Transforming the science of transformation toward sustainability: the case of ammonia and reactive nitrogen

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SYNOPSIS

This perspective frames chemistry in sustainability space and uses a case-study of ammonia and reactive nitrogen to demonstrate how systems thinking tools can better position chemistry to contribute to sustainability science

ABSTRACT

Chemistry has played a central role over the past century in the large-scale anthropogenic transformation of matter into diverse materials that have improved the quality of life for many people on our planet. The lens of chemistry is fundamentally necessary to understand the resulting flux of chemical substances in Earth system processes, the unintended consequences of those transformations, impacts on food supply security, water and energy concerns, ways to mediate and adapt to climate change, loss of biodiversity, and how best to build and maintain resilient ecosystems. Reactive nitrogen compounds (Nr) such as ammonia from the industrial fixation of atmospheric nitrogen exemplify both the central importance of chemistry in providing food and meeting basic human needs for a global population of 7.9 billion people and the sustainability challenges arising from the intended and unintended consequences of large-scale human production and release of Nr. The chemistry profession can use the Planetary Boundaries framework as a systems thinking tool to understand and address challenges facing the entire Earth system resulting from the altered biogeochemical flows of nitrogen. This analysis has compelling priority due to the roles Nr currently plays in global food production and ammonia's potential role as an energy carrier for large-scale human activities in a future low carbon economy. As this example illustrates, navigating the complex benefits and challenges large-scale human activity imposes on Earth system processes requires the convergence of chemistry research, industrial practice, and education. Since the chemical reactions and processes that transform matter are foundational to sustainability challenges, this perspective maps multiple levels at which chemistry can contribute toward the emergence of sustainability of the Earth system. We conclude with recommendations for steps the profession of chemistry can take to make education relevant and engaging and to connect chemistry research and practice to cross-disciplinary sustainability challenges.

Introduction

Chemistry is the science of transformation of matter. The extraordinary extent to which chemistry, in collaboration with other disciplines in science, technology, and engineering has created materials to support and improve the human condition for many over the last couple of centuries may be viewed as a triumph of achievement. But for chemists, that triumph carries with it the absolute necessity to be conscious of the impact of their work and the responsibility they share with the entire global community to ensure long-term sustainability of the planetary environment we co-inhabit.

Many of the intertwined sustainability challenges our planet faces in the 21st Century arise from the great acceleration in the second half of the 20th Century of the release of chemical substances into the atmosphere, biosphere, hydrosphere, and cryosphere because of the scale of human activity transforming matter. That production of anthropogenic material reached an extraordinary crossover point in 2020, when the global mass of human-made material exceeded all living biomass for the first time in our planet's history. Using established material flow analysis methods from industrial ecology, the growth in anthropogenic mass, defined as the dry weight embedded in inanimate solid objects made by humans, is estimated to have doubled every 20 years since 1900, reaching an average of 30Gt per year over the past five years. This is equivalent to each of the 7.9 billion people on Earth producing their own body weight in anthropogenic mass every week. Juxtaposed with this trend, human activities of deforestation, forest management, and other land use changes have resulted in the loss of about 50% of global living plant biomass in the 3,000 years since the first agricultural revolution. In 2020 (+/- 6 years), anthropogenic and biomass amounts cross over at ~1.1 trillion tonnes, and by 2040, if current trends continue, anthropogenic mass will be triple the value of biomass.[1]

The mass of anthropogenic material is a simplistic and coarse-grained measure of the scale of human activity to transform matter from near-surface geological deposits, the atmosphere, and other sources into materials and objects that are useful to society. This measure is coherent, however, with multiple lines of evidence that human transformation of materials has accelerated so rapidly over the past 70 years that humans are now the dominant force shaping our planet. Analysis by the Anthropocene Working Group of the International Commission on Stratigraphy of the International Union of Geological Sciences has led the group to recommend a transition on the Geologic Time Scale from the Holocene Epoch to a new

Anthropocene Epoch[2], beginning in the 1950s. Declaration of a new epoch in the geologic time scale requires robust and persistent global evidence that will be incorporated into deposits in the future geological record. In the case of the Anthropocene determination, many of the primary lines of evidence relate to material transformations involving chemical processes and reactions, including radionuclides dispersed across the planet by above-ground nuclear tests, fly ash from combustion, aluminum and concrete particles, high levels of phosphates and nitrates in soils from large-scale fertilizer application, and plastic pollution.[3]

There is no question that human transformation of materials in the Anthropocene to produce everything from structural constituents (concrete, asphalt, bricks, metals, plastics, glass, and wood products make up the largest portion of anthropogenic mass) to synthetic fibers, agricultural products, drugs, petrochemical products, materials for energy production, and many other materials, has dramatically improved the quality of life for many people on the planet. However, unintended consequences of the scale of human activity to transform materials have led to rapidly emerging global challenges to Earth system processes, including global climate change, air pollution, eutrophication of water bodies, stratospheric ozone depletion, and rapid loss of biodiversity. In many cases these effects result from the flux of substances into the environment from the production, use, or degradation of human-made materials.

While other science and engineering domains play significant roles in aspects of this material transformation, the chemical sciences, with a scope ranging from basic and applied science to technological innovation, focus~~es~~ primarily on chemical and physical transformations of matter[4].

In this perspective we explore the role for chemistry, in convergence with other disciplines, to address the sustainability challenges that arise from the large-scale transformation of matter by (a) locating chemistry in the sustainability space, including the requirement for convergences within and beyond chemistry needed to address those challenges; (b) illustrating the challenge and steps toward solutions using NH_3 and Reactive Nitrogen (Nr) species as an example; and (c) concluding with recommendations for steps the profession of chemistry can take to transform itself toward sustainability.

Framing chemistry in the sustainability landscape

We begin by characterizing sustainability and then considering how a systems approach can position chemistry to help guide human activity toward sustainability of the Earth system.

We draw on three of many definitions of sustainability or sustainable development that have been put forward. Perhaps the most frequently cited one comes from the Brundtland Report, which defined sustainable development as: "meeting the needs of the present without compromising the ability of future generations to meet their own needs."[5] Two limiting features of this definition are that it focuses only on human well-being and it requires a common understanding of the concept of essential human "needs," with the Report suggesting that overriding priority be given to the needs of the world's poor. UNESCO's long-standing Education for Sustainable Development (ESD) initiative defines ESD as "a process of learning how to make decisions that consider the long-term future of the economy, ecology, and social well-being of <u>all</u> communities."[6] An important clarification here is whether the use of the term "communities" assumes humans are integral parts of larger ecological communities. Finally, in the context of describing chemistry's role in sustainability, we have previously characterized sustainability as "how present and future generations can live within the limits of the natural world."[7]

Building on these previous definitions and emphasizing that sustainability applies to all communities[8], we understand sustainability as *supporting present and long-term future well-being of all human and ecological communities under economic, social, and environmental conditions that position development within safe limits of Earth system processes*. An important feature of sustainability is that it is an emergent property of the whole Earth system and not simply a property of individual elements of the system.[9] Figure 1 depicts a systems thinking (ST) approach to inform our understanding of how chemistry can contribute at multiple levels to the landscape of disciplinary and interdisciplinary approaches, orientations, tools, and frameworks that guide human activity toward an emerging realization of sustainability of Earth as a system.

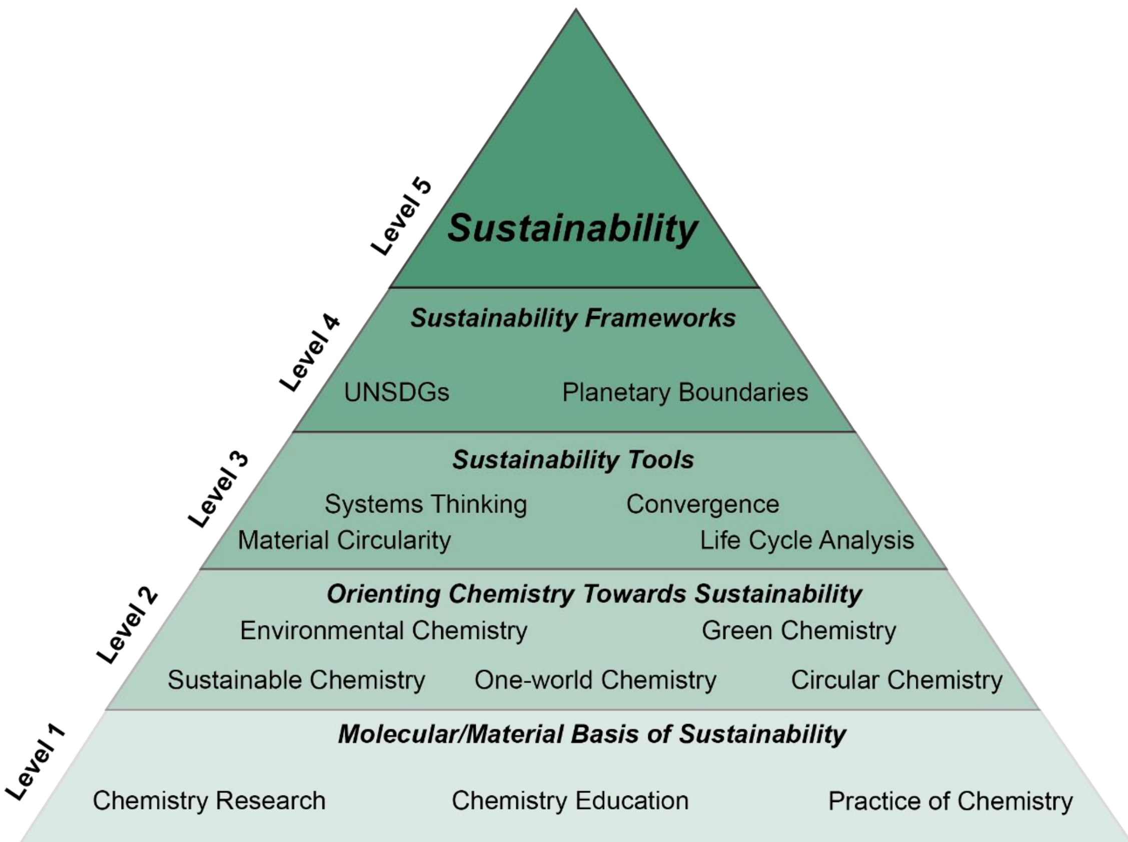


Figure 1. A systems approach to understanding how chemistry is embedded in and can contribute at multiple levels toward the emergence of sustainability of the Earth system.

As the science of transformation of matter, chemistry provides the material basis platform for working towards sustainability[10] through the combined efforts of education, research, and practice (*Fig. 1, Level 1*). Orienting these efforts has, in recent years, involved the development and incorporation of several complementary guiding principles and approaches (*Fig. 1, Level 2*). Historically, environmental chemistry has drawn attention to the unintended consequences of material transformation through the release of contaminants into different interconnected environmental sub-systems. The development of green chemistry from the 1980s onwards marked a shift from pollution identification and control to pollution prevention, offering a set of guidelines in the 12 Principles of Green Chemistry, published[11] in 1998. Described[12] as "the design of chemical products and processes that reduce or eliminate the generation of hazardous substances", the field of green chemistry has continued to grow,[13] widening its scope to embrace considerations from sustainable sourcing to optimizing waste disposal. The term 'sustainable chemistry' has sometimes been treated as similar to, or synonymous with, green chemistry.[14] However, it has also been described[15] as chemistry that "contributes in a sustainable manner to sustainability" and "simultaneously both a path and a goal", asking questions[16] such as 'why?', 'for what purpose?' and 'for whom?' One-world chemistry[17] adopts the 'one-health' principle which affirms the fundamental interconnectedness among the health of people, animals, and the environment, and calls for systems-based and cross-disciplinary approaches to tackle sustainability challenges. Circular chemistry[18] also extends green chemistry, incorporating circular economy concepts to provide its own 12 principles that direct attention to a hierarchy of choices.

Approaching sustainability requires integrated consideration of factors related to the impacts of human activity on systems that include the economy, society, and the environment.[19] Several tools are available to assist in understanding the interactions between chemistry and these Earth and societal systems and in operationalizing the sustainability principles (*Fig. 1, Level 3*). Systems thinking (ST), which has been identified as a critical competence for sustainability,[20] affords a set of synergistic analytic skills used to improve the capability of identifying and understanding systems, predicting their behaviors, and devising modifications to them to produce desired effects. Although ST had long been applied in some other disciplines, including biology and engineering, only since 2016 has it begun to be adopted[17] as a tool in chemistry, with a growing body of work that focuses on bringing ST into chemistry education at foundational secondary and post-secondary levels.[7,21–26] Recognition that working across disciplinary approaches is essential in understanding the implications and impacts of human activities and material transformations on Earth and societal systems,[27] there has also been increasing attention to convergent approaches of chemistry and other sciences to meet society's needs.[28] Growing convergence research is listed as one of the US National Science Foundation '10 big ideas', where convergence is defined as "the merging of ideas, approaches, and technologies from widely diverse fields of knowledge to stimulate innovation and discovery." The need to spotlight chemistry in the cross-disciplinary mix of disciplines shaping developments toward sustainability is highlighted by the absence of chemistry in the list of knowledge domains headlined in 2014 by American Association for the Advancement of Science president Sharp[29] as essential to positioning convergence as "the next scientific revolution" after the molecular biology and genomics revolutions. Material circularity focuses on the material component of the circular economy, adapting the latter's approaches to reduce waste and ensure that materials are recaptured and further used at the highest possible value that is technically, economically, and environmentally practical.[30] This is assisted by conducting life cycle analysis, adjusting for the scale of production.[31]

Important frameworks have emerged that provide guidance on the pathways to sustainability (*Fig.1, Level 4*). The UN Sustainable Development Goals (SDGs)[32] agreed in 2015 provide a time-bound and specific set of goals and targets, mostly to be achieved by 2030 as milestones on the pathway to sustainable development. The Planetary Boundaries framework[33] provides assessments of the extent to which human activity, including transformations of matter, is within or exceeding safe operating limits, with many of the control variables for the nine boundaries being chemical entities. Recently, the roles of anthropogenic chemicals and material transformations have been assessed as major components of the 'novel entities' planetary boundary, concluding that the safe operating space of this planetary boundary is exceeded since annual production and releases are increasing at a pace that outstrips the global capacity for assessment and monitoring.[34] The human security framework, presented by the UN Development Program[35] in 1994, was later adopted by the UN as an overarching, integrative approach that provides an effective analytical lens and programming framework for the SDGs.[36] Recently, it has been examined from a chemistry perspective.[37] Chemistry contributes in diverse ways to all seven dimensions of human security and, in particular, is deeply involved in the material dimensions (environment, health, food and economic security) and their interactions with the societal dimensions (personal, community and political security). Importantly, chemistry offers approaches to helping strengthen the resilience of these interconnected Earth and societal systems as a contribution to building the sustainability of people and planet.[38]

Reactive nitrogen (Nr) in the coupled human/planetary system

One particularly important 20th Century crossover point in the transformation of material by humans is a consequence of the large scale production of ammonia, the primary source of all anthropogenic Nr, from relatively unreactive atmospheric nitrogen and hydrogen, via the Haber-Bosch (HB) process.[39] A primary motivation for synthesizing ammonia from its elements (nitrogen fixation) was the growing demand for food, which required an increase in the production of Nr for N-fertilizers (ammonia, urea, ammonium nitrate, etc.) that are essential for crop growth. In the English translation of Fritz Haber's Nobel lecture in 1920: "it was clear that the demand for fixed nitrogen, which at the beginning of this century could be satisfied with a few hundred thousand tons a year, must increase to millions of tons".[40]

Figure 2 shows that since the 1960s, increased use of agricultural N-fertilizer[41,42] has facilitated world population growth, currently at ~ 7.9 billion.[43] It is estimated that up to ~50% of the world population is supported by N-fertilizer use in food production.[39] This underscores the essential nature of ammonia in supporting the human population, considering that ~80% of ammonia produced through the Haber-Bosch process is used directly or indirectly as sources of N-fertilizer.[39]

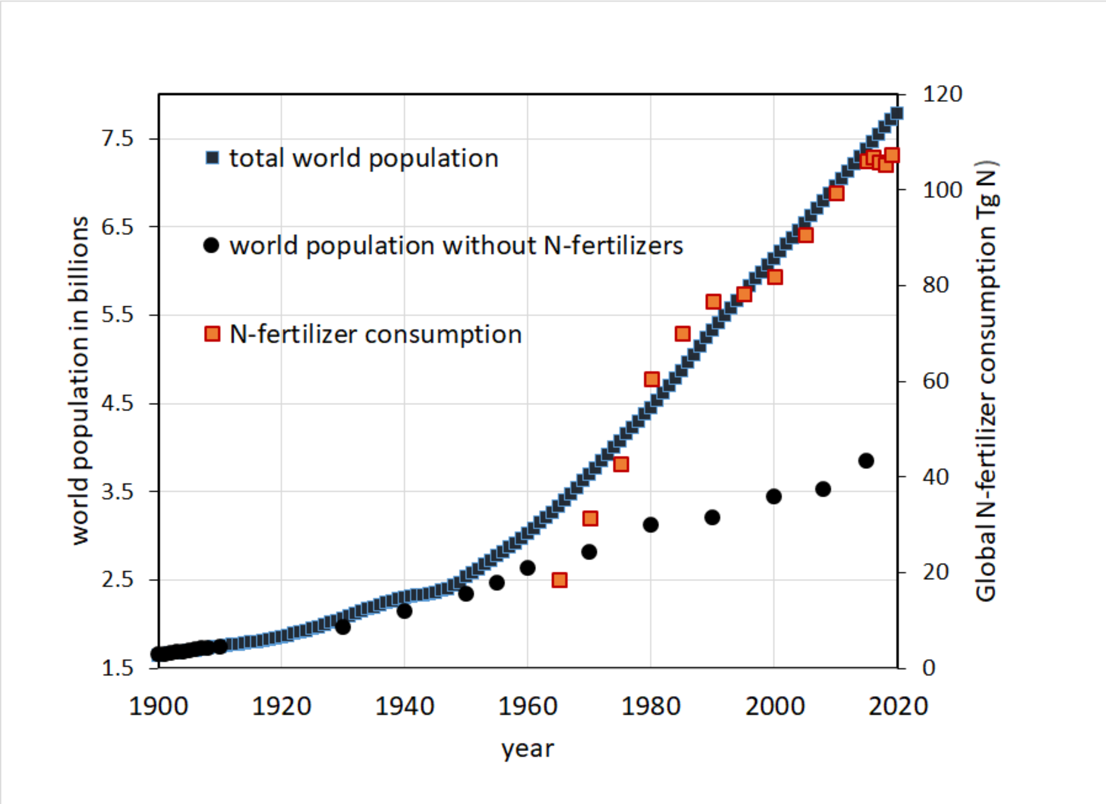


Figure 2. Correlation between total world population (1900-2021) and consumption of global agricultural N-fertilizers (1965-2019). An estimate of world population without N-fertilizers (to 2014) indicates that ~50% of the current world population is supported by food produced from agricultural N-fertilizer use.

The use of agricultural N-fertilizers has become the dominant driver of the global nitrogen cycle. In 2010, total anthropogenic Nr was estimated by Fowler et al[44] to be ~210 Tg N, exceeding natural sources of Nr, estimated at 203 Tg N. Of anthropogenic sources, N-fertilizers contributed more than half (~120±10% Tg N), the remainder being Nr from biological nitrogen fixation in crops (~60±30% Tg N) and NO_x from fossil fuel combustion (~30±10% Tg N).[44] Nitrogen use efficiencies vary considerably across agricultural regions globally,[45,46] with significant amounts of Nr lost to the environment. The Planetary Boundaries Framework (Figure 1, Level 4) is a helpful tool to understand and address the resulting cascade of unintended negative Earth system impacts, including eutrophication of water, acid rain, production of greenhouse gases, tropospheric air pollution, stratospheric ozone depletion, and loss of biodiversity.[47]

The Planetary Boundaries Framework and Sustainability Consequences of Nr production

Chemistry plays a key role in the Planetary Boundaries sustainability framework (Figure 1, Level 4) that can help understand and address the environmental sustainability challenges resulting from the scale of human activity. The framework (Figure 3), measures the Earth's stability and resilience amid rapid global change, including materials transformation. The framework comprises nine Earth system processes whose health and dynamic interactions describe the biophysical state of our planet: climate change, novel entities, stratospheric ozone depletion, atmospheric aerosol loading, ocean acidification, biogeochemical flows of nitrogen and phosphorus, freshwater use, land-system changes, and biosphere integrity. In seven of the nine Earth system processes, control variables have been identified and quantified that indicate, with a green/yellow/red "stoplight" color scheme, whether that Earth system process is still in a safe operating zone (below the planetary boundary), a zone of increasing risk, or a zone of high risk because of human activity. Moreover, it has just been proposed that, in the case of the 'novel entities' category, the production of plastics could be taken as one of the indicators and that the safe operating limit for this has also already been exceeded.[48] The chemistry profession has the right tools to expand the use of this powerful framework, for the dynamics of Earth's physical and biological systems are shaped and revealed through chemistry.[49] Most of the control variables measuring the state of each Earth system are directly related to the production and measurement of chemical substances in the atmosphere, hydrosphere or lithosphere. Yet chemistry's role in the framework has been largely invisible and unexplored by either the chemistry profession or the sustainability community.

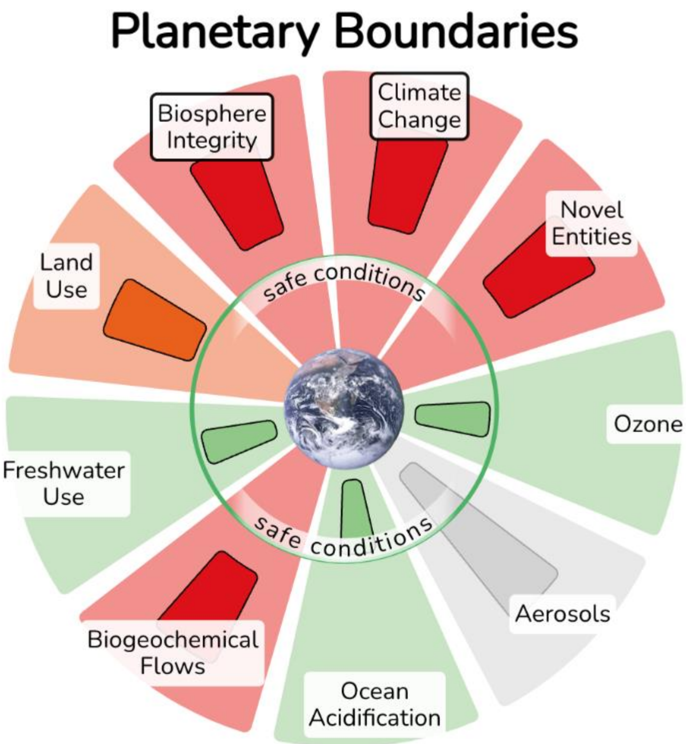


Figure 3. Planetary Boundaries framework, from the King's Centre for Visualization in Science planetary boundaries interactive learning resource at www.planetaryboundaries.kcvs.ca, adapted from the Stockholm Resilience Centre (Steffen et al., Science 2015).[33]

The altered biogeochemical flow of nitrogen at a planetary level illustrates ways in which the chemistry profession can use this framework to understand and address challenges facing the Earth system as a whole. The Framework's control variable for the biogeochemical flow of nitrogen is the amount of industrial and agricultural biological fixation of atmospheric nitrogen. Exploring the status of the control variable for the biogeochemical flows Earth system process in the interactive resource in Figure 3 shows the change in the anthropogenic nitrogen fixation rate over the past century: negligible before the Haber-Bosch process in 1910 and accelerating rapidly to the present-day value of 240 Tg N/y, measured as the total amount of industrial and intentionally biologically fixed nitrogen. The safe level for the nitrogen fixation control variable (the planetary boundary) has been determined to be 78 Tg N/year, placing the nitrogen Earth system processes in a zone of high risk.[45]

The biogeochemical flow of nitrogen, in which a variety of chemical and biochemical processes across different Earth environments result in a cascade[47] of Nr, cannot be considered as an isolated Earth system process. Rather, the Planetary Boundaries framework can serve as a tool to understand how a particular Earth system process connects integrally and dynamically to other Earth system processes in the framework and to the Earth system as a whole. Figure 4 illustrates key connections between the biogeochemical flow of nitrogen and other Earth system processes. For example, nitrous oxide produced by soil microbes as a result of application of N-fertilizers is now the fourth most significant contributor to atmospheric warming and the largest contributor to stratospheric ozone depletion.[48] The complexity of interactions is further illustrated by the observation[49] that, while the amount of Nr resulting from application of N-fertilizers in agriculture increased massively during the 20th Century, N availability has been declining in many non-agricultural ecosystems worldwide in the same period. This has been attributed to cross-system effects of a combination of (mainly) elevated atmospheric CO_2 levels and globally rising temperatures.

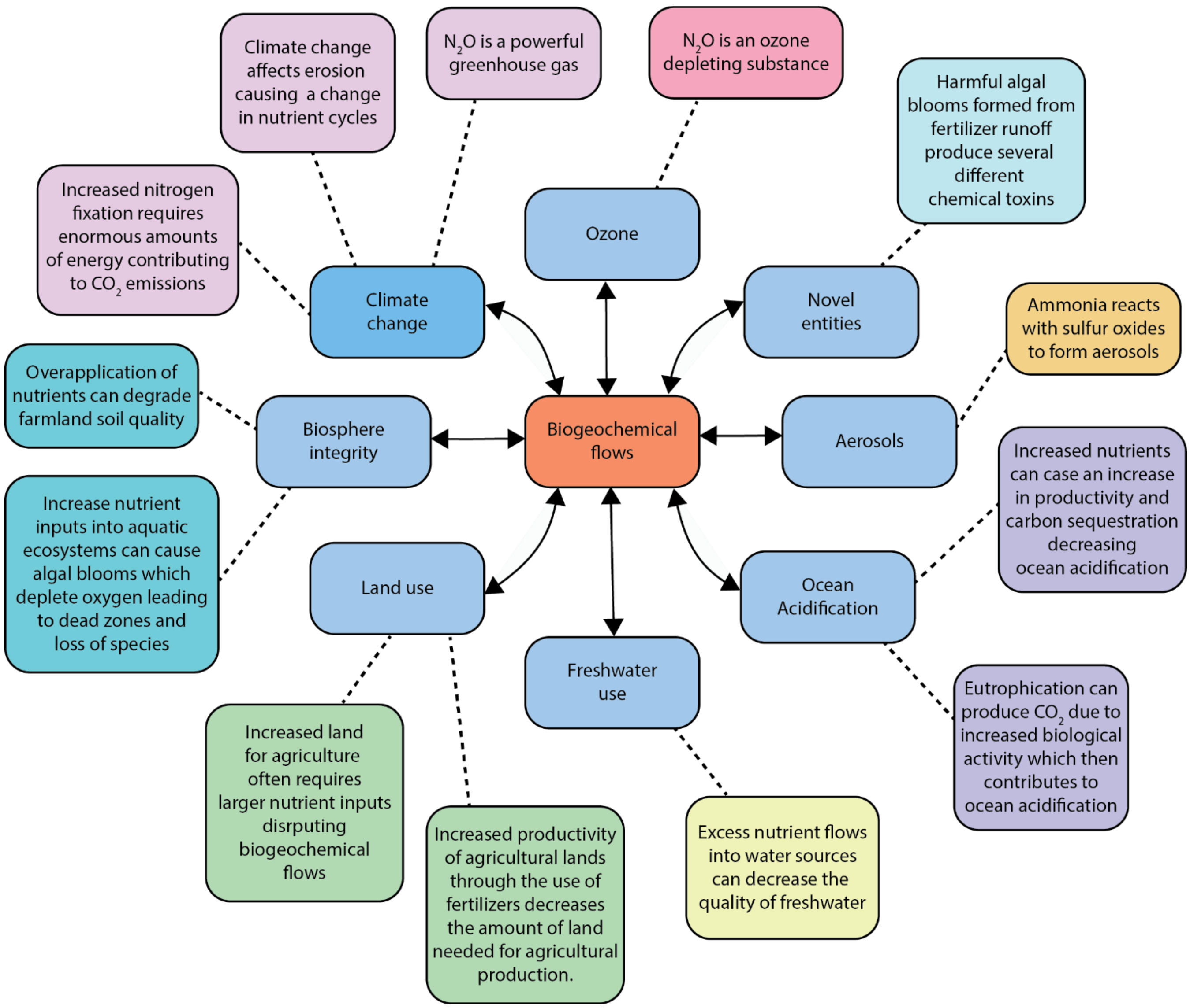
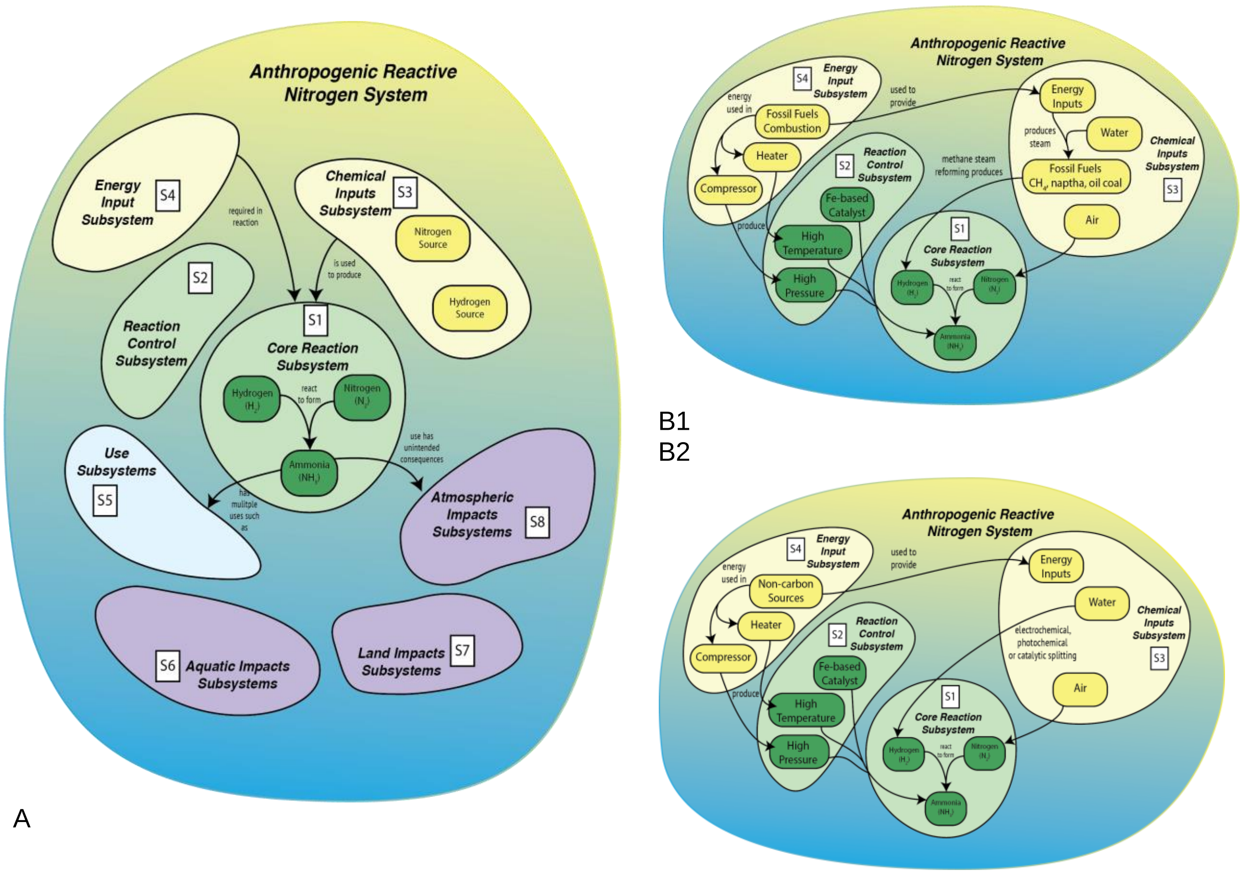
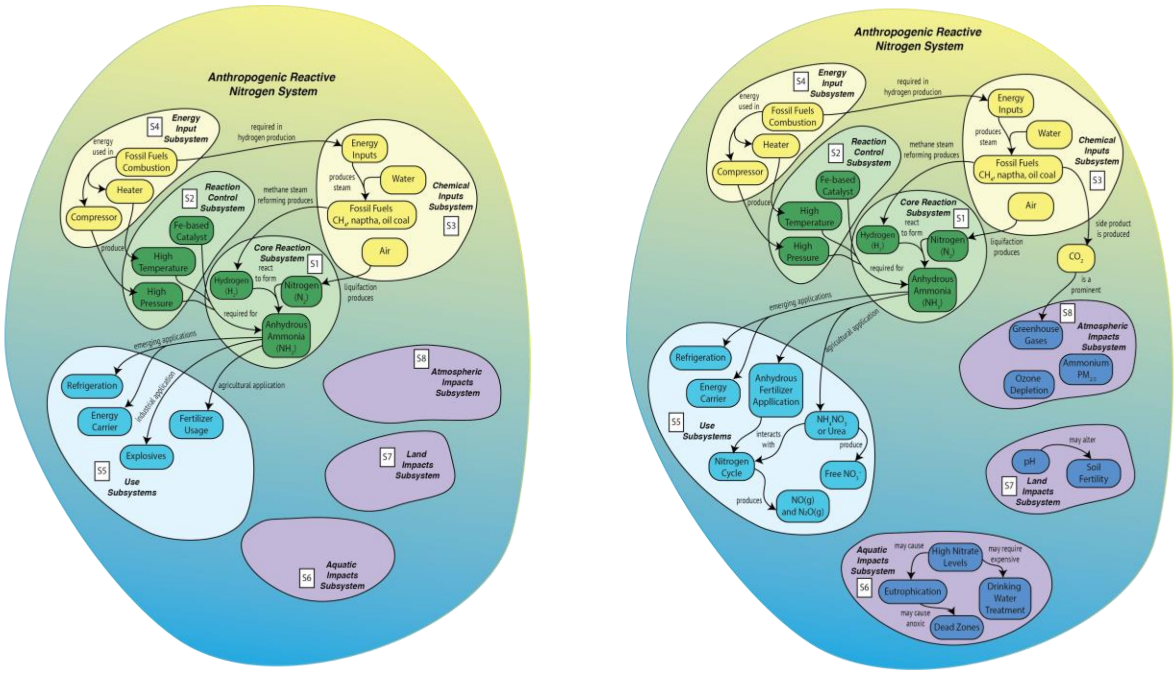


Figure 4. Interconnections among the biogeochemical flow (focusing on Nr) Earth system process and each of the other Earth system processes in the Planetary Boundaries framework, demonstrating the importance of viewing discrete Earth system processes as dynamic parts of the larger Earth system.

Addressing the environmental impacts of Nr requires an appreciation of the degree to which the functions of human society depend upon the production and use of the various forms of Nr which are all derived from NH_3. Emerging uses of ammonia (energy carrier and refrigeration) also need to be evaluated in the context of their possible future impact on Earth systems. Since these need to be implemented on a global scale to meet emerging human needs, such an evaluation is critical.

This can be accomplished through an examination of the SOCME (Systems-Oriented Concept Map Extension) for global NH_3 production and use, including unintended environmental consequences (Fig. 5). Figure 5A provides an overview, with details in expanded diagrams (Fig. 5 B-D) that will be referred to in the text below.





C D

Figure 5. Stages in building a SOCME for reactive nitrogen, illustrating some major subsystems of interest (panel A: subsystems S1-S8)) and how these can be expanded to explore alternative processes for the synthesis of ammonia (panels B1 and B2) and following through for the Haber-Bosch manufacture of ammonia (panel B1) to explore different uses (panel C: subsystem S5) and, in the case of N-fertilizers, implications for major (aquatic, land, atmospheric) biophysical subsystems of the planet (panel D: subsystems S6-S8)

Current Global Ammonia Production from Fossil Fuels

The broader context of global ammonia production is illustrated by considering the energy and chemical inputs for achieving reaction conditions that maximize yields of NH_3 from the core reaction of N_2 and H_2 (Fig. 5A; S1-S4). Reaction conditions vary depending on individual manufacturers, however in all cases the processes are energy intensive, with fossil fuel combustion providing the bulk of the energy for heating and compression/expansion cycles to achieve the high T and P conditions for the so-called NH_3 synthesis loop (Fig 5B1; S1, S2, S4). N_2 is obtained from cryogenic cooling of air, and in 99.5% of global NH_3 production, H_2 is produced from the energy intensive high P and T steam reforming of fossil fuels (Fig 5B1; S3-S4).[50,51] Since fossil fuels are the source of H_2 as well as the bulk of energy for the overall process[51], the market price of ammonia is influenced by often volatile fossil fuel costs.[52]

In the Haber-Bosch process fossil fuel combustion and steam reforming produce CO_2 (Fig 5D; S8), with the amount dependent on the age of the facility and the fossil fuel source. The CO_2 footprint ranges from 1.5 – 4.5 t of CO_2 for every 1t of NH_3.[53] Global NH_3 production accounts for 1.9% of global anthropogenic CO_2 released to the atmosphere[54] contributing to atmospheric loading with greenhouse gases (Fig 4: biogeochemical flows of greenhouse gases including CO_2 and N_2O, are responsible for climate change).

The need to decouple NH_3 production from fossil fuels is widely known and an area of active research and development. Technologies that can be scaled up in the short term are being intensively explored worldwide and will be discussed in *Emerging Technologies* below. They primarily involve H_2 production from electrolysis of water (Fig. 5B2; S3), with renewable electricity providing energy for the entire process (Fig. 5B2; S4).

Economically Important Processes Dependent on Ammonia

Approximately 80% of industrially produced NH_3 is used to make N-fertilizers in various forms, to enhance crop growth to help meet food demands globally (Fig. 2). Common forms of applied N-fertilizer include anhydrous NH_3 (Fig 5D, S5), NH_4NO_3 and urea (S5). NH_4NO_3 is synthesized by reaction of NH_3 and HNO_3, with the latter itself being synthesized from NH_3 by Ostwald Oxidation via NO and NO_2 (S5).[55] Urea is produced from the reaction of NH_3 and CO_2 (Fig 5D, S5),[56] usually as an ancillary process to ammonia synthesis.

After N-fertilizers, the remaining 20% of NH_3 accounts for the bulk of Nr production and consumption, including chemical intermediates, pharmaceuticals, pesticides, synthetic fibers, resins, polymers, dyes, paints, and explosives. All these materials ultimately end up in the environment (S6-S8), with often poorly understood decomposition pathways.[57] This is of increasingly pressing concern in relation to biogeochemical flows and their impacts on Earth systems, as depicted in the Planetary Boundaries (Fig. 4) and human security[37] framings.

A detailed SOCME resulting from the above process of incremental assembly is shown in Figure 6. It is emphasized that this SOCME for the anthropogenic Nr system is not 'final'. It reflects choices made at every stage concerning materials, processes, applications, and disposal methods, as well as evolving understanding of intersystem linkages and impacts. Its value lies in the opportunities it presents to stimulate system thinking and explore the feasibility and likely impacts of alternatives, encouraging the search for green chemistry processes and sustainable sourcing and handling of materials, with sustainability of the entire Earth system as the overarching goal.

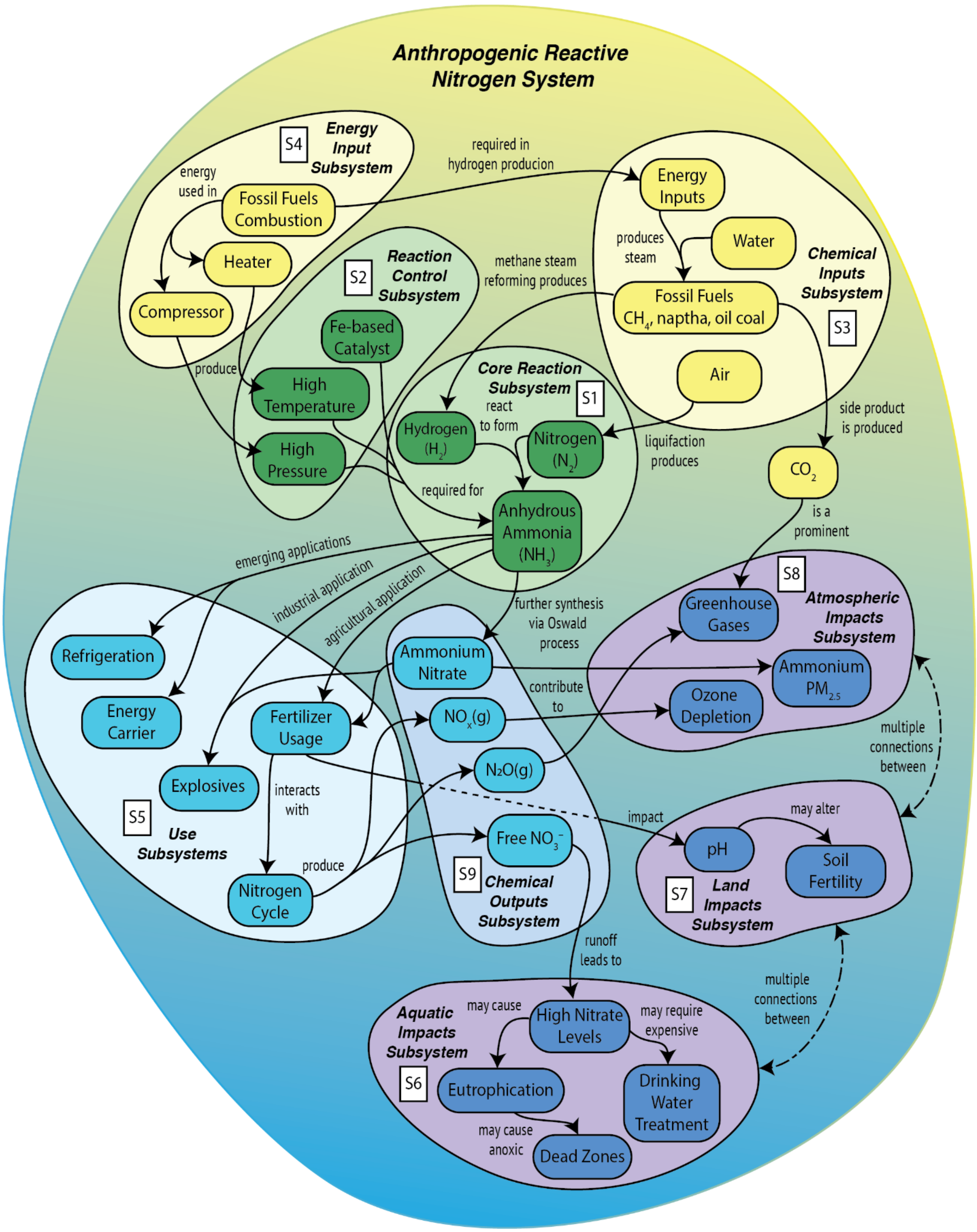


Figure 6. SOCME for anthropogenic reactive nitrogen system, illustrating current pathways for production of NH_3, its transformation into N-fertilizers and major elements of the resulting environmental impacts, as well as expanding use of NH_3 as a refrigerant and its emerging use as an energy carrier.

Ammonia and Derivatives, Agriculture, and the Environment.

Currently, the agricultural practice system is very inefficient with respect to Nr, since about 80% of N-fertilizers applied to fields are released to the environment,[58] largely due to over-application to compensate for losses (Fig. 6). This massively increases the biogeochemical flow of Nr in the nitrogen cycle (S6). A significant portion of NH_3 introduced as N-fertilizers volatilizes,[59] resulting in formation of solid aerosols of NH_4^+ salts, which are major contributors to $PM_{2.5}$ in agricultural areas and linked to negative human health impacts[60] as well as greenhouse effects (Fig. 4).[61] NH_4NO_3, (S9) which is applied primarily as an aqueous solution, releases NO_3^- to aquatic systems, leading to widespread eutrophication (S6).[58] Excess N-fertilizers accumulating in soil (S7) and waters (S8) are metabolized[62–64] to produce N_2O in large amounts (S9), with this aspect of the nitrogen cycle (S5) contributing significantly to climate change and ozone depletion (Fig 6: S8 and Fig 4),[44,65] and impacting on a wide range of biosphere components (Fig. 6: S6-S8 and Fig. 4). Efforts to reduce N-fertilizer over-application include regional application management strategies and development of controlled release N-fertilizers.[66,67]

Global Food Security.

An important aspect of the human security framework is its emphasis on the interconnected nature of different security dimensions,[37] a feature which is prominent in the example of NH_3 production. Owing to the energy intensive nature of ammonia production from fossil fuels, (Fig 6; S4), the cost of natural gas accounts for up to 85% of the cost of ammonia production.[52] Further, agricultural fertilizers, of which Nr is the dominant contributor (Fig. 6; S5), account for about a third of the cost of agricultural food production in the United States, with values projected as high as 45% in 2022.[68] As a result, in our current global system, the price of food, N-fertilizer and fossil fuels are linked.[52,69,70] This linkage has resulted in increased global food prices, contributing to political instability and conflict[71,72] More recently, unprecedented price rises in 2021[73,74] (Fig 7) have contributed to a growing global cost-of-living crisis.[75] Further sensitivity of food security to energy supplies comes from the global food distribution system which relies on energy for food transportation and refrigeration (see also the role of ammonia in *Refrigeration* below).

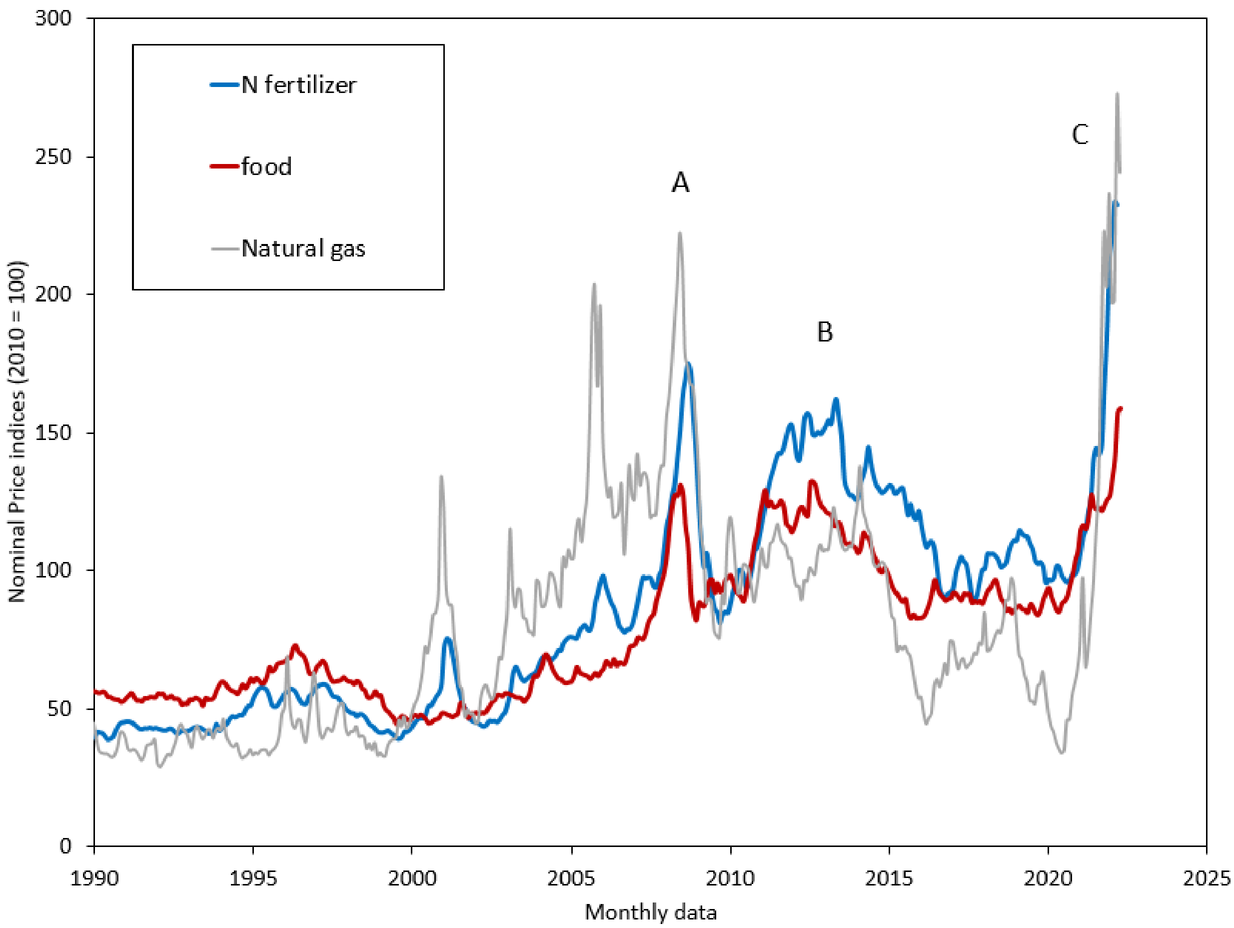


Figure 7. Nominal price indices show price correlations for globally traded N-fertilizer,[76] food[77] and natural gas.[77] Price spikes in 2008 (A) and 2011 (B) are contributors to food riots and subsequent political instability in North Africa and the Middle East. Price spikes in 2021 and 2022 (C) surpass those in 2008 and 2011.

Emerging Technologies

Greener Ammonia Production. The need to decouple ammonia production from fossil fuels is apparent in the discussions above. Viable scalable Haber-Bosch technologies exist using renewable electricity to generate H_2 from electrolysis of water (Fig. 5B2; S1). As of 2022 announcements of production scale projects for greener ammonia production are increasingly frequent.[78]

Rapid developments worldwide have focused on reducing the carbon footprint of ammonia production and finding more sustainable alternatives (Fig 5B2).[79,80] Other efforts include reducing the energy consumption of the core reaction through innovations in catalysts and novel electrochemical reactions, as well as processes for CO_2 capture[81] and transformations[81,82].

Resurgence of Ammonia in Refrigeration. NH_3 is the current heat transfer fluid of choice for large scale industrial and commercial refrigeration applications (Fig 6: S5) (e.g., office building air conditioning, supermarket heat pumps, food shipping and storage, winter sports arenas).[83] Due to its toxicity, use of NH_3 in residential applications (home air conditioning and refrigeration) has been very limited since the 1930s, when it was replaced by the newly-developed synthetic chlorofluorocarbons (CFCs).[84] However, CFCs were phased out under the 1987 Montreal protocol due to their high ozone depletion potential (ODP) (Fig. 4) and replaced by hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). The Kyoto protocol (1997) scheduled the phase-out of HCFCs by 2030 due to their ODP and global warming potential (GWP) (Fig. 4); HFCs are scheduled for drastic reduction by 2045 under amendments to the Montreal protocol (2014) and European F-gas legislation (2014).[85] Ammonia has negligible ODP and GWP and is seeing a resurgence as one of the few candidates to replace HFCs in refrigeration systems.[86] Toxicity issues associated with NH_3 are being addressed through modern system designs.[83]

Ammonia as Energy Carrier in the Future Low-Carbon Economy. NH_3 is being evaluated as an energy carrier (S6) to meet the unavoidable need for a liquid fuel to replace hydrocarbons in a future low-carbon economy. Central to this is the scale up of green ammonia synthesis. Attractive features of ammonia include its low cost of liquefaction and storage, and existing storage and transportation infrastructure.[81] Ammonia is a possible enabler of hydrogen-based energy production technologies, due to its ease of conversion to H_2 for use in fuel cells.[87] Significant worldwide R&D is also focused on the development of NH_3 as a fuel in direct combustion applications such as internal combustion engines for vehicles[88] and gas turbines for stationary power generation,[89,90] as well as an alternative to heavy fuel oil in sea transportation vehicles.[91] The combustion reaction of O_2 and NH_3 has N_2 and H_2O as the thermodynamic end products, making NH_3 in principle an emission-free fuel. However, in practice significant challenges exist in mitigating NOx intermediates.[89,90]

Future synthesis and use of ammonia

Ammonia or its derived Nr are likely to remain central to food production, as a source of N-fertilizers, for the foreseeable future. However, sustaining the growing global population is currently taking place at the expense of the environment. The global flow of Nr from HB ammonia is already well past the safe limit set in the Planetary Boundary Framework. If the demand for NH_3 also rises substantially more due to its adoption for other large-scale uses, such as in domestic refrigeration and energy production, the challenges will become even greater. They will include not only those directly related to the environment, but also those arising from interlinkages to other aspects of human security. In particular, economic sensitivity to factors affecting the scale of production, availability, and supply of NH_3 will become more acute, and global competition between uses of NH_3 as fertilizer and energy carrier could significantly increase the costs of foodstuffs and the resilience of food security.

Overall, it must be questioned whether it is possible to manufacture and use NH_3 at the scale envisaged by its growing areas of application, while reducing the impacts to levels that are compatible with Earth system safe operating spaces and human security needs. The interlinkages suggest that significant efforts will be needed to manage NH_3 production, supply and uses as its importance grows as a global commodity. Given both the urgency of action and the complexity and inter-connectedness of steps required, incremental approaches will be necessary towards reducing the multiple environmental footprints of Nr to levels compatible with sustainability. Chemistry and other sciences will have important roles to play, along with economic and political sectors. There will need to be a focus on:

- Managing Nr emissions in agriculture
- Decoupling NH_3 production from fossil fuels (transition to green production)
- Carefully evaluating the scaling-up of NH_3 production to meet the demands of emerging markets (energy and refrigeration):
    - Avoid large increase in Nr release to the environment, considering that Nr already exceeds the safe planetary boundaries limit
    - Effect of competition with N-fertilizer market and impact on global food prices and security
- Evaluating and managing the impact of emerging markets on N-fertilizer availability and pricing, and subsequent food prices and threats to global human security

Recommendations for re-centering the role of chemistry toward sustainability

We conclude this perspective with recommendations for central emphases, tools, and strategies to guide the transformation of chemistry (people, policies, and practice) toward sustainability. One of the key lessons emerging from considering Nr as a case study is the central importance of systems thinking in transforming the profession of chemistry towards sustainability. To realize a more effective and central role in understanding and addressing the grand challenges for society and the environment posed by large-scale material transformation, we recommend that the chemistry profession consider the following:

- Systems thinking approaches and tools provide the perspective required by the chemistry profession to look beyond optimizing reactions in a lab and processes in a manufacturing plant and to give attention to steering the complex and dynamic interactions of anthropogenic material transformation toward sustainable outcomes. Sustainability is not an outcome of individual reactions or processes, but rather a system property that emerges from transdisciplinary system-level consideration of the chemistry enterprise in its Earth and societal contexts.[9] (Overall *Figure 1: A systems approach to understanding how chemistry is embedded in and can contribute at multiple levels toward the emergence of sustainability of the Earth system.)*
- The scale and scope of the anthropogenic transformation of matter requires that chemists in research and industry, educators, and learners across the chemistry enterprise be deeply aware of the interconnectedness of material transformation and the sustainability of our planet. (*Figure 1, Level 1: Molecular/Material Basis of Sustainability)*.
- Education in chemistry at all levels, from the first introductions to the science of transformation in K-12 science education, to the professional development of chemists, requires a paradigm shift.[92] Beyond refocusing content on sustainability issues, this must equip learners to use systems thinking tools to connect chemistry research and practice to make education relevant and engaging, and to address the challenges and opportunities students will encounter as scientists and citizens. (*Figure 1, Level 1: Molecular/Material Basis of Sustainability)*.

- Environmental chemistry, which has historically focused on measuring and understanding the risks of environmental contaminants in Earth's geosphere, biosphere, cryosphere, hydrosphere, and atmosphere, has provided grounding for new orientations that move chemistry further toward sustainability. Strong support is needed to further integrate orientations such as green chemistry, sustainable chemistry, and one-world chemistry into chemistry research, practice, and education. (*Figure 1, Level 2: Orienting Chemistry towards Sustainability)*.
- Chemistry research and development should be combined with the transdisciplinary approaches needed to orient outcomes toward the advocacy required to achieve sustainability goals.[93] This convergence is not universally familiar territory across the chemistry enterprise; achieving it will require both education and professional development. (*Figure 1, Level 3: Sustainability Tools)*
- Contributing to global sustainability drivers such as the UN Sustainable Development Goals and the Planetary Boundaries framework should be a primary concern for professionals across the chemistry enterprise. The lens of chemistry, which draws attention to multiple dimensions of the molecular basis of sustainability,[94] is fundamental to understanding material transformations, the flux of chemical substances in Earth system processes, unintended consequences of those transformations, impacts on food supply security, water and energy concerns, ways to mediate and adapt to climate change, loss of biodiversity, and how best to build and maintain resilient ecosystems. (*Figure 1, Level 4: Sustainability Frameworks).*

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Author Contributions

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ABBREVIATIONS

CFC, chlorofluorocarbon

HFC, hydrofluorocarbon

HCFC, hydrochlorofluorocarbon

GWP, global warming potential

HB, Haber-Bosch process for industrial fixation of nitrogen

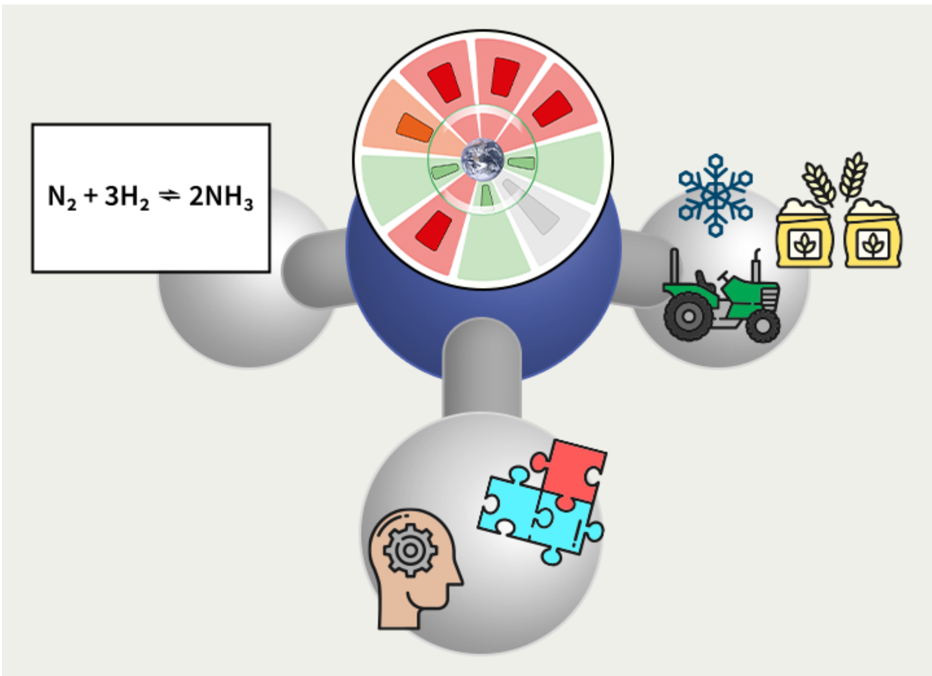
N-fertilizer, compounds used in global agriculture to enrich soil with bioavailable nitrogen (ammonia, urea, ammonium nitrate, etc.)

Nr, Reactive Nitrogen - all N species except N_2

NUE, nitrogen use efficiency

ODP, ozone depletion potential

TOC/Abstract Graphic.



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