> </ul>



Method	Description
<b>Chemical</b>	
<b>Chemical precipitation and crystallization</b>	<ul style="list-style-type: none"> <li>- The most common chemical technology for phosphate recovery from municipal wastewater</li> <li>- The formation of struvite has been commercialized as a treatment process for phosphorous and ammonia recovery from wastewater sludge dewatering*<sup>45</sup></li> <li>- For phosphate recovery, the crystallization of calcium phosphate has been performed using calcites as seeds<sup>46</sup></li> <li>- <b>Products:</b> <math>\text{Ca}_5(\text{OH})(\text{PO}_4)_3</math> (hydroxyapatite) and <math>\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}</math> (struvite)</li> </ul>
<b>Ion-exchange membrane electrolysis (ED)</b>	<ul style="list-style-type: none"> <li>- Extraction of nutrients from wastewater occurs via the application of ion-exchange membranes<sup>47</sup></li> <li>- Advanced methods such as selective ED and simultaneous anionic/cationic selective ED are even more efficient<sup>48,49</sup></li> <li>- <b>Products:</b> <math>(\text{NH}_4)^+</math>, <math>\text{K}^+</math>, <math>\text{Ca}^{2+}</math>, <math>\text{Mg}^{2+}</math> and <math>(\text{PO}_4)^{3-}</math></li> </ul>
<b>Physical</b>	
<b>Incineration, gasification, and pyrolysis ash nutrient recovery</b>	<ul style="list-style-type: none"> <li>- Incinerator ash is rich in nutrients such as phosphorus and can be used as a part of fertilizer feedstock</li> <li>- Pyrolysis includes waste heating under a limited supply of oxygen. It is a very important process to manage livestock waste.<sup>50</sup> Bio-oil and biochar or charcoal are produced from pyrolysis</li> <li>- Gasification is a form of pyrolysis that applies to higher temperatures producing mainly gases and a small amount of biochar<sup>51</sup></li> <li>- <b>Products:</b> Ash; and bio-oil, biochar or charcoal (pyrolysis)</li> </ul>
<b>Forward Osmosis (FO)</b>	<ul style="list-style-type: none"> <li>- FO is a technique that uses an osmotic pressure gradient as a driving force and semi-permeable membranes to separate dissolved solutes from water<sup>52,53</sup></li> <li>- The use of selective osmotic membranes improves phosphate and ammonium nutrient recovery from wastewater<sup>52,53</sup></li> <li>- <b>Products:</b> Phosphate and ammonium nutrients</li> </ul>
<b>Adsorption, absorption, and sorbents</b>	<ul style="list-style-type: none"> <li>- Natural adsorbents such as zeolites, clays, biopolymers, and biochar have been investigated for nutrient recovery<sup>54-56</sup></li> <li>- Biochar was applied to recover 96% of ammonium and phosphate from swine wastewater<sup>54</sup></li> <li>- Na- and K-zeolites were used for ammonium and phosphorus recovery in conjunction with MgO to stabilize bobierite or struvite,<sup>55</sup> while Ca-zeolites facilitated the recovery of phosphates from wastewater via formation of Ca-phosphates<sup>56</sup></li> <li>- <b>Products:</b> Struvite and calcium phosphate</li> </ul>
<b>Membrane filtration</b>	<ul style="list-style-type: none"> <li>- Useful for nutrient recovery from anaerobically digested slurries</li> <li>- The combination of microfiltration, ultrafiltration, and nanofiltration membranes allows recovery of &gt;94% of nitrogen from digestate<sup>57</sup></li> <li>- Recovery of both ammonia (30-36%) and phosphate (83-95%) has also been demonstrated by nanofiltration<sup>58</sup></li> <li>- <b>Products:</b> Phosphate and ammonium nutrients</li> </ul>

\*Struvite precipitation can be classed as a biological and physical method of nutrient recovery.



## Highlights and trends in nutrient recovery

The CAS Content Collection™ is an expert-curated resource that was used to evaluate methods of nutrient recovery and the concepts driving innovation to foster a more circular economy.

### Publications and topics

A **broad fertilizer search** retrieved 121,213 patents and 125,228 journal publications over the 2001–2021 period. The number of journal and patent publications grew steadily and following a peak in 2017, has since been decreasing (**Figure 2**). Trends in patent publications during this period appeared to be influenced primarily by China, who was responsible for a substantial number of patents in the field.

Topics associated with **journals** were related to the effects of fertilizers on crop plant growth, biological responses, and soil fertility, with some focusing on nutrient removal (in terms of their role as potential pollutants) or recovery for fertilizer use. Topics associated with **patents** focused strongly on organic substances and processes associated with fertilizer nutrient recovery and formulations, including bio-waste-related topics, e.g., manure, ashes, and fermentation.

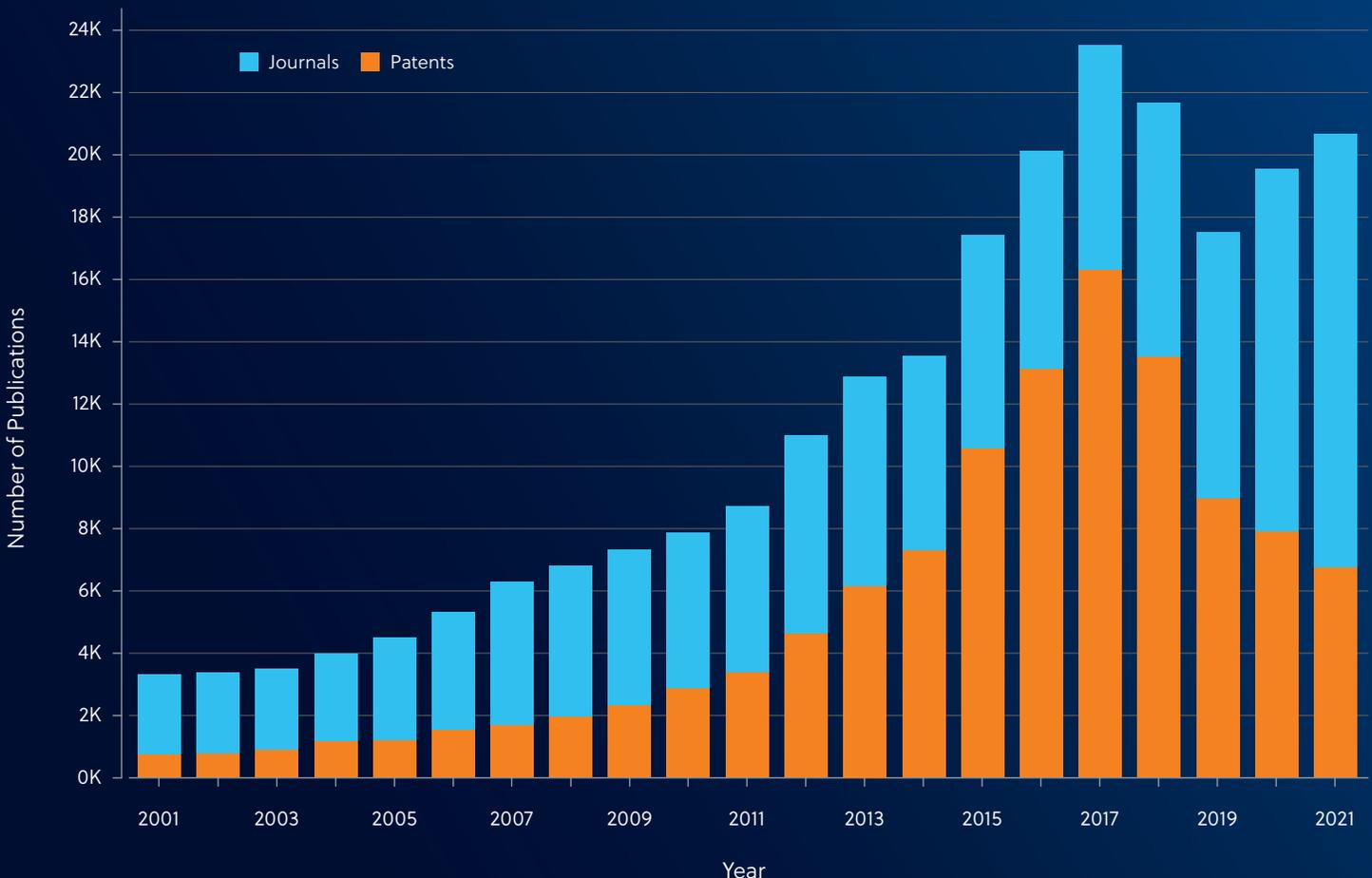


Figure 2. Journal and patent publication numbers (2001–2021) for a broader search of fertilizers, sustainability, recycling, and recovery topics



Substance classes that were discussed for nutrient recovery included “elements”, “oxides” and “hydroxides”, “metal salts”, “minerals”, and “polymers”. Carbon was the most popular element, featuring in almost 14,000 publications. Oxides were mostly represented by silicon (1,214 publications), calcium (917

publications), and magnesium (882 publications) oxides, while the most frequently cited hydroxides included calcium, magnesium, and aluminium hydroxides. Calcium carbonate (1,820 publications) was the most frequently reported compound, used as both a precipitating agent and sorbent.

### Nutrient recovery from waste and wastewater

Findings showed that biological processes were the most prominent methods for nutrient recovery from wastewater, having increased by 40% between 2001 and 2018, while physical and chemical methods were associated with a 20% and 27% increase in publications, respectively, during the 2002 to 2012 period.

Patents comprised a significant proportion — 53% — of publications on physical methods, while making up 49.5% of publications for chemical methods and 37% of publications for biological methods.

The number of documents concerning nutrient recovery from wastewater treatment sludge, biochar, and ashes increased in number during the period of study, while the number associated with sewage sludge fertilizers remained low. A clear increasing trend in **charcoal/biochar** topics was noted in patents and journals, with journal publications demonstrating continued growth despite a slight drop in 2019. Patent publications have grown, especially since 2013, although the numbers year on year have been somewhat variable (**Figure 3**).

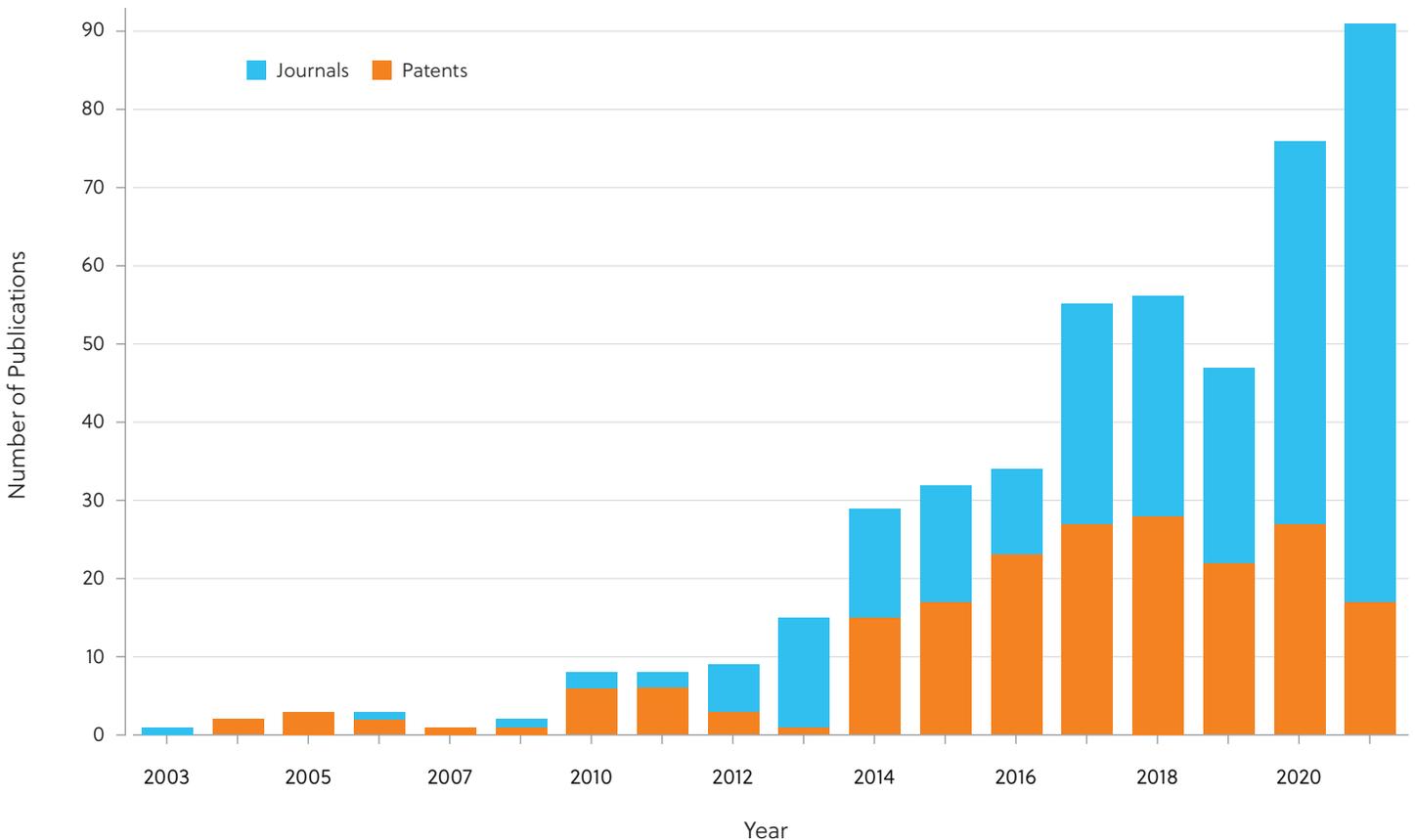


Figure 3. Patents and journals (2000–2021) including the CAS term for biochar for narrower search of fertilizers, sustainability, recycling, and recovery topics related to wastes and wastewaters. 2001, 2002 and 2008 had values of zero (not shown)

**Struvite** publications increased substantially, where hexahydrate  $[(\text{NH}_4)\text{Mg}(\text{PO}_4)\cdot 6\text{H}_2\text{O}]$  was the dominant form studied — little has been published on potassium struvite  $(\text{MgK}(\text{PO}_4)\cdot 6\text{H}_2\text{O})$ . “Precipitation wastewater treatment” was a major concept relating to struvite

production, comprising >90% of all concepts listed, followed by “crystallization wastewater treatment”. Both concepts are directly related to struvite recovery (**Figure 4**).

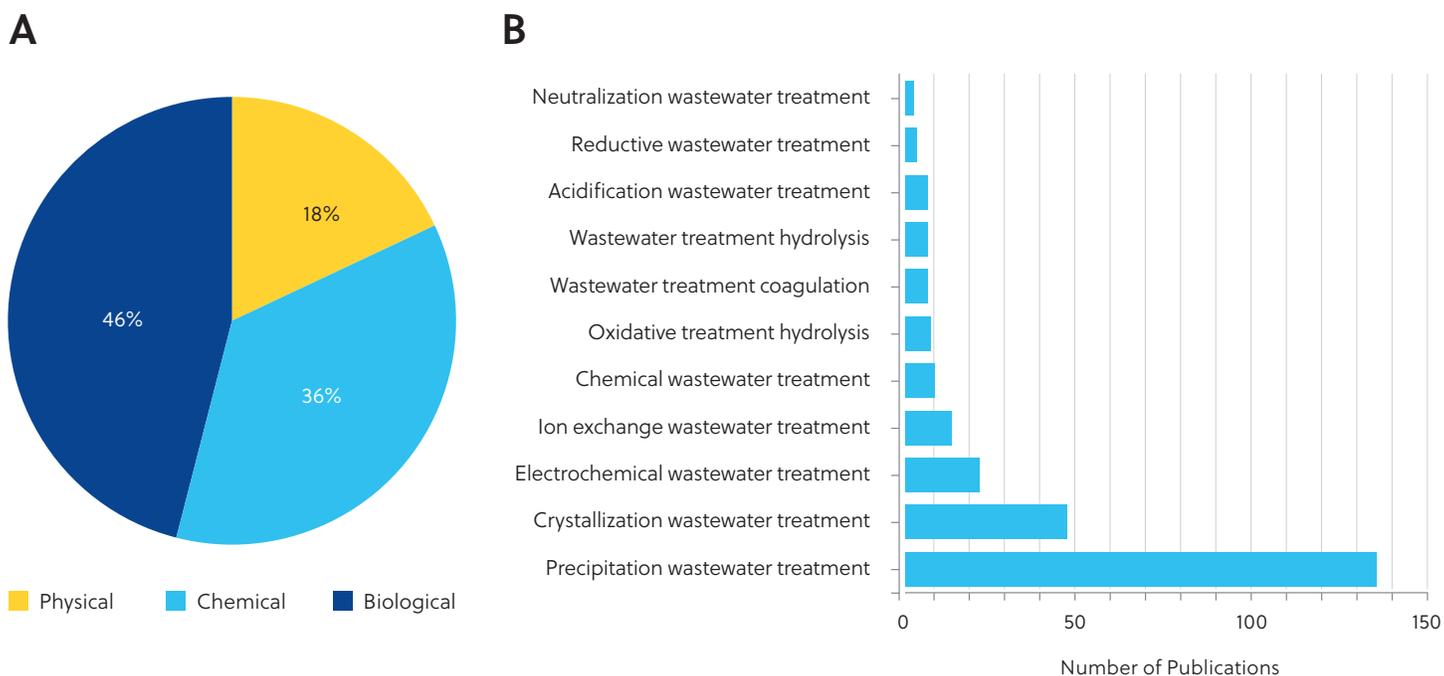


Figure 4. A) Publications on biological, chemical, and physical methods associated with wastewater treatment for struvite precipitation and B) Chemical treatment concepts for struvite production

### Green ammonia synthesis

The process of making ammonia 100% renewable and carbon-free, using renewable energy, nitrogen, and water — was discussed primarily in journal publications, with patent documents reaching 20% of the total publication volume in 2020. There was a dramatic growth in substances with a role in catalytic green ammonia synthesis from 2017 to 2021; numbers increased from less than 100 distinct substances in 2017 to nearly 500 distinct substances in 2021.

Specific subsets of substance classes, such as inorganic materials, organic/inorganic small molecules, elements, and co-ordination compounds make up many of the new catalysts used in green ammonia synthesis (**Figure 5**).

“Electrochemical reduction” and related concepts were among the most frequently occurring concepts noted in green ammonia and nitrogen reduction reaction, with “photocatalysts” occurring less frequently. The proportion of journal publications featuring

photocatalytic or electrocatalytic nitrogen reduction grew from 1% in 2001 to 25% in 2021. In terms of catalyst evaluation, 52% (1,167/2,256) of documents discussed reaction “rate,” “yield,” or “mechanism.” More than 40% of 1,500 documents with a focus on electrocatalysis discussed faradaic efficiencies, consistent with an emphasis on the potential efficiency of ammonia production. Only 4.1% of the 2,256 documents discussed the use of  $^{15}\text{N}$  or other isotopically labeled reagents; the use of these reagents is important to determine the source of the ammonia produced by a method and its reproducibility, implying that more consistent use of control experiments is likely needed.



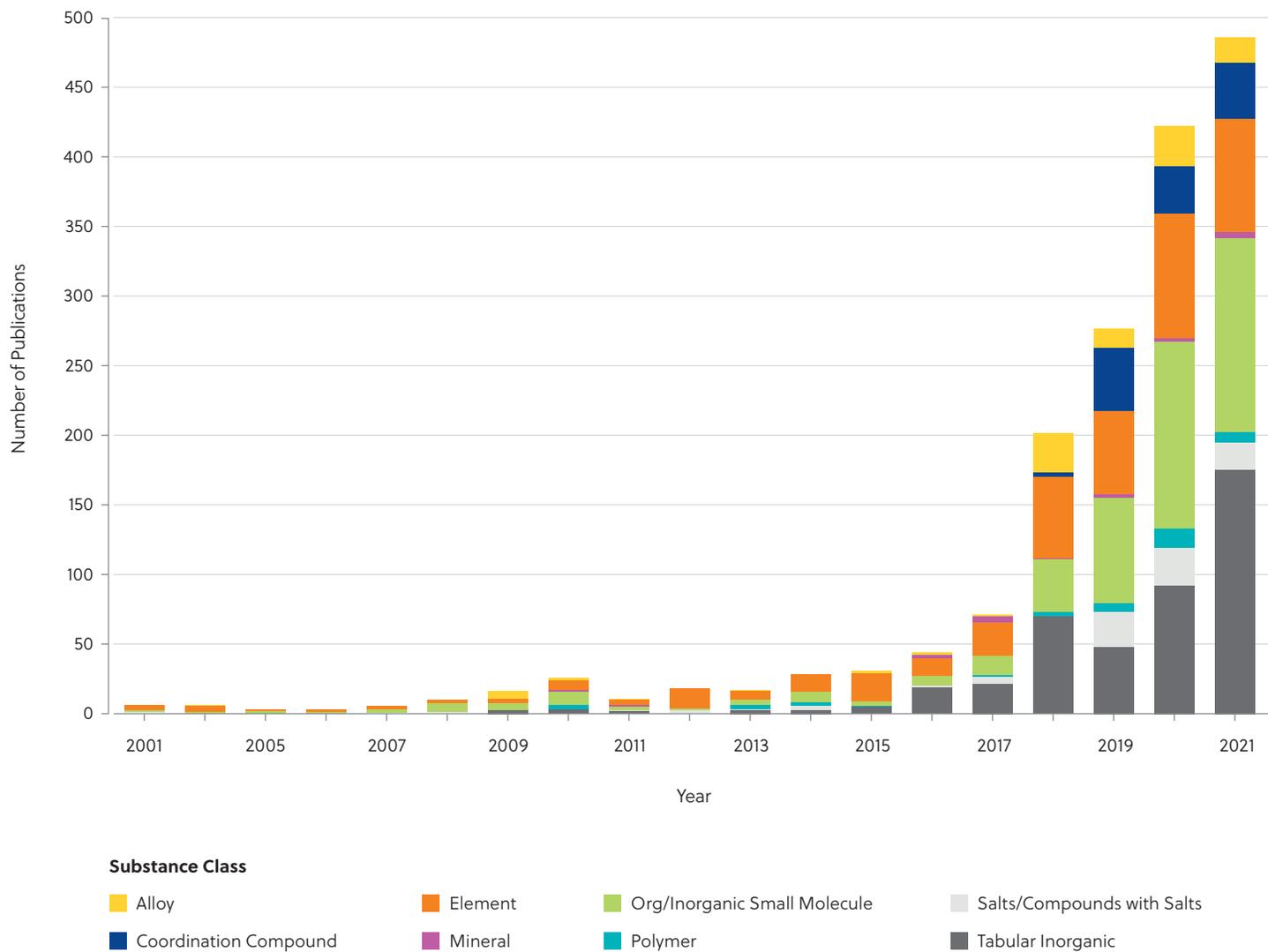
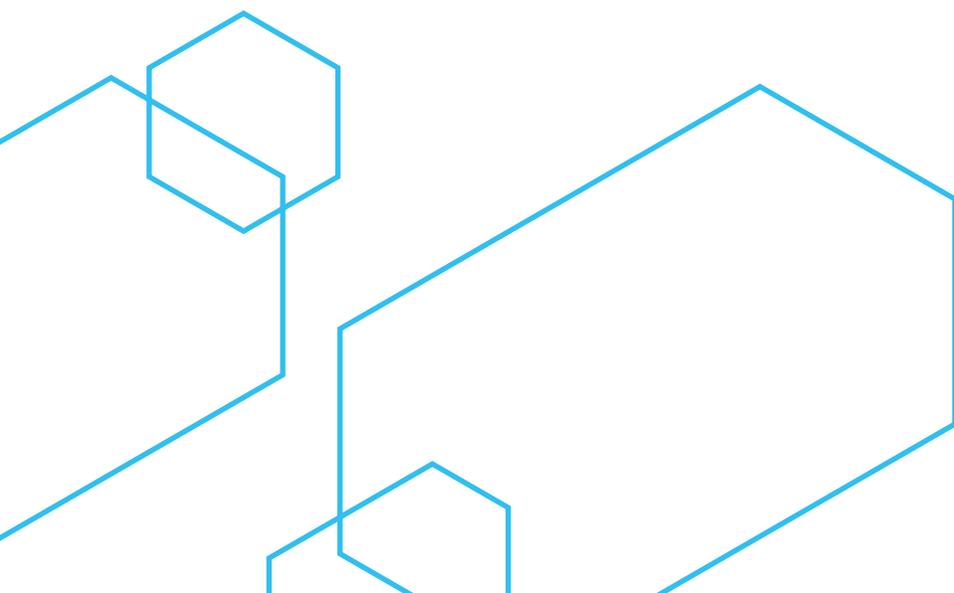


Figure 5. Publication trends and distinct substances used for catalysts by year (2001–2021) in green ammonia synthesis research. Data for 2003–2004 is not available



## Looking to the future

This analysis using the CAS Content Collection serves as a snapshot of popular and emerging methods to recover, recycle, and reuse fertilizer nutrients from various wastes and wastewater generated by humans in food, livestock, and industrial production.

Proactive recovery of fertilizer macronutrients from waste would reduce energy consumption and eliminate future concerns regarding finite global reserves. Alternative “greener” processes for fertilizer production include green ammonia synthesis and recovery of fertilizer nutrients from phosphorus-containing wastes. The feasibility of integrated systems has been demonstrated, where multiple processes can be used together to produce a variety of products with minimal waste. For example, during industrial algae production as a “biofuels crop”, nutrients are required for microalgal growth in the cultivation media to produce biomass for use in the biorefinery system for biofuels production.<sup>59</sup> Animal-derived wastewaters and anaerobically digested manures have been used to supply nutrients to systems such as one using lipid-rich pig wastes, to grow a lipid-accumulating algal biomass that can be used for biodiesel production.<sup>60</sup> Aquaculture wastewaters integrated into hydroponic or aquaponic plant growth systems is another example of such systems, which can be used for the combined production of plant biofuels or food products.<sup>61</sup>

Several processes involving phosphorus and/or nitrogen recovery have been commercialized.

These include:

- AirPrex® Patented Sludge Optimization Process (CNP Cycle GmbH) removes struvite from biosolids<sup>62</sup>
- Ostara’s proprietary Pearl® and WASSTRIP® technologies are designed to recover phosphorus and nitrogen to create an environmentally responsible fertilizer (Crystal Green®)<sup>63</sup>
- Metso Outotec's AshDec® Thermochemical P-Recovery recovers phosphorus from sewage sludge ash<sup>64</sup>
- RecoPhos have developed the thermoreductive RecoPhos-Process for phosphorus recovery from sewage sludge and sewage sludge ashes<sup>65</sup>

These examples of waste recovery innovations are proof that sustainable agriculture will be a key contributor to the circular bioeconomy by minimizing energy consumption and protecting the finite nature of global phosphorus, nitrogen, and potassium reserves.

As an expert-curated resource, the CAS Content Collection was employed to perform a quantitative analysis of fertilizer and waste recovery processes over time, across countries/regions, specific research areas and substances. It is hoped that by highlighting these trends in nutrient waste recovery, researchers in relevant industries will feel equipped to augment fertilizers with alternative nutrient resources while improving the efficiency and sustainability of waste management.



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