

Using ammonia as a shipping fuel could disturb the nitrogen cycle

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Ammonia has been proposed as a shipping fuel, yet potential adverse side-effects are poorly understood. We argue that if nitrogen releases from ammonia are not tightly controlled, the scale of the demands of maritime transport are such that the global nitrogen cycle could be substantially altered.

Introduction

Human activities have caused warming of Earth's surface temperature by more than 1°C relative to pre-industrial levels through emissions of CO₂ and other greenhouse gases (GHGs) [1]. In an effort to reduce CO₂ emissions, electricity and hydrogen are seen as potentially valuable energy carriers, as they are carbon-free and can be produced from a variety of low-emissions technologies. However, both options do have technical and economic challenges, particularly for long-term energy storage as well as for mobile applications with large on-board fuel storage requirements. The latter is required for maritime shipping, which is responsible for 2.9% of global energy-related CO₂ emissions [2]. One solution that has been proposed to address these challenges is to use ammonia (NH₃) (made from renewable energy) as a shipping fuel source [3]. While studies address various benefits and costs of this technological strategy [4, 5, 6], none have assessed it in the context of the global nitrogen (N) cycle.

The global nitrogen cycle has already been dangerously disrupted by human activities, which convert inert nitrogen gas (N₂) to NH₃ or other forms of reactive nitrogen (N_r) at the rate of about 254 Tg per year (in 2015, see Figure 1). This is comparable to the natural rate of N_r conversion of 110 Tg N per year on land and 140 Tg N per year in the oceans [7]. N_r widely exists in the earth system, in a wide range of forms, and is critical for many ecosystem functions such as biosphere primary production. However, excessive N_r in water and air leads to environmental damages such as eutrophication and air pollution, threatening ecosystems and human health. N_r added to the environment can be converted back to N₂ mainly through the denitrification process, which usually emits N₂O as a by-product. N₂O itself is a potent GHG with a global warming potential of about 265–298 over a 100-year time horizon.

Considering these adverse environmental impacts, the planetary boundary for the human disturbance to the nitrogen cycle has been estimated at 62–82 Tg N. This boundary describes the level of N_r that can be safely added to the earth system by human activities without irreversible damages [8]. As mentioned above, human activities have already far exceeded that boundary. Additional needs for NH₃, such as for maritime shipping fuel production, could exacerbate this trend, and as a consequence, it is critical to understand the potential scale of any such disturbance as well as options to minimize it.

36 Potential nitrogen cycle disturbance

37 Our initial assessment shows that switching maritime shipping fuels from diesel fuel and residual fuel oil to ammonia
38 fuel would by itself require N_r production of approximately 586 Tg per year (see Box 1). While the actual amount of
39 that N_r that ends up in the environment is unknown, without technological advances and tight regulatory control,
40 ammonia-powered shipping could substantially contribute to disruption of the global nitrogen cycle. For example,
41 if 14% of that amount were to be released into the environment (e.g. through leakage, combustion and other
42 pathways), the amount of N_r production would equate to 82 Tg N, which is equal to the estimated upper limit of
43 the planetary boundary (which has already been exceeded by a factor of three).

44 The rate of 586 Tg N per year is more than twice the present global total and would exceed the upper limit
45 of the planetary boundary by more than 700%, indicating a potentially large-scale disruption of the global nitrogen
46 cycle. Note that the current level of ammonia production was 176 Tg in 2018 [3] while the amount of ammonia
47 needed to power the maritime shipping sector would be 711 Tg, implying a four-fold increase.

48 In contrast to the sources of N_r shown in Figure 1, the ammonia fuel cycle should return the majority of the
49 N_r in the fuel to the atmosphere as N_2 . For example, selective catalytic reduction (SCR) converts NO_x emissions in
50 the exhaust to N_2 [6], to the extent that catalytic converters are installed, maintained, and operated on ammonia-
51 powered ships. The convention in the literature for combustion-related nitrogen production and release is to not
52 count the NO_x that is generated by combustion but immediately scrubbed by catalytic converters. Because these
53 transformations happen instantaneously and within individual facilities and vehicles, there are no inventory data of
54 this volume of temporary NO_x production. In contrast to within-tailpipe NO_x , the ammonia-for-shipping fuel cycle
55 would separate the production of N_r and the potential return to the atmosphere as N_2 into very different times
56 and places, with many opportunities for escape along the way (e.g., production, loading and unloading, transport,
57 storage, fueling, and incomplete combustion).

58 Uncertain climate benefits

59 N_2O emissions from the use of ammonia as a maritime shipping fuel, including both direct emissions from combustion
60 and SCR, as well as indirect emissions from environmental denitrification, could significantly reduce the climatic
61 benefits of ammonia fuel. While N_2O emissions can be largely avoided in stoichiometric combustion conditions (in
62 which ammonia engines would probably tend to operate), these conditions in turn give rise to NO emissions however
63 which can partially convert into N_2O at the end of the exhaust [9]. At present, global maritime shipping produces
64 approximately 1056 Tg of CO_2 , from 330 Tg of fuel [2]. If 0.4% of the nitrogen in ammonia fuel were to become
65 N_2O , whether directly or indirectly, these emissions would completely offset the GHG emissions benefits of switching
66 fuels in the first place (see Box 2), irrespective of nitrogen cycle perturbation and ecosystem impacts, and even if
67 the ammonia production and distribution produced zero GHG emissions. Experimental data on N_2O emissions from
68 ammonia combustion and SCR is extremely rare and fairly dated [10, 11]. Research from 2012 [10] suggests that
69 combustion of ammonia in a small (8.6 kW) diesel engine increases N_2O emissions by about 1 g per kWh (about 0.4%
70 of the N in NH_3) compared to diesel combustion which would completely offset the combustion-phase GHG benefit
71 of ammonia over diesel. N_2O can also be a by-product of the SCR system if not properly tuned [11]. Furthermore,
72 the SCR process itself has the potential for NH_3 slippage [12].

73 An alternative to ammonia combustion would be cracking of ammonia into hydrogen and N_2 with subsequent use
74 of hydrogen in a proton-exchange membrane fuel cell (or other fuel cell technologies) [3]. While such ammonia-based
75 fuel cell technologies could potentially entail less N_r emissions from ship operations than ammonia combustion, the
76 actual operational rates of N_r release are not known for any ammonia-fueled ship technologies. Moreover, advanced
77 ship technologies do not address the potential for N_r release upstream of the ships. Note that hydrogen itself is an
78 indirect GHG and increased emissions would contribute to anthropogenic climate change [13].

79 In summary, ammonia as a maritime shipping fuel has the potential to release environmentally significant quanti-

80 ties of N_r on a global scale. Without mitigation of N_r species, ammonia use would amplify existing issues in nitrogen
81 cycle management. In addition, N_2O emissions associated with ammonia use could also offset or, if too large, negate
82 any GHG emissions benefits from switching fuels.

83 **Managing NO_x and NH_3 leakage**

84 Ammonia's decarbonization potential, therefore, is practical only if the leakage and emissions rates of N_r from all
85 stages of the full fuel cycle are kept to a minimum. The US National Emissions Inventory Data [14] implies that only
86 about 0.01% (in 2017) to 0.02% (in 2014) of the ammonia produced leaked from production facilities, but none of
87 the public inventory data that we reviewed provides any information about NH_3 leakage from ammonia distribution,
88 handling, and storage from the present-day supply chain. Leakage from ship refueling and operation would need
89 to be assessed similarly. In the future, upstream NH_3 emissions can be mitigated through technological change,
90 increases in the prices of the product, or pricing on their emissions, but some non-zero quantity of emissions should
91 be expected due to the nature of producing and transporting a commodity that is gaseous at standard atmospheric
92 conditions.

93 NO_x emissions of marine ammonia engines have been addressed in the literature, though the uncertainties are
94 significant, spanning two orders of magnitude [5]: from about 0.02–0.2%, which is similar to present marine diesel
95 engines, to about 0.2–2% of the nitrogen in ammonia fuel becoming NO_x [15]. Importantly, the estimates to this
96 point are not based on observational data from ammonia ships operating in real-world conditions, as this technology
97 is not deployed at present.

98 Any NO_x emissions resulting from incomplete combustion could be reduced by 90–99% through post-combustion
99 SCR [6], but the proposed catalytic reaction pathways require at least one molecule of NH_3 per each molecule of
100 NO_x to be reduced, which implies a parasitic energy loss associated with operating the SCR units. Any parasitic
101 energy loss and additional cost associated with the installation, operation and maintenance (e.g., due to degradation
102 of the catalytic efficiency affected by aging [16] or lubricant oil additive poisoning [17]) of the SCR and auxiliary
103 systems correlates with risk that such systems would not be operated at sea. Advanced injection principles could
104 be employed to reduce NO without sacrificing large portions of the engine efficiency. However, these systems may
105 require hydrocarbons as supporting fuels, which would in turn result in CO_2 emissions [18].

106 Of the potential nitrogen pollution from ammonia-based maritime shipping, N_2O escape will probably prove
107 the most difficult to quantify because direct emissions from combustion and SCR are not the only relevant sources.
108 N_2O emissions also occur indirectly due to a process within the 'nitrogen cascade' known as denitrification [19]. The
109 portion of N_r in agricultural fertilizers that becomes N_2O has been estimated at between 1–2% [20] with the use of
110 simplified estimation methods. However, observational studies find a wide range of N -to- N_2O emissions fractions,
111 about 0.1–20%, with the variability generally attributed to environmental conditions [21]. No studies that we are
112 aware of address what this fraction would be for maritime emissions of N_r species. Regardless of what the actual
113 fraction is, indirect N_2O emissions from ammonia-powered maritime shipping can be expected to scale with other
114 N_r emissions.

115 Other human health and environmental impacts can also occur after spillage and accidents involving liquid NH_3
116 as well as from formation of fine particulate matter from nitrogen oxides and ammonia. These additional health,
117 environmental and safety risks would have to be evaluated as well if future ammonia production were to be increased.

118 **Sailing ahead**

119 This Comment aims to provide a summary of the information presently available for estimating the potential nitrogen
120 cycle implications of the use of ammonia as a maritime shipping fuel, as the literature on this technological strategy
121 for decarbonization has not yet considered this perspective. We demonstrate that if nitrogen releases from ammonia
122 are not tightly controlled, the scale of the demands of maritime shipping fuel are such that the technology could

123 significantly alter the global nitrogen cycle. Further, some of the released nitrogen would ultimately resolve to
124 N_2O , which would offset at least some of the climatic benefits afforded by switching maritime shipping fuels. The
125 environmental cost–benefit analysis depends crucially on the exact emissions rates of NH_3 , NO_x , and N_2O at all stages
126 of ammonia fuel production, transportation, refueling, and consumption, and in all of the environmental conditions
127 in which ships travel. A second key question is what portion of the NH_3 and NO_x emissions will indirectly resolve
128 to N_2O on a multi–year timescale. We suggest that these questions should be at the forefront of ongoing research,
129 development, and deployment of ammonia as an alternative maritime shipping fuel.

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137 Ethical declarations

138 Competing interests

139 The authors declare no competing interests.

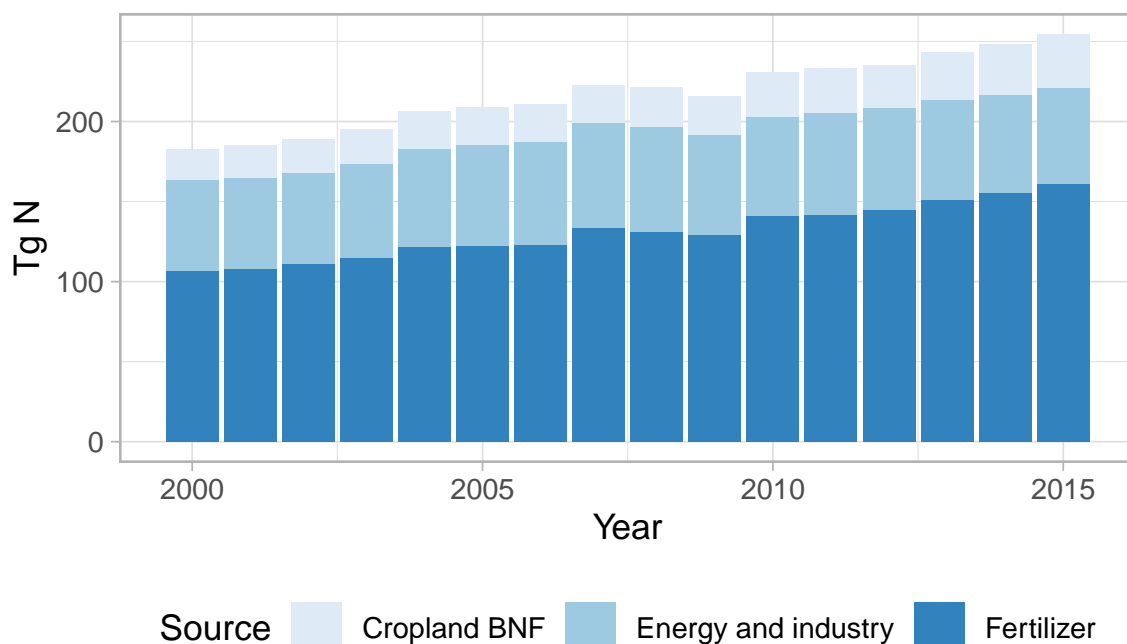


Figure 1: Global anthropogenic reactive nitrogen production by source, 2000–2015. BNF=biological nitrogen fixation. Data sources: [22, 23].

Box 1: Calculating the amount of N_r due to switching shipping fuels to NH_3

We calculate the amount of N_r due to switching shipping fuels to NH_3 (586 Tg N) according to Equation 1:

$$Q_n = Q_f \times \frac{l_f}{l_a} \times \mu_a \times \frac{e_f}{e_a} \quad (1)$$

where

- Q_n denotes the amount of N_r produced from NH_3 combustion
- Q_f denotes the amount of shipping fuels combusted in 2018 (330 Tg) [2]
- l_f denotes the weighted lower heating value of current shipping fuels (40.5 MJ/kg)
- l_a denotes the lower heating value of NH_3 (18.8 MJ/kg)
- μ_a denotes the molar mass of N in NH_3 (14 g/mol / 17 g/mol \approx 0.824)
- e_f denotes the efficiency of current ship engines
- e_a denotes the efficiency of NH_3 engines

Note that we assume that ammonia engines would have about the same thermal and mechanical efficiency as current shipping fuel engines, so that the term $\frac{e_f}{e_a}$ simply becomes one. While the thermodynamic engine efficiency and the quantity of energy demanded by maritime shipping are both uncertain and subject to technological improvement over time, the other variables in this calculation are immutable physical properties.

Box 2: Calculating the amount of N₂O that would negate climate benefit of NH₃

The amount of N₂O that would negate the climate benefit of ammonia as a shipping fuel (0.4%) is calculated using Equation 2:

$$p_{no} = \frac{Q_c}{Q_n} \times \frac{\mu_n}{g_{no}} \quad (2)$$

where

- p_{no} denotes the percentage of N turned into N₂O
- Q_c denotes the amount of CO₂ emitted from shipping fuel combustion in 2018 (1056 Tg CO₂) [2]
- Q_n denotes the amount of N_r emitted from ammonia combustion (586 Tg N)
- μ_n denotes the molar mass of 2N in N₂O ($2 \times 14 \text{ g/mol} / 44 \text{ g/mol} = 0.\overline{63}$)
- g_{no} denotes the 100-year global warming potential of N₂O (298 kg CO₂e/kg N₂O) [24]

An alternative way of deriving p_{no} is shown in Equation 3:

$$p_{no} = q_{no} \times l_a \times \gamma_e \times \gamma_m \times \mu_n \times \mu_a \quad (3)$$

where

- p_{no} denotes the percentage of N turned into N₂O
- q_{no} denotes the amount of N₂O produced per energetic unit of NH₃ (1 g N₂O/kWh NH₃) [10]
- l_a denotes the lower heating value of NH₃ (18.8 MJ/kg)
- γ_e denotes energy conversion between kWh and MJ (1 kWh/3.6 MJ)
- γ_m denotes mass conversion between t and g (1 t/1,000,000 g)
- μ_n denotes the molar mass of 2N in N₂O ($2 \times 14 \text{ g/mol} / 44 \text{ g/mol} = 0.\overline{63}$)
- μ_a denotes the molar mass of N in NH₃ (14 g/mol / 17 g/mol \approx 0.824)

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