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RESEARCH ARTICLE

PROPOSED INNOVATION REFORM MODEL FOR THE MINERAL NITROGEN FERTILIZER INDUSTRY IN CHINA TO REDUCE GREENHOUSE GAS EMISSIONS

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KEYWORDS

carbon accounting, life cycle assessment, policy, product structure

HIGHLIGHTS

- The carbon footprint of the nitrogen fertilizer chain has decreased significantly over the last decade.
- Different nitrogen fertilizer products have different carbon footprints.
- Structural improvement of N fertilizer products can achieve carbon reduction.

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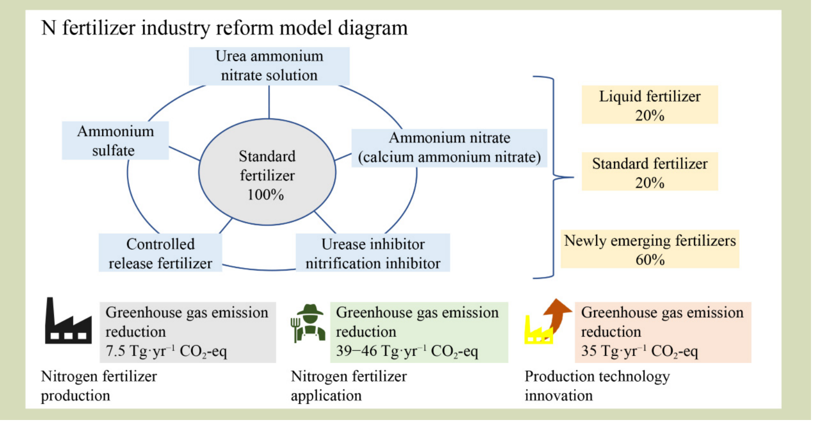
GRAPHICAL ABSTRACT



ABSTRACT

Globally, the reduction of excessive N losses and greenhouse gas (GHG) emissions is a central environmental challenge in the 21 century. China has huge associated emissions during both production and land application phases. In addition, 70% of N fertilizer in China is produced and land applied as urea, which has high associated emissions. This study utilized life cycle analysis to compare the carbon emission capacity of different N fertilizers and quantified GHG emissions from different N fertilizer chains within China. This enabled a new innovative reform model to be proposed, which aims to decrease the carbon footprint and increase the net ecosystem carbon budget of China. The results showed that the carbon footprint of the N fertilizer industry was about 229 $Tg\cdot yr^{-1}$ CO_2-eq in 2020. Through changes away from urea through the production and land application of a mix of newly emerging fertilizers, liquid fertilizers and standard fertilizer reductions to 174–182 $Tg\cdot yr^{-1}$ CO_2-eq. Through the upgrading of mineral N fertilizer production technology, the carbon footprint of N fertilizer chain can be reduced by 34.8 $Tg\cdot yr^{-1}$ CO_2.eq. Such reductions would reduce China's total GHG emissions to 140–147 $Tg\cdot yr^{-1}$ CO_2-eq.

1 INTRODUCTION

The production of synthetic mineral nitrogen fertilizers have surpassed naturally synthesized N from biological N fixation and lightning, and have become the main source of N used by humans[1]. Continued world population growth leads to increasing demand for N fertilizers and it is expected to rise to 236 Mt by 2050[2]. For developing countries with more people and less potential for biological N fixation, the dependence on N fertilizer is also greater[3]. However, much of the N applied to cropland escapes the agricultural system and becomes reactive N cascading through the environment (water and gaseous phases). Nearly 300 Tg of N are activated through human activities annually, but about 70% of N enters the atmosphere and water in the form of nitrous oxide, nitrate, nitrogen oxides (NO_x) and ammonia[4]. In fact, N emissions from human activities are already beyond the safe range for the sustainability of the planet[5]. N_2O produced by N fertilizer is an important greenhouse gas (GHG)[6], and 62.4% of all N_2O emissions in China are attributed to agricultural activities[7]. The European assessment showed that the environmental cost of reactive N in Europe reached as high as 70 billion to 320 billion EUR[8]. Harnessing the positive effects of N fertilizers and reducing its negative impacts, especially GHG emissions, requires a concerted global effort.

China, as a dominant force in the international N fertilizer market, is central to both the problem and solution of mineral N production, as well as its global use and emissions. Between 1990 and 2009, 61% of the global growth in N fertilizer production and 52% of the global growth in N consumption occurred in China[9]. In 2015, N fertilizer production, consumption and exports peaked and a total of 47.2 Tg N were produced, of which 30.1 Tg N were consumed in agriculture, accounting for 30% of the global demand for agricultural N fertilizers[9]. The Chinese government has actively responded to the call to control global climate change and proposed policies for carbon peaking and carbon neutrality (the dual-carbon strategy). In China, the energy consumption of the fertilizer industry accounts for 20% of the total energy consumption of the petrochemical industry; the energy consumption of the synthetic ammonia industry accounts for 2.5% of the national total energy consumption[10]. The N fertilizer industry is an important source of carbon emissions, and its emission reduction is essential for realizing the dual-carbon strategy.

The assessment of the emission reduction potential of the N fertilizer chain is considered of great significance for formulating a dual-carbon strategy for the N fertilizer industry. However, different studies generate widely-varying estimates of GHG emissions from N fertilizer chains in China, from 9.6 to 31 t CO_2-eq t^{-1} N[11–13]. This phenomenon may be caused by the complexity of N fertilizer types and the differences in emission factors at different stages of the life cycle. Over the past 20 years, the ratio of urea to other types of N fertilizers was about 7:3[14]. There are various N fertilizers such as ammonium sulfate (AS), ammonium nitrate (AN), ammonium bicarbonate (ABC) and ammonium chloride (ACl), and their market share is between 2% and 10%[9]. In recent years, with the development of the concept of green agriculture in China, newly emerging fertilizers such as stabilized fertilizers with nitrification inhibitors (NI), urease inhibitions (UI) and controlled-release fertilizers (CRF) have appeared on the market, but their market share is quite small[15].

In addition, differences in accounting methods regarding production processes and fertilizer application processes to farmland result in varied figures regarding total emissions of GHG. As far as the production process is concerned, the energy structure, technology level and N fertilizer types are all important factors contributing to the final emissions[13,14]. The main raw material for ammonia production in China is coal rather than natural gas, which is the main raw material globally. It is estimated that the amount of GHG using coal as raw material is twice that of natural gas[16]. China's GHG emission in synthetic ammonia production is 6.98 t CO_2-eq t^{-1} N[17], while the global average emission is 3.18 t CO_2-eq t^{-1} N. If the optimal process is used, the emission can be stabilized at 2.37 t CO_2-eq t^{-1} N[18]. Zhang et al. reported that the comprehensive carbon emission factor of N fertilizers in China was 6.0 t CO_2-eq t^{-1} N[13]. It was stated, that the default value for direct N_2O emissions from fertilizer application was 1% and 0.3% for indirect N_2O emissions[19]. Different N fertilizer products have different N_2O emission factors, such as 1.1% for urea and 0.8% for AN. Fertilizer type also influences the emission factors of NH_3 and a higher value (1.45%) is found when using urea, and a lower value is observed when using AS (0.60%) or AN (1.07%)[20]. The N-containing gas loss rate of urea is highest among various N fertilizers at about 15%–20%[16]. Newly emerging fertilizers with the potential to reduce the carbon footprint, have been shown to be important ways to reduce N losses by 20%–70%[21]. Therefore, due to the different emission factors of different N fertilizer products, it is urgent to evaluate whether adjusting the structure of N fertilizer products is a feasible GHG emission reduction measure.

Over the past 20 years, the N fertilizer industry experienced tremendous changes. Since 2010, there were three major policies issued successively, i.e., the optimization of production capacity in the synthetic ammonia industry, the implementation of energy consumption quotas, and a zero growth of N fertilizer policy, indicating the technological progress and output changes of the N fertilizer manufacturing industry. Therefore, the conclusions of past studies are no longer representative of the current state, and GHG of the N fertilizer chain also needs to be recalculated.

This study aims (1) to compare the carbon emission capacity of different N fertilizers; (2) to quantitatively assess GHG emissions from different N fertilizer chains in China using baseline data from 2010 to 2020; (3) to propose a new innovative reform model for China; and (4) to quantify the potential of this reform model to decrease the carbon footprint and increase the net ecosystem carbon budget in China.

2 MATERIALS AND METHODS

2.1 N fertilizer industry reform model diagram

One of the reasons for the serious pollution of N fertilizers in China is that the production process and resource are being ignored, while the focus is on the accurate application amounts of fertilizers in relation to agricultural requirements. The physical composition of N fertilizers is dominated by solid particles. Current urea production has a high environmental impact (12.1 t CO_2-eq t^{-1} N). Europe and the USA regard the development of a variety of new N fertilizer products as a feasible method to improve the utilization rate of N fertilizer. For example, liquid N fertilizer products, such as liquid-ammonia and urea ammonium nitrate (UAN), account for more than 45% in the USA[22]. At the same time, related equipment is provided for the production, storage, transportation and application of liquid N fertilizer. Unlike the USA, policy in Germany means that solid fertilizers are the main commodities and therefore nitrate products are developed. Nitrate accounts for 28% of the N form. Calcium ammonium nitrate accounted for the largest proportion of the products at 45%[22]. Through the combined application of ammonium nitrogen (NH_4^+-N) and nitrate nitrogen (NO_3^--N), a balance between supply of nutrients and environmental protection can be achieved.

It is widely accepted that a balanced supply of nutrients is the prerequisite for plant growth. Plant roots can simultaneously absorb and utilize NH_4^+-N and NO_3^--N. NO_3^--N tends to increase the root to shoot ratio, increase the soluble sugar content and metabolic enzyme activity in the root system, and promote the absorption of K^+, Ca^{2+} and Mg^{2+}[23]. The anion antagonism of NO_3^--N can reduce the absorption of Cl^- by plants, which is beneficial to the growth of chlorine-avoiding plants[24]. NH_4^+-N tends to promote leaf growth. N forms have different effects on crop growth, but a large number of studies have shown that the synergistic supply of NH_4^+-N and NO_3^--N is the key to achieving high yield and high quality of plants. The concentration of NH_4^+-N in the plant growth environment will produce ammonium toxicity, which is manifested as leaf edge necrosis, leaf yellowing and chlorosis[25]. This imbalance can be mitigated when NO_3^--N is supplied at the same time. Adding NH_4^+-N can also lower the reducing power and photon energy consumed by high concentration NO_3^--N. Simultaneous supply of NH_4^+-N and NO_3^--N can significantly increase the photosynthetic rate of plants[26]. According to the International Fertilizer Industry Association (IFA), the proportion of NO_3^--N in China is only 0.3%. The disparity in the proportion of N fertilizer products makes it difficult for plants to obtain a coordinated supply of NH_4^+-N and NO_3^--N. Therefore, it is urgent to increase the proportion of NO_3^--N in N fertilizer products.

According to statistics, the drip irrigation area is 10 Mha in China, accounting for 10% of the total cultivated land area. With the development of water and fertilizer integration technology, it will reach 20% in the future. Therefore, increasing the proportion of liquid N fertilizer to 20% is in line with the development requirements. AS, a byproduct of the steel industry mainly for export, is an inexpensive N fertilizer with low energy consumption[16,20]. The annual output of AS accounts for 20% of the total N input, and all of it is put into agricultural production, which can replace 15% of urea, which can not only reduce the carbon footprint of N fertilizer, but also reduce the unit cost. Newly emerging fertilizers, such as CRF, NI and UI, have been shown to be an important way to reduce the carbon footprint[21]. The object of successful commercial attempts is to apply this technology to urea (as CRF, UI and NI), NH_4^+-N fertilizer (as NI). Upgrading this type of standard N fertilizer product with newly emerging fertilizers holds promise in reducing GHG emissions. The high price of newly emerging fertilizers makes it difficult compete with traditional fertilizers in market share. However, as a simple way to achieve the goal of green agriculture, many countries promote newly emerging fertilizers in the form of mandatory laws and financial subsidies. To realize the development of low-carbon agriculture in China, emission reduction at the fertilizer application processes is an important link. With the increasing awareness of new fertilizers, it is necessary to promote the healthy development of the newly emerging fertilizers industry in the future. Under the conditions of policy support and farmers' approval, the market share is expected to increase to more than 60%.

In this study, the transformation of urea with inhibitors, other ammonia and nitrate forms of N to develop a new strategy for the synthetic N fertilizer industry is proposed (Table 1), which would be an urgent requirement for achievement of the dual-carbon strategy. The product optimization structure model, referring to the level of NO_3^--N in Germany, increases the proportion of NO_3^--N to 20%. The proportion of urea is reduced to 20%, and the nutrients in this part are replaced by AS, AN and UAN, increasing their proportion by 15%, while maintaining the ratio of ACl and compound production. In this way, the ratio of amide: NH_4^+-N: NO_3^--N in the N fertilizer product can reach 3:5:2. Compared with the current ratio (7:2:1), the supply of various N nutrients can be more coordinated and can be adapted to more scenarios, such as water and fertilizer integration, after the adjustment of the product structure. There are various N fertilizer products, and the proportion fluctuates slightly with market changes. Therefore, the average proportion of different products from 2015 to 2020 is used as the product structure to explain the goals and effects of the reform.

2.2 Life cycle assessment scope

The life cycle assessment is a method for summarizing and evaluating the potential impact of inputs and outputs on the environment of a product (service system) throughout its life cycle.

This study evaluated the resource and environmental costs of different types of N fertilizers for the entire life cycle, starting from the production of synthetic ammonia and ending with the farmland application of N fertilizers. It included the entire process of N fertilizer production, transportation and application. In the field application section, direct and indirect N_2O emissions from N fertilizer application were included (Fig. 1).

2.3 Data collection

Statistical data were collected for analysis. There are three channels for statistics on N fertilizer production and application in China, namely the IFA, the Chinese N Fertilizer Industry Association (CNFIA), the China National Chemical Information Centre are cited (CNCIC) and the National Bureau of Statistics of China (NBSC). Due to different statistical scope and methods, the annual data are slightly different for different channels. To keep in line with international standards and to keep the data professional, this paper used the CNFIA as the main channel.

N fertilizer production capacity, output (including total N fertilizer output and output of each product) and consumption data came from the CNFIA. Newly emerging fertilizers production and capacity data came from the CNCIC. The total N fertilizer production and product data for Germany and the USA came from the IFA. Agricultural N fertilizer application rates were obtained from the NBSC. The emission factors during the production and application of different N fertilizers were summarized from published literature data.

2.4 GHG emissions from ammonia synthesis

The GHG emission factors before and after the reform of the

Table 1 N fertilizer structure in future. Product structure is calculated based on N

Types of fertilizers	Now	Product structure optimization objective
Composition of main N fertilizer types (%)		
Urea	65.4	20
Ammonium bicarbonate	2.8	0
Ammonium chloride	7.5	10
Ammonium sulfate	5.0	20
Ammonium nitrate	4.0	20
Compound and other products[1]	16.0	15
Urea ammonium nitrate	–	15
Composition of product type (%)		
Standard fertilizers	99.5	20
Newly emerging fertilizer	0.5	60
Liquid fertilizer	0	20

Note: [1]Compound and other products represent compound fertilizers which were made from synthetic ammonia.

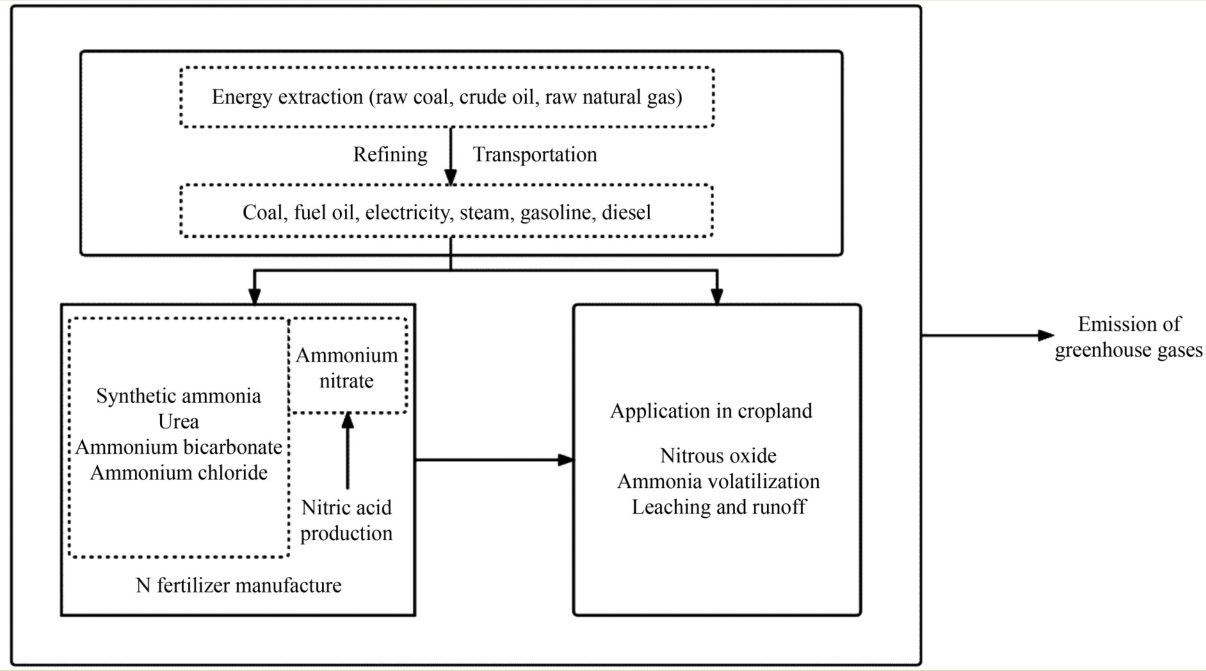


Fig. 1 Life cycle assessment boundaries for N fertilizers.

ammonia industry were evaluated in the present study. Information on fossil fuel energy consumption, electricity usage, and total energy consumption in ammonia plants in 2005 was obtained from the survey by Cao[27]. The result of this data calculation was before industrial upgrading. According to the Chinese government's "Twelfth Five-Year Plan" requirement, by 2015 the energy consumption of synthetic ammonia using anthracite lumps as raw material was less than 39.6 GJ; the energy consumption of synthetic ammonia using natural gas as raw material was less than 33.7 GJ. Therefore, this paper termed the energy consumption required by the policy to estimate the energy consumption of synthetic ammonia after 2015 as after industrial upgrading.

Emission factors for each type of ammonia plant were calculated using policy energy consumption caps and IPCC default values:

$$\mathrm{EF}_{\mathrm{Am}i} = \sum \mathrm{W}_{\mathrm{M}ij} \times (R_{\mathrm{CO_2}} + R_{\mathrm{N_2O}} \times 298 + R_{\mathrm{CH_4}} \times 25)_{ij} \quad (1)$$

where $\mathrm{EF}_{\mathrm{Am}i}$ is the GHG emission factor (t CO_2-eq t^{-1} N) for the production of synthetic ammonia at different plants, $\mathrm{W}_{\mathrm{M}ij}$ is the raw material consumed per unit of ammonia N production ($t \cdot t^{-1}$ N), and R_{CO_2}, R_{N_2O}, and R_{CH_4} are CO_2, N_2O, and CH_4 emission factors, respectively, for feedstock combustion ($t \cdot t^{-1}$ N). The average energy consumption of synthetic ammonia is calculated as a weighted average according to the structure of synthetic ammonia feedstock.

2.5 GHG emissions from N fertilizer product manufacturing

The data on the total consumption of the main production materials of urea, AN, ABC and ACl are from the CNFIA fertilizer plant survey. The consumption of different N fertilizer production materials includes the consumption of synthetic ammonia. Emission factors for each type of N fertilizer were calculated as:

$$\mathrm{EF}_{\mathrm{S}i} = \sum \mathrm{W}_{\mathrm{S}ij} \times (\mathrm{R}_{\mathrm{CO_2}} + \mathrm{R}_{\mathrm{N_2O}} \times 298 + \mathrm{R}_{\mathrm{CH_4}} \times 25)_{ij} + \mathrm{EF}_{\mathrm{HNO_3}} \quad (2)$$

where $\mathrm{EF}_{\mathrm{S}i}$ is the carbon emission coefficient (t CO_2-eq t^{-1} N) of a certain N fertilizer N production process, $\mathrm{W}_{\mathrm{S}ij}$ is the raw material consumed per unit of N fertilizer production and $\mathrm{EF}_{\mathrm{HNO_3}}$ is the raw material nitric acid with a carbon emission factor of 5.4 t CO_2-eq t^{-1} N[13]. Nitric acid is an upstream product of AN and is only counted when calculating energy consumption for AN production.

2.6 GHG emissions from N fertilizer application to croplands

The data on the farmland emission factors of different N fertilizer products and the effect of N fertilizer abatement technology are from published literature, covering N fertilizer products including urea, ABC, ACl, AN, AS and UAN. In addition, the effects of newly emerging fertilizers, NI, UI and CRF, on N loss are reviewed.

Emission factors for different N fertilizers were calculated as:

$$\mathrm{EF}_{\mathrm{A}i}=\sum(\mathrm{EF}_{\mathrm{N_2O}i}+\mathrm{EF}_{\mathrm{NH_3}i}\times 1\%+\mathrm{EF}_{\mathrm{NO_3}i}\times 0.75\%)\times\frac{44}{28}\times 298 \tag{3}$$

where $\mathrm{EF}_{\mathrm{A}i}$ is the carbon emission coefficient (t CO_2-eq t^{-1} N) during the application of a certain N fertilizer, and $\mathrm{EF}_{\mathrm{N_2O}i}$, $\mathrm{EF}_{\mathrm{NH_3}i}$, and $\mathrm{EF}_{\mathrm{NO_3}i}$ are the losses (%) of different N fertilizer loss pathways, respectively.

2.7 GHG emissions from the entire N fertilizer chain

The total GHG emissions of the N fertilizer chain were calculated as:

$$\mathrm{GHG}_{\mathrm{T}i}=\sum(\mathrm{EF}_{\mathrm{S}i}+\mathrm{EF}_{\mathrm{A}i})\times \mathrm{W}_{\mathrm{F}i} \tag{4}$$

where $\mathrm{GHG}_{\mathrm{T}i}$ is the total amount of GHG emissions in the N fertilizer chain in China in a specific year and $\mathrm{W}_{\mathrm{F}i}$ is the amount of specific N fertilizer (Tg N).

3 RESULTS

3.1 Changes in the structure of N fertilizer products

As shown in Fig. 2, from 2002 to 2015, the production of N fertilizers in China showed a rapid growth trend. In 2002, the total output of synthetic ammonia was 30.1 Tg N, and the total output of N fertilizer was 27.4 Tg N. In 2015, the total amount of synthetic ammonia increased by 82.7% compared with 2002, reaching 55.0 Tg N, which is the peak of synthetic ammonia production. At the same time, N fertilizer production also peaked at 47.9 Tg N in 2015, up 74.7% from 2002.

After 2015, in response to the zero growth of N fertilizer initiative from the Chinese government, the production of synthetic ammonia showed a negative growth rate for three consecutive years from 2016 to 2018. From 2015 to 2016, the negative growth rate of synthetic ammonia production was the largest, reaching 9.1%. In 2018, the output of synthetic ammonia was stable at 56 Tg. A slight recovery was noted in 2020 (58.8 Tg). With the decline of synthetic ammonia production, N fertilizer production showed a similar trend, with a negative growth rate of 12.8% from 2015 to 2016. It can be seen that the market shrinkage caused by policy influence had a huge impact on the production volume.

During this period, the N fertilizer product structure has also undergone major changes (Fig. 2). From 2002 to 2015, urea increased from 58.5% to 68.2%, whereas ABC dropped from 21.6% to 4.2%. By 2020, the proportion of ABC further decreased to 2.2%. Due to the increase in the proportion of various N fertilizer types and fluctuations in the price of urea, in 2020 the proportion of urea decreased by 3.5% compared with 2015. With the development of combined alkali production, ACl increased slightly which is a byproduct of combined alkali production. By 2020, the output of ACl was 2.2 $\mathrm{Tg\cdot yr^{-1}}$ N, accounting for 8.5% of the output of N fertilizer, an increase of 0.9% compared with 2002. Since 2002, AN has been included in the management of civil explosive products and cannot be directly used as agricultural N fertilizer. However, due to the growing demand for nitro-compound

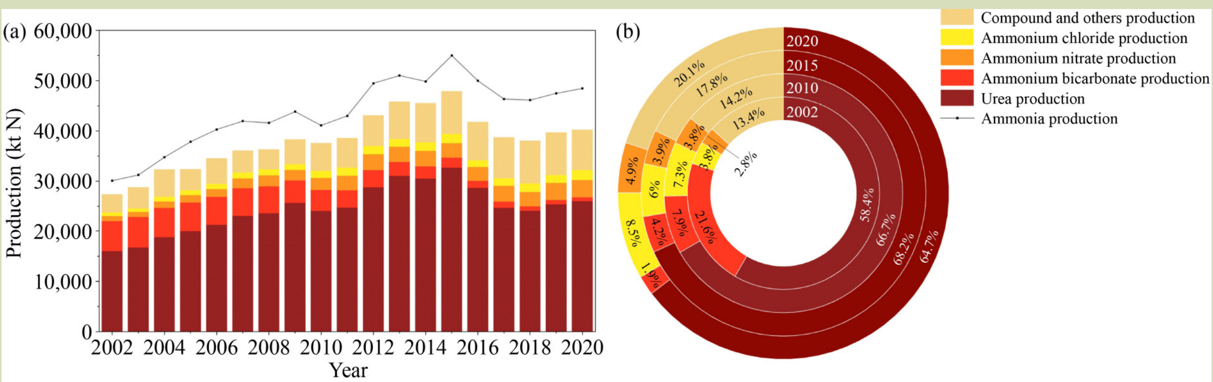


Fig. 2 Temporal changes in N fertilizer production. (a) Changes in N fertilizer production from 2002 to 2020 in China. (b) Proportion of N fertilizer products in different years. Data were sourced from the China N Fertilizer Association. Compound and other products represent compound fertilizers which were made from synthetic ammonia (the same below).

fertilizers, the production of AN is also on the rise. In 2020, the output of AN was 2.0 Tg· yr^{-1} N, accounting for 4.9% of N fertilizer. Compound fertilizers and other fertilizers, such as and multi-compound fertilizers, showed an increasing trend, from 13% in 2005 to 20% in 2020. AS is a byproduct of the iron and steel industry. As a response to the requirements of environmental protection and comprehensive utilization the output reached 2.2 Tg·yr^{-1} N by 2020. Due to advocacy of scientific fertilization, the output of compound fertilizer also has increased rapidly.

3.2 Carbon emission coefficients during the production and application of different N fertilizer types

3.2.1 Carbon emissions in the production of synthetic ammonia

The ammonia synthesis process is the link with the highest energy consumption in N fertilizer production, and the level of energy consumption is directly related to the cost of N fertilizer production. China's synthesis of ammonia uses coal and natural gas as the main raw materials, of which coal accounts for 76% and natural gas accounts for about 21%[9]. The energy consumption of the ammonia synthesis, the production process and its scale will affect the final amount of energy used. In 2005, CNFIA conducted a survey on the fossil fuel energy consumption, electricity use and total energy consumption of 230 of the 570 ammonia addition plants in the country, and found that the energy efficiency of ammonia synthesis of large enterprises using coal and natural gas as raw materials was 53.5 and 44.7 GJ·t^{-1} N, respectively, and GHG emissions were 7.4 and 2.5 t CO_2-eq t^{-1} N, respectively[13]. Energy efficiency was 12.2%–20.3% higher than that of small and medium-sized enterprises. Overall GHG emissions decreased by 22.1%–35.9% (coal) and 6.3%–43.2% (natural gas)[13].

Combing the comprehensive energy consumption of synthetic ammonia in China's history, it was found that the comprehensive energy consumption of synthetic ammonia dropped from 96.6 GJ·t^{-1} N in 1980 to less than 56.0 GJ·t^{-1} N in 2011 (Table 2). However, due to the increased demand for synthetic ammonia from industry and agriculture, the production of synthetic ammonia rose from 30.1 to 55.0 Tg N in 2002–2015 (Fig. 2). The total energy consumption of ammonia synthesis increased of 43.7% compared with 2002. After 2015, synthetic ammonia production declined. By 2020, the total energy consumption figure dropped by 11.9%.

Due to the improvement of production efficiency, the carbon emission per unit of ammonia production in China has dropped from 5.1 t CO_2-eq t^{-1} N in 2005 to 3.9 t CO_2-eq t^{-1} N in 2015 (Table 3). GHG emissions increased from 154 Tg CO_2-eq in 2002 to 214 Tg CO_2-eq in 2015 due to the rapid increase in synthetic ammonia production. It dropped to 189 Tg CO_2-eq in 2020. The world's advanced synthetic ammonia technology emits 2.6 t CO_2-eq t^{-1} N. Through technological upgrades, there is still room for 33.3% carbon emission reduction per ton of products.

Table 2 Temporal changes of ammonia energy consumption in China

Year	Comprehensive energy consumption (GJ·t^{-1} N)
1980[1]	96.6
1995[1]	66.9
2006[1]	59.1
2011[1]	56.0
2015[2]	46.5

Note: [1]Data were summarized from Huang[28]. [2]Calculated data according to the technical requirements of the "Twelfth Five-Year Plan", weighted by the proportion of fuel used in coal (78%) and natural gas (21%).

3.2.2 Carbon emissions from N fertilizer production

Compared with the energy consumption of synthetic ammonia production, the energy consumption during the process of producing N fertilizer from synthetic ammonia has not received much attention. In this study, the comprehensive energy consumption of different fertilizer production processes was calculated, including the ammonia synthesis process (Table 3).

Due to the different types of N fertilizers, the energy consumption during the production of synthetic ammonia into N fertilizers is different. Urea is the most important N fertilizer in China. From 2002 to 2015, carbon emissions decreased from 6.3 to 5.1 t CO_2-eq t^{-1} N. The main reason for the reduction in carbon emissions was the reduction in energy consumption in the ammonia synthesis process.

Nitrate N fertilizer, represented by AN, is the fertilizer with the highest GHG emissions during the production process. The main reason for this is that nitric acid is the main raw material, and the production of nitric acid emits N_2O. The nitric acid production process can supply 7.1 GJ·t^{-1} N of heat through an exothermic reaction[29], which can reduce the fuel consumption. However, the reaction produces N_2O, and the world emission averages 8.1 t CO_2-eq t^{-1} N[31]. After 2015, China's AN production GHG emissions is 9.8 t CO_2-eq t^{-1} N.

Table 3 GHG emission factors for different N fertilizers during fertilizer manufacturing

N fertilizer type	Chinese factors[1] (t CO_2-eq t^{-1} N)		Advanced technology[2] (t CO_2-eq t^{-1} N)
	Before industrial upgrading	After industrial upgrading	
Synthesis ammonia	5.1	3.9	2.64
Urea	6.3	5.1	2.52
Ammonium bicarbonate	5.4	4.2	–
Ammonium nitrate	11.0	9.8	3.03
Ammonia chloride	5.4	4.2	–
Ammonium sulfate	–	0.35	0.11
Compound and other products[3]	–	6.1	–
Urea ammonium nitrate solution	–	–	2.44

Note: [1]Recalculated data from previous studies by the research team[13,28]. [2]Advanced technology is organized according to the International Fertilizer Industry Association[29,30], including all industrial links starting from ammonia synthesis. [3]Compound and other products represent compound fertilizers which were made from synthetic ammonia.

The emission reduction contribution of the optimized ammonia synthesis technology is 1.2 t CO_2-eq t^{-1} N, and the AN emission factor of the world's advanced technology is 3.0 t CO_2-eq t^{-1} N. It can be seen that the industrial technological innovation of AN should start with the control of N_2O in the nitric acid emission process, and then N_2O emissions can be reduced by 70%–95% through N_2O decomposition technology[6,32].

ABC is the main N fertilizer product for small N fertilizer plants in China. It uses the shift gas in the synthetic ammonia production process to pass into the concentrated ammonia water tower, absorbs CO_2 in the shift gas, and produces ABC crystals. This process fixes CO_2, so GHG emissions are lower[13]. With the reduction of energy consumption for ammonia synthesis, the carbon emission in the production of ammonium bicarbonate is reduced from 5.4 to 4.2 t CO_2-eq t^{-1} N.

The main sources of ammonium N fertilizer in China are the chemical and steel industry. The production of ACl does not cause additional GHG emissions. Combining the emission calculation of synthetic ammonia production in China, it can be concluded that CO_2 emissions in the ACl link are 4.2 t CO_2-eq t^{-1} N. AS, as a byproduct of steel, lacks energy records, so it is calculated using the world average GHG emissions of 0.35 t CO_2-eq t^{-1} N.

UAN is the main variety of liquid N fertilizer. During the production process AN and urea are melted, then stirred and cooled, and the additional energy consumption is about 0.7 GJ·t^{-1} N. Compared with the solid fertilizer granulation and drying process, the energy consumption is significantly lower[33]. The optimal technical CO_2 emission of UAN is 2.44 t CO_2-eq t^{-1} N[29]. The USA developed a UAN solution, and transported it through pipelines and liquid storage, which can reduce CO_2 emissions in granulation, packaging, transportation and other links. However, UAN is still in its infancy in China and lacks corresponding storage and transportation conditions.

3.2.3 Carbon emissions during N fertilizer application

Scientific development of N fertilizer products is one of the most effective ways to improve farmland utilization efficiency and to increase production and environmental protection. Fertilizer type affects the final emission factor (Table 4). Urea and ABC are the products with the highest gas loss rate among the common N fertilizers, with carbon emissions of 8.2 and 7.0 t CO_2-eq t^{-1} N, respectively. However, AS can be as low at 3.9 t CO_2-eq t^{-1} N. Except for ABC, the emission factors of other fertilizers are only 47.9%–80.3% of urea. In terms of direct N_2O emissions, urea (1.4%), ABC (1.2%) and ACl (1.2%) were higher. Direct N_2O emissions from AS are only 0.6%. In terms of ammonia volatilization, both urea and ABC are above 12%. For ammonium N fertilizers, chemical changes in the soil lead to higher ammonia volatilization, such as AS (6.4%) and ACl (7.4%), due to the presence of NH_4^+.

In conclusion, rational adjustment of the N fertilizer structure is of great significance to reduce N loss during fertilizer application. As a multicomponent liquid N fertilizer, N loss during the application process of UAN is 30% lower than that of urea. For every ton of N supplied by AS instead of urea, GHG emissions can be reduced by 4.29 t, and the potential for energy conservation and emission reduction is significant.

Table 4 GHG emissions from different fertilizers applied to farmland

N fertilizer type	N_2O (%)	NH_3 volatilization (%)	Leaching and runoff (%)	Emission factors (t CO_2-eq t^{-1} N)
Standard fertilizers[1]				
Urea	1.45	12.9	24	8.24
Ammonium bicarbonate	1.2	12.1	24	7.03
Ammonium nitrate	1.07	2.1	24	5.95
Ammonia chloride	1.16	7.4	24	6.62
Ammonium sulfate	0.6	6.4	24	3.95
Compound and other products[2]				5.20
Newly emerging fertilizers[2]				
Nitrification inhibitors	0.49	10.2	13.3	3.26
Urease inhibitions	1.2	4.7	27.2	6.79
Controlled-release fertilizers	0.91	3.85	8.18	4.71
Liquid fertilizer[3]				
Urea ammonium nitrate solution	1.09	4.26	13.2	5.77

Note: [1]Data were summarized from various sources[20,21,28,30]. [2]Compound and other products represent compound fertilizers which were made from synthetic ammonia. [3]Estimate of the emission factors of newly emerging fertilizer based on the main marketed commodities in this category. Urease inhibitions was estimated by the emission factors of urea and ammonium N fertilizer, nitrification inhibitors and controlled-release fertilizers were estimated by the EF of urea. Use the mean instead of the test result.

3.2.4 Newly emerging fertilizers-inhibitors and stabilized fertilizers

China has less than 8% of the world's total cultivated land, but accounts for 21% of the world's total reactive N flux flowing into farmland. Also, the N input per unit area is much higher than the world average[34]. To meet the needs of improving N use efficiency in farmland systems, the fertilizer industry has been continuously working on product upgrades to reduce losses in N fertilizer application.

In China, stabilized fertilizer refers to a type of fertilizer in which UI or NI are added during production. NI targets ammonia oxidizing bacteria and inhibits nitrification by inactivating the ammonia monooxygenase system[35]. UI reduce N loss by temporarily blocking soil urease and preventing urea hydrolysis[36]. Integrating data from 203 field samples around the world shows that UI can reduce NH_3 and N_2O losses by 63.2% and 17.3%, respectively; NI can significantly reduce N_2O emissions by 53.9% and NO_3^- leaching by 44.6% but increases NH_3 emissions by 15.3% (Table 4). In addition, different crop systems, soil types and climatic conditions affect the degradation time and effect of inhibitors[37].

The IFA expects total global stable fertilizer production to reach 27 Mt by 2026, while the inhibitor market in China has not yet opened[38]. As shown in Fig. 3(a), in 2010, the sales volume of inhibitors in China was about 1.6 kt, the production capacity of stable fertilizer was 1.56 Mt, and the output was 300 kt; in 2021, the sales volume of inhibitors was about 9.1 kt, the production capacity of stable fertilizer was 3.8 Mt, and the output was 1.9 Mt. From 2010 to 2021, the average annual growth rate of inhibitor sales and stabilized fertilizer production capacity and production was 17%, 8% and 18%, respectively. At present, the production capacity of stable fertilizers with NI and UI in China is only 1% of the total N input. In the existing N fertilizer product structure, increasing the proportion of stable fertilizers is of great significance for reducing carbon emissions during N fertilizer application. The main limiting factors for its promotion are large variations in effect, high cost of addition, and low awareness of growers. With the accelerated pace of China's agricultural green development, stable fertilizers will become an important product type.

3.2.5 Newly emerging fertilizers-controlled-release fertilizer

CRF can prolong nutrient release time and match nutrient release with crop needs. The coating material is the core of the product, which determines the nutrient release rate. Depending on the different coating materials, CRF can be divided into inorganic coated fertilizers and organic coated fertilizers. Inorganic coating materials mainly include sulfur, sulfate and other non-metallic minerals (e.g., attapulgite and kaolin)[39]. The organic coating materials are mainly synthetic polymer

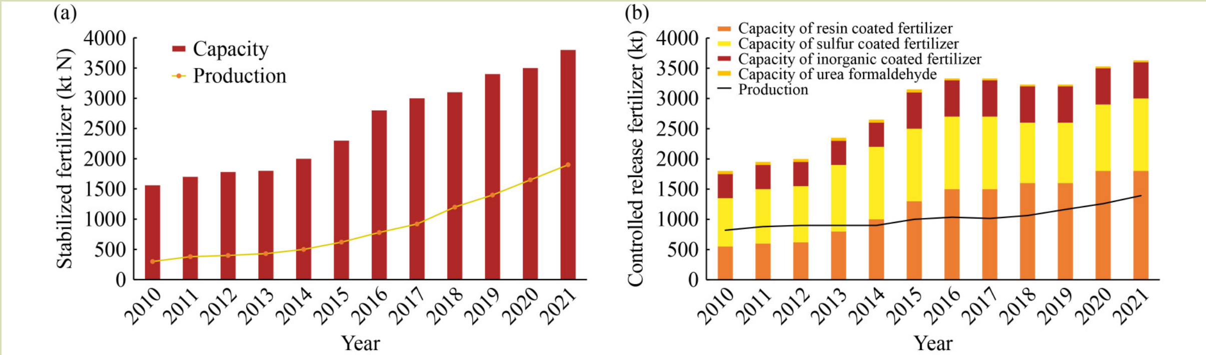


Fig. 3 Production capacity and output changes of newly emerging fertilizers in China from 2010 to 2021. (a) Production capacity and output changes of stabilized fertilizers. (b) Production capacity and output changes of controlled-release fertilizers. Data were sourced from the China National Chemical Information Centre.

materials, including thermoplastic polyolefins and thermosetting resins. Generally, the wear resistance of organic coated fertilizers is satisfactory, and the nutrient release cycle is more controllable than that of inorganic coated fertilizers. However, non-degradable coating materials may lead to environmental pollution[40]. In previous studies, the effect of CRF on a global scale was calculated, and the results showed that CRF can reduce NO_3^- leaching and NH_3 and N_2O losses by about 66%, 70% and 38%, respectively[21].

In 2000, the world's consumption of CRF was about 600 kt, and China's consumption was less than 5 kt. In recent years, as the Chinese government encourages the research and development of eco-efficient fertilizers, CRF has developed rapidly. As shown in Fig. 3(b), in 2010, China's production capacity of CRF reached 1.8 Mt, with an output of 0.82 Mt. In 2021, the production capacity reached 3.63 Mt, with an output of 1.39 Mt. From 2010 to 2021, the average annual growth rate of production capacity and output was 7% and 5% respectively. Main CRF products in China are resin-coated fertilizers, sulfur-coated fertilizers and inorganic coated fertilizers. In terms of types, resin-coated fertilizers have developed most rapidly. In 2021, the production capacity was 1.8 Mt, and the output was 0.48 Mt. The average annual growth rate of production capacity and output of resin-coated urea from 2010 to 2021 was 11% and 6%, respectively. For sulfur-coated fertilizers, the values are 6% and 4%, respectively. The fused calcium magnesium phosphate is a slow-release technology independently developed in China. The coating material adopts inorganic fertilizers such as calcium, magnesium and phosphate rock powder. In the past 10 years, the production capacity, which has remained between 400 and 600 kt, and output have been relatively stable.

4 FRAMEWORK FOR N FERTILIZER INDUSTRY REFORM

4.1 Carbon emission reduction potential of N fertilizer product structure optimization

NBSC statistics show that China's farmland N fertilizer input was 18 Tg N in 2020. Under the condition of maintaining the current N application level, a scenario assumption method was used to evaluate the carbon emission reduction effect of structural improvement of N fertilizer products in GHG emissions in the N fertilizer chain.

Ammonium sulfate to replace urea. The CO_2 produced per ton of AS produced and applied is 4.3 t CO_2-eq, which is only 35.4% of urea. Using the best technology, the production process can reduce carbon emissions by an additional 0.24 t CO_2-eq t^{-1} N. According to the target, 15% of urea will be replaced by 15% of AS, so that the proportion of AS will increase to 20%. The amount of CO_2 emitted during AS production is 1.3 and 14.5 $Tg \cdot yr^{-1}$ CO_2-eq during the application process. Compared to emissions before the adjustment, a reduction of 11.8 $Tg \cdot yr^{-1}$ CO_2-eq during the application process and a reduction of 13.1 $Tg \cdot yr^{-1}$ CO_2-eq during the production process was observed.

Ammonium nitrate to replace urea. The purpose of replacing urea with AN is to make the nutrient supply more balanced. The proportion of AN is increased to 20%, which will generate 57.8 $Tg \cdot yr^{-1}$ CO_2-eq. GHG emissions from the application process will be reduced by 6.3 $Tg \cdot yr^{-1}$ CO_2-eq. The production process does not show any carbon emission reduction, mainly because N_2O is generated, which increases the risk of carbon emission. Therefore, it is also important to pay attention to production technology innovation while increasing the proportion of AN. The industrial technological innovation of AN should start with the control of N_2O during the nitric acid emission process. The N_2O decomposition technology can reduce N_2O emissions by 70%–95%[32]. The emission factor for AN production in world advanced technology is 3.03 t CO_2-eq t^{-1} N[29].

Urea ammonium nitrate to replace urea. UAN contains three forms of N, namely ammonium N, nitrate N and amide N. It simplifies granulation, drying, packaging and other links, and energy consumption for production, storage and transportation is low. CO_2 emissions can be reduced by 7.3 Tg·yr^{-1} CO_2-eq in the production process and 6.8 Tg·yr^{-1} CO_2-eq in the application process. It is expected to reduce CO_2 emissions by 14.1 Tg·yr^{-1} CO_2-eq in total.

New emerging fertilizer to replace standard N fertilizers. The production process of new emerging fertilizer is no different from that of standard fertilizer, with associated emission reductions reflected in the application process[41]. Since different types of standard fertilizers can be upgraded to new emerging fertilizer, three scenarios were set when estimating emission reduction potential (Fig. 4). All three scenarios assumed the addition of NI to AS and ACl. In particular, the first scenario assumed standard urea was upgraded to UI-containing urea; the second scenario assumed that standard urea was upgraded to controlled-release urea; and the third scenario assumed that UI-containing urea and controlled-release urea were divided equally. On the basis of adjusting the structure of traditional fertilizer products, upgrading traditional fertilizers to new types of fertilizers can reduce emissions by 14.5–21.6 Tg·yr^{-1} CO_2-eq. The GHG emissions for UI, NI and CRF are 24.4, 17.9, and 17.3 Tg·yr^{-1} CO_2-eq, respectively, which are 5.8, 8.7 and 12.9 Tg·yr^{-1} CO_2-eq less than for standard urea fertilizer.

4.2 Past, present, and future emissions

From 2010 to 2020, the amount of N fertilizer used in agriculture decreased by 22.1%. The biggest change in the N fertilizer industry was increased control of blind fertilization and control of the total amount of N fertilizer. According to product structure estimation in 2010, the GHG emission by N fertilizer production and application in China was 141 and 172 Tg·yr^{-1} CO_2-eq, respectively. From 2010 to 2020, GHG emissions decreased by 84.4 Tg·yr^{-1} CO_2-eq, to which the production process contributed 46.3 Tg CO_2-eq. Over the past 10 years, reducing N application levels and optimizing synthetic ammonia technology have made outstanding contributions to the reduction of GHG emissions in the N fertilizer industry.

In the future, the N fertilizer industry will need to reformed in order to optimize the N fertilizer structure. By replacing urea with AS, AN and UAN, a total emission reduction of 32.4 Tg·yr^{-1} CO_2-eq can be achieved, of which the contribution rate of the production process is 23.1% and the contribution rate of the application process is 76.9%. The large gap between the existing production technology and advanced technology in terms of GHG emissions is the main reason for the low emissions in the production process. Advanced ammonia synthesis technology and urea production technology can reduce carbon emissions by 1.3 and 2.6 t CO_2-eq t^{-1} N, respectively. Through N_2O decomposition technology, carbon emission during AN production can be reduced to 3.0 t CO_2-eq t^{-1} N. In China, total emissions from N fertilizer production,

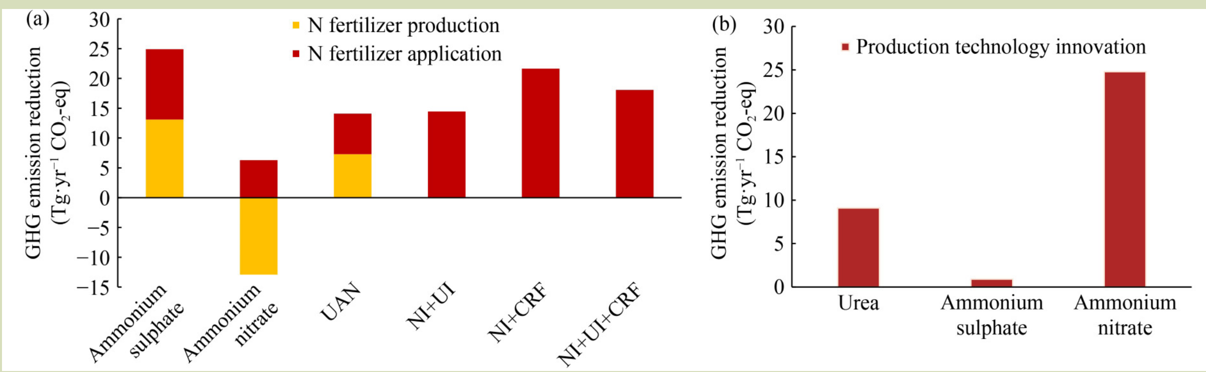


Fig. 4 The N fertilizer chain GHG emission reduction that can be realized by the improvement of the N fertilizer product structure. (a) GHG reduction capacity of production and application process. (b) GHG emission reduction capability through production technology innovation.

packaging, storage and distribution are about 5.2 t CO_2-eq t^{-1} N[13]. In developed countries, the numerical value can be reduced to 3.3 t CO_2-eq t^{-1} N[42]. When the production technology is further optimized, the GHG emission reduction during the production process of urea, AS and AN is 9.1, 0.9 and 24.8 Tg·yr^{-1} CO_2-eq, respectively. A total of 34.8 Tg·yr^{-1} CO_2-eq of GHG emission reduction can be achieved through technology upgrades.

In 2010, GHG emissions from the N fertilizer chain were 312.9 Tg CO_2-eq, which decreased to 228.5 Tg CO_2-eq in 2020, showing the positive results from controlled N application. The current N input has dropped to 18–20 Tg·yr^{-1} N in China, which has reached the balance point between nutrient supply and demand[13]. For food security, it is difficult to achieve carbon reduction by reducing N application. Therefore, an innovative approach needs to be considered. According to the results of this paper, it is estimated that technological innovation can be achieved under the new model of product structure, and CO_2 emissions can be reduced by 81.7–88.9 Tg·yr^{-1} CO_2-eq. As a result, the GHG emission of the N fertilizer chain will be 140–147 Tg·yr^{-1} CO_2-eq, which is 53.6% lower than in 2010 and 36.5% lower than in 2020, for targets of the dual-carbon strategy to be achieved.

5 CONCLUSIONS

In the coming decades, responding effectively to the dual-carbon strategy is a major issue for China from 2010 to 2020, a reduction of N fertilizer GHG emissions by 84.4 Tg·yr^{-1} CO_2-eq was achieved through the utilization of scientific N management technologies. In this paper, a proposed innovative reform model in China was suggested to move away from a high dependence on standard urea to a mix of new emerging, liquid and standard fertilizers, which can be achieved by utilization of advanced production technologies to reduce the energy consumption and GHG emission during the production process. If the key measures are combined, the carbon reduction potential is up to 81.7–88.9 Tg·yr^{-1} CO_2-eq in the future. The emission reduction of the N fertilizer synthesis process is 42.3 Tg·yr^{-1} CO_2-eq (industrial upgrading process emission reduction is 34.8 Tg·yr^{-1} CO_2-eq), and the emission reduction of the N fertilizer application process is 39.4–46.6 Tg·yr^{-1} CO_2-eq. The results presented herein should guide policy pertaining to fertilizer inputs, which has the potential to enable the targets of the dual-carbon strategy a reality.

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Compliance with ethics guidelines

Dongjia Li, Rui Liu, Li Chen, Yu Gao, Xuanyu Gu, Yu-hua Shi, Jiahuan Liu, and Weifeng Zhang declare that they have no conflicts of interest or financial conflicts to disclose. All applicable institutional and national guidelines for the care and use of animals were followed.

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