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Perspective

Ammonia Volatilization from Fertilizer Urea—A New Challenge for Agriculture and Industry in View of Growing Global Demand for Food and Energy Crops

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Abstract: The growing world population and the necessity to meet its nutritional needs despite the limited area of agricultural land pose a serious challenge for agriculture. Agriculture is responsible for 80–95% of total ammonia emissions to the atmosphere, but at the same time it has great potential to reduce them. Fertilisation with mineral nitrogen (in particular urea) is responsible for 19.0–20.3% of total ammonia emissions emitted from agriculture. Ammonia emissions have a negative impact on the environment and human health, therefore it is important to minimize the volatilization of ammonia and increase fertiliser efficiency. This is important due to the need to mitigate the negative impact of anthropopressure on the environment in terms of air pollution, negative effect on soils and waters. The application of urease inhibitors during fertilisation with nitrogen fertilisers is one method to reduce ammonia emissions from plant production. Another option to achieve this goal is to reverse the global trend toward maximizing the production of energy crops (intensive fertilisation inevitably increasing ammonia emissions to the environment) for the production of biofuels, which is growing rapidly, taking up arable land that could be used for food production. The aim of the review is to identify the impact of recently introduced technologies for reducing ammonia emissions from urea on agricultural productivity, environment, and crops. It is of importance to reconsider optimization of crop production in arable land, possible owing to the progress in the production, modification, and application of mineral fertilisers and changes in crop structure. A broad debate is necessary with policymakers and stakeholders to define new targets allowing introduction of technologies for conversion of energy crops into energy with a minimal impact on food production and environmental issue.

Keywords: ammonia emission; urease inhibitors; biofuels; food production; bioenergy crops; N fertilisers

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1. Introduction

Urea is one of the most popular nitrogen fertilisers worldwide. It has high content of nitrogen (46%) with very high bioavailability. However, it is characterized by a high degree of losses in contact with soil, in comparison with other fertilisers. NH_3 emission per kilogram of urea converted to nitrogen ranges from 159 to 168 g, depending on soil pH and climatic conditions [1]. This undesired ammonia emission is an economic problem resulting in reduction of crop yields due to nitrogen loss and has a negative long-term impact of agriculture expansion into the environment [2]. At the same time, the growing world population, and the need to meet global demand for food, make for a continuous increase in the production of fertilisers, including urea [3,4].

The necessity to reduce ammonia emission and the associated nitrogen losses from fertilisers introduced into soil, especially urea-based formulations, has resulted in the implementation of the National Emission Ceilings (NEC) Regulation (directive of the European parliament and of the council (EU) 2016/2284 of 14 December 2016) [5–7].

The reduction of ammonia emissions accompanying the application of urea fertilisers has recently been achieved by use of nitrogen conversion inhibitors (urease inhibitors) in the soil [8–10]. It should be noted that the global urea production in 2019 reached approximately 209 million tons and is systematically growing [3], with about 10% produced in Europe [11]. Worldwide industrial urea production facilities (except for European installations which already meet the new requirements of European law [5–7]) are not adapted to the coating of urea granules with urease inhibitors. These installations require costly, technical changes to achieve this goal.

Moreover, urease inhibitors should have appropriate physico-chemical properties to be applicable at specific conditions both in the manufacture and application. Urease inhibitor-containing commercial mixtures currently released on the EU market are adapted to various forms of application, e.g., simultaneous application together with fertiliser in the field or coating of granules by the producer or the final client [12,13]. The use of separate fertiliser and inhibitor by the client might not ensure precise dosage. The current requirements of this technique assume a 70% average reduction of ammonia emissions for solid urea [13].

The emissions of ammonia or other gases from agricultural production may be additionally reduced by a change in the structure of plant production, which is one of the dilemmas faced by agriculture, e.g., raw materials for production of biofuels [14]. The dynamically growing production of energy crops (as raw materials for biofuels) is characterized by high fertiliser demands, resulting in associated ammonia emissions, and high pesticide applications [15,16]. The production of biofuels has been touted as a solution for mitigating the negative impact of fossil fuels on the environment. The expansion of biofuels leads to growth in the production of agricultural raw materials for biofuels and can indirectly lead to changes in land use structure [16].

Agriculture, being strongly linked to the conditions of industry that provides resources as well as processing capacities for agricultural products, must secure food production in the long term, despite changes in the environment affecting agricultural productivity in various regions of the world. [16] This should be attained with care for preserving the natural environment and ensuring appropriate amounts of produce for food and fodder. Thus, the aim of the review is to point out the impact of recently introduced policies and technologies aimed at limiting ammonia emission from urea fertiliser on agriculture productivity, including the use for the purposes of food and energy crops.

2. Challenges to the Market of Agricultural Products

Agriculture and other areas of human activity associated with food production will have to adapt to climate change and, at the same time, meet the future nutritional needs of the growing population. It is predicted that the world population will reach approximately 9.1 billion by 2050 [17,18], with substantial population growth to be recorded in developing countries. Approximately 70% of the global population are expected to live in cities (vs. 49% today) and urbanization will proceed at an accelerated pace. To feed the increasing urban population, food production (excluding food raw materials that are currently used for production of biofuels) must increase considerably. The annual production of cereals and meat will have to increase to approximately 3 billion tons and 470 million tons, respectively [17,18]. Improvement of the standard of living will be accompanied by an approx. 30% increase in the calorific value of consumed meals, compared to values recorded in 2015 [18]. Additionally, considering the expected expansion of agriculture by 2050, it will be necessary to convert 593 million ha of land into arable fields, with respect to the area of agricultural land in 2010 [17].

Climate change is one of the threats to the safety of long-term food supplies. An unresolved issue is the necessity to reduce the 11-gigaton greenhouse gas emissions produced in agriculture from the amounts predicted for 2050 to the level required to curb global warming below 2 °C (an indispensable level to prevent major negative climate change effects). Progressive climate change will force cultivation of heat-tolerant plants and induce other limitations to agriculture [17,18]. Increasing air temperature and its impact on soil wetness were shown to be main environmental drivers of ammonia emission [19].

3. Emission of Ammonia from Agriculture

Agriculture is the main source of ammonia emissions to the atmosphere. It is responsible for 80–95% of the total emissions of this gas, where mineral fertilisers account for 20.3%, animal husbandry for 48.6%, and biomass combustion for 13.3% of emissions, while fossil fuel combustion and industry account for 0.7% of emissions [20]. Ammonia emission is also strongly dependent on soil use, emissions from bare unfertilised soils are estimated at up to 3 kg $N\text{-}NH_3 \cdot ha^{-1} \cdot year^{-1}$ as compared to about 1.2 kg $N\text{-}NH_3 \cdot ha^{-1} \cdot year^{-1}$ from forests [20]. It is expected that emission from uncultivated lands may increase due to increasing atmospheric N deposition [21].

Ammonia volatilization during mineral nitrogen fertilisation [9] accounts for 19.0–20.3% [19,20] of the percent of total ammonia emissions emitted from agricultural activities. Ammonia emission is an economic problem, resulting in reduction of crop yields due to nitrogen loss, and has a negative impact on the environment [8]. Gaseous ammonia emitted to the atmosphere enters a cycle of chemical transformations, which may ultimately cause negative effects on soil and water environments [2,9,18,22] and degradation of susceptible ecosystems [2,23], leading to acidification of water and soils and eutrophication of natural terrestrial and aquatic ecosystems. As a consequence, these emissions exert adverse effects on the biodiversity of the entire ecosystem, including soil biodiversity, which is of fundamental importance for the evolution and durability of life-supporting systems in the biosphere [2,22]. NH_3 is a secondary source of N_2O; thus, it is indirectly responsible for global warming and ozone depletion in the stratosphere, N_2O is a GHG of high global warming potential [9,24–27]. Moreover, after fertiliser application in soil urea hydrolysis starts, which results in emission of not only ammonia but also CO_2, especially when high doses of nitrogen fertilisers are used [8,12,26].

4. Fertiliser Consumption and Demand

The growing demand for agricultural products, together with the growing world population size, has been stimulating the global production of fertilisers for years.

The total fertiliser consumption ($N + P_2O_5 + K_2O$) in 2009 equal to 161 mln tons increased to 184.7 million tons in 2014 and was predicted to reach 186.6 million tons in 2015 [3]. Forecasts of the world demand for nitrogen, phosphorus, and potassium ($N+P_2O_5+K_2O$) used as fertilisers assume a demand of 200.9 million tons in 2022 [4]. The data on fertiliser consumption in 2009–2015 [3] and predictions for 2022 [4] show a continuous increase in the demand for these products, whereas the International Fertilisers Association (IFA) outlook [11] for fertilisers predicts the use of 197 million tons in 2024. The latest forecast includes disruptions in 2020/21 due to the negative impact of COVID-19 on the global fertiliser supply chain, the global recession, the economic downturn and uncertainty about the pace of economic recovery, record-breaking unemployment figures, and size of global grain stocks [11].

5. Production of Biofuels vs. Ammonia Emissions

One of the important areas of agriculture is the cultivation of bioenergy crops for production of biofuels, i.e., biodiesel, HVO (hydrotreated vegetable oil), and ethanol. Biofuels are serious competitors for food plants and an indirect source of ammonia emission associated with the high fertiliser demands [14]; they occupy arable land that could be used for food production. Due to the high use of fertilisers and pesticides, production of energy crops adversely affects the environment and biodiversity [26,28,29]. The production of commonly used biofuels, such as rapeseed biodiesel and maize bioethanol, depending on the nitrogen doses applied, according to updated calculations, can contribute to global warming as much as energy production from fossil fuels [30]. Crops with less N demand have a more favourable effect on the climate change.

The global production of biofuels in 2018 reached 154–167.9 billion litres [15,31] and increased by approximately 10 billion litres compared to 2017 [31], whereas only 49.9 billion litres were produced in 2005. Biofuel production is predicted to increase by 25% between 2019 and 2024. The largest biofuel producers are China, Brazil, the USA, and the ASEAN countries [26,31]. In 2018, 16.1% of maize grain, 1.7% of wheat grain, 3.3% of other feed grains, and 13.5% of vegetable oil were processed into biofuels globally [15].

A strong shift in maize cultivation from the food sector to the biofuel sector can be seen from data shown in Figure 1. Maize production as raw materials for biofuels increased rapidly from 51.3 million tons of grain in 2005 up to 181.7 tons in 2018 when it occupied a cultivation area of 30.29 million ha [15]. A typical nitrogen dose for maize ranges between 150 kg N ha^{-1} [10,32,33] and 240 kg N ha^{-1} [32,34], which is equal to 5.2 million tons of N to 7.3 million tons of N in urea per year, (assuming maize production 181.7 million tons of grain as raw materials for biofuels). The nitrogen emission accompanying maize cultivation for biofuel production can be quite significant depending on the region, climate, and crop management. Maize is one of the three main primary crops (along with wheat and rice), which collectively account for 72% of NH_3 emissions related to the use of mineral fertilisers in global agriculture [35]. At the same time, its requirements for nitrogen and pesticides are higher than in other crops [36]. Mineral fertilisers were found to be responsible for about 73% of all energy inputs in the production of maize [37]. However, high nitrogen rates have a negative impact on bioenergy crops. It was shown that the increasing N doses increased plant overall carbon content and specific biochemical compounds, e.g., lignin, which is an unfavourable component during ethanol production [38].

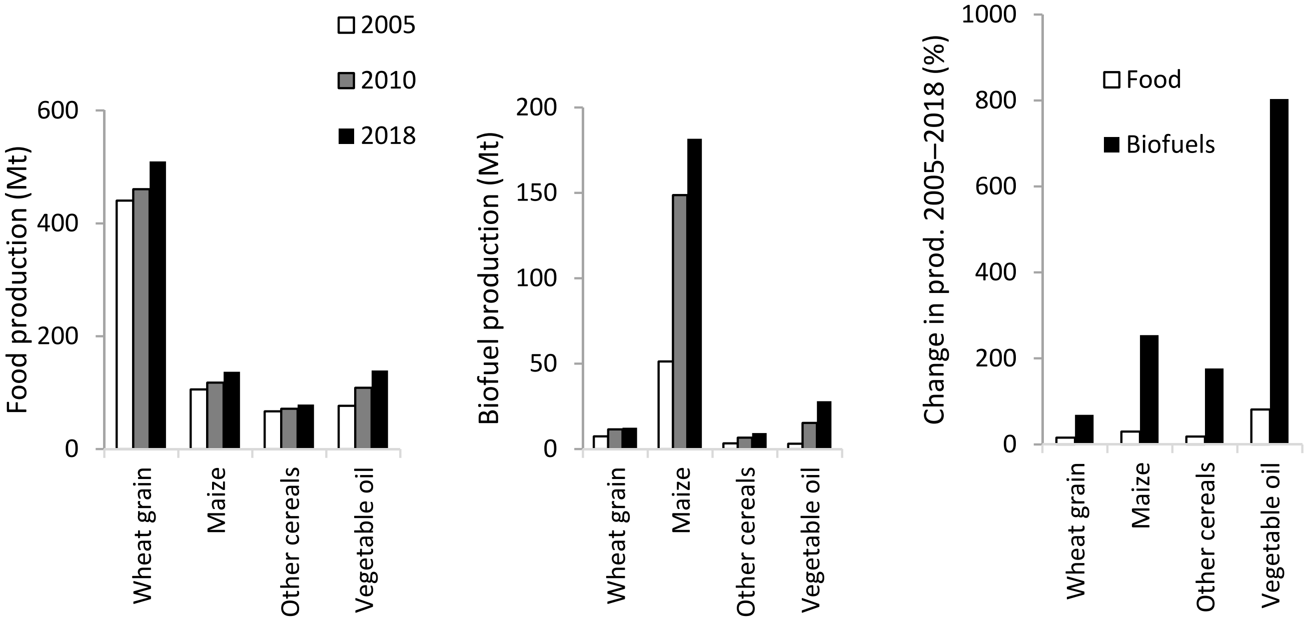

Figure 1. Production of agricultural raw materials for the food and biofuel sectors [15].

The development of biofuel markets is strongly related to the macroeconomic environment and, in particular, to the level of crude oil prices. Since the beginning of the 21st century, the development of global biofuel markets has been driven by policies supporting increased biofuel production and use. The government support for the biofuel industry ranges from tax policies to financial support for investment projects. On the other hand, there are trends where the cultivation of energy crops is beginning to be perceived as controversial [30] due to the uncertainty about net GHG savings and the potential competition with land use for biodiversity and food production.

The possibility of reduction of net greenhouse gas emissions and ammonia emissions in the production and use of biofuels depends on the type of crop plants, the location with its specific climatic conditions, soil type and the level of nitrogen fertilisation. Some studies [26,30] show that the GHG balance for the production of biofuels is questionable in comparison with that of fossil fuels, and real N_2O emissions may be 2–3 times higher than those estimated from field measurements. Measurements of the net balance of greenhouse gases are encumbered with substantial uncertainty and largely depend on the plant species concerned, nitrogen fertiliser doses, soil conditions, climate, and agricultural management practice [26]. The potential reduction of ammonia emissions in cultivation of plants intended for biofuel production will improve its net GHG balance. Currently, the production of biofuels (especially first-generation liquid biofuels, bioethanol, and biodiesel) is responsible for emission of ammonia and greenhouse gases. To alleviate this problem, it is necessary to implement new technologies for converting agricultural biomass into energy, in particular, the biomass obtained without competing against food production. The use of new technologies to produce biofuels will reduce the consumption of nitrogen fertilisers and thus the emission of ammonia to the atmosphere. [15,16]. Analysis of land suitability for energy crops [39] shows that about 40% of land area suitable for bioenergy crops is area potentially suitable also for food production.

6. Evaluation of Ammonia Emissions from Mineral Fertilisers with Focus on Urea

Reported ammonia emission after application of nitrogen fertilisers differs in wide ranges depending on soil properties (moisture, density, pH), climatic conditions, etc. The values of ammonia emission factors for temperate climate range from 159 to 168 g of nitrogen per 1 kg of applied urea, depending on soil pH and climatic conditions [1]. Emission of ammonia during and after the fertilisation process results in a loss of the fertiliser. It reduces the effectiveness of fertilisation and at the same time increases the costs of plant production. The ammonia emission factors determined [1] for a specific fertiliser usually reach the lowest values at natural pH and low temperatures, whereas their highest values are recorded at high pH and high temperatures. In the case of ammonium nitrate, depending on the soil pH in temperate climate, the NH_3 emission per kilogram of applied ammonium nitrate converted to nitrogen is much lower ranging 16–33 g [1,40,41]. Guidance from the UNECE Task Force on Reactive Nitrogen shows that NH3 emissions from urea-based fertilisers (typically 5–40% N loss as NH3) are much greater than those based on ammonium nitrate (typically 0.5–5% N loss as NH30 [13]. Noteworthy, nitrogen accounts for 32% in ammonium nitrate and 46% in urea; therefore, nitrate doses differ from urea doses for the same crops.

Application of urea into the soil may lead to high nitrogen gas losses amounting on average c.a. 18% of applied N [42]. However, very high N loses were often reported: 50% [43], 64% [42], 82.4% [44]. An increase in air temperature from approx. 2 to 30 °C was responsible for an increase in N losses from about 0 to 60% [45].

In field experiments on maize, NH_3 emissions were shown to increase with increase in fertilisation rates (150 and 270–300 kg N ha^{-1}); the emissions were responsible for 4–38% and 18–61% of applied N for lower and higher urea doses depending on soil type [9,10,46].

Due to the high heterogeneity of soil properties, ammonia emissions from the soil immediately after fertilisation are characterized by considerable spatial and temporal variability. This has been confirmed by numerous reports showing a wide range of nitrogen losses through NH_3 emissions at a level of 2–43% for arable land and 10–58% for grassland [12].

Although urea hydrolysis catalysed by the urease enzyme depends on temperature, emission from urea is affected by temperature and the effect is diminished by the enzymatic activity of the soil [40,47], which is highly variable.

7. Urea Production Capacity and Process Limitations

The global urea production capacity is approximately 209 million tons (2019) [11], (including 10% produced in Europe, with regulations already in place to limit ammonia emissions [5–7]). The currently constructed installations worldwide will have increased the global urea production capacity to 225 Mt by the end of 2021, which implies an increase by 17 Mt (+8%) to reach 230 Mt in 2024. In 2019–2024, the production capacity is expected to increase in South Asia (mainly in India and Bangladesh), Africa (Nigeria and Egypt), Eastern Europe, and Central Asia (Russia and Uzbekistan), i.e., regions with no regulations on ammonia emission reduction. Urea demand is expected to rise in almost every region, but to a lesser extent in East Asia. South Asia will account for almost 25% of the potential global growth in the demand. Urea demand is also expected to increase significantly in Latin America and Africa. Forecasts suggest an increase in the proportion of urea to 2/3 of the production of all nitrogen fertilisers in medium-term prospects [11].

The operating and the newly constructed industrial facilities for urea production are characterized by high production capacities. Currently, installations based on proven technical solutions with a capacity of up to 3 million tons of urea per year are being built in the world. The construction of five such facilities is underway with varying degrees of advancement [48].

Commercial synthesis of urea involves reaction of ammonia with carbon dioxide at high pressure to form ammonium carbamate, which is then dehydrated by thermal treatment yielding urea and water [49]:

$$2NH_3+CO_2 \underset{(a)}{\Leftrightarrow} \underbrace{NH_2COONH_4}_{\text{Ammonium carbamate}} \underset{(b)}{\Leftrightarrow} CO(NH_2)_2+H_2O \tag{1}$$

Both reactions (1) take place in the liquid phase in the same reactor and are in equilibrium. Their performance depends on various process parameters. The most typical production conditions are presented in Table 1, which shows the high requirements of urea production. Reaction (a) is fast and exothermic, whereas reaction (b) is slower and endothermic. Usually, 50–80% conversion (based on CO_2) is achieved. It increases with the rise in temperature and the NH_3/CO_2 ratio and decreases with the increasing H_2O/CO_2 ratio [49].

Table 1. Typical process parameters of urea production [49].

Process Parameter	Process Values
Pressure (bar)	140–250
Temperature (°C)	180–210
NH_3/CO_2 ratio (molar)	2.8:1–4:1
Retention time (minutes)	20–30

The melting point of urea is 130 °C, above which the compound is degraded. This property allows solidification of urea on an industrial scale at a slightly lower temperature than the melting point. The temperature determines the possibility of addition of e.g., a urease inhibitor, in accordance with the new EU regulations. It is recommended [13] to reduce ammonia emissions from urea-based fertilisers by using urease inhibitors, e.g., NBPT, mainly in liquid form for coating urea fertiliser granules [8]. Other recommended techniques to reduce ammonia from urea-based fertilisers include slow-release coatings, injection into soil, rapid incorporation into soil and irrigation immediately after application [13].

8. Urease Inhibitors—Mechanism of Action

Urea hydrolysis in soil with the involvement of urease results in intensive release of the ammonium form of nitrogen NH_4 in the reaction:

$$(NH_2)_2CO\ (\text{urea}) + 2H_2O + H^+(\text{urease}) \leftrightarrow 2NH_4^+ + HCO_3^- \tag{2}$$

which further proceeds as follows:

$$H_4^+ = NH_3 + H^+ \ pKa = 9.25 \quad (3)$$

The equilibrium of this reaction depends on pH and temperature and shifts significantly towards the formation of NH_3 at a higher pH value and a temperature rise. For example, the driving force (relative concentration of NH_3 in the soil solution) of ammonia emission was assumed as 1 at pH 7 and the temperature of 25 °C but at pH 8 and 20 °C was assumed as 5. This explains the NH_3 loss (7%) at soil pH not exceeding 7, even if the temperature rises to 45 °C. In turn, the driving force at constant soil pH increases with temperature. It was reported that the driving force of ammonia emission at pH 8 and a temperature of 30 °C was three times lower than at 10 °C [50].

$$CO_3^- + H^+ \leftrightarrow CO_2 + H_2O \quad (4)$$

Uea nitrogen losses are also largely dependent on soil properties, e.g., the content of clay and sand fractions. The negatively charged surface of clay particles contributes to adsorption of NH_4^+. In turn, higher soil porosity associated with high sand content facilitates gas exchange between deeper soil and the atmosphere [51].

Various urease inhibitors are commercially available on the EU market. Table A1 (Appendix A) presents the chemical compositions of urease inhibitors for application through urea spraying treatments and material safety data sheets provided by the manufacturers. At present, the knowledge of the potential impact of chemicals used with N fertilisers to decrease urease activity on food safety is limited. The data on the composition of urea inhibitors may contribute to consumers' awareness of food safety; nevertheless, long-term effects should be evaluated to ensure positive reception of these new modified fertilisers [52].

N-butyl thiophosphoric triamide (NBPT) is the most common active agent in commercial urease inhibitors used worldwide. A mixture of two compounds, i.e., NBPT (N-butylthiophosphoric triamide) and NPPT (N-propylphosphorothioic triamide), is used as well [53]. Currently, it is recommended that these commercially available urease inhibitors should be applied with urea in two forms: in the coatings of urea granules or liquid urease inhibitor solutions applied to the soil after urea fertilisation, which is associated with their physicochemical properties (boiling point, flash point).

Analysis of many experiments shows that, compared to pure urea, NBPT-treated urea reduces NH3 losses by approximately 53%. The average yield increase upon NBPT application is 6.0% depending on the crop species and cultivation conditions. It may range from 0.8 to 10.2% [8]. However, there are studies showing much higher efficiency of urease inhibitors. It was shown [43] that depending on soil type NBPT as a urease inhibitor contributed to reduction of the total NH_3 loss by up to 85% in clay soil and up to 81% in sandy loam soil. Better results were achieved at lower soil temperature and moisture in both cases. In maize cultivation at elevated temperatures in tropical climate conditions (average temperature 26.7 °C), NBPT reduced urease activity for 9 days, resulting in 42% reduction of total NH_3 emissions through slower release of NH_4^+ into the soil solution in the urea hydrolysis process [47].

The rate of urea hydrolysis in the presence of NBPT also depends on soil pH. The hydrolysis process is inhibited by 17.0 and 86.2% at 20 °C and by 53.3 and 92.1% at 0.5 °C in acidic and alkaline soils, respectively. Investigations have confirmed higher stability and activity of NBPT in alkaline soils, as shown by field observations [54,55]. The effect of the content of soil organic matter and organic residues present on the soil surface on the NBPT yield is not clear and much less important than soil pH and clay content. As demonstrated on different types of soils [51], the efficiency of NBPT declines significantly (two or three times) with decrease in soil pH.

Another commercial inhibitor, N-propylphosphorothioic triamide (NPPT), applied with urea on sandy loam soil was reported to inhibit NH_3 volatilization by over 50% within the first 11 consecutive days after fertilisation [53]. The application of a mixture of 0.05% NPPT and 0.05% NBPT as a urease inhibitor reduced ammonia emissions by 23.8% and 28.8%, compared with single applications of NBPT or NPPT, respectively [56].

The commercially available urease inhibitor mixture called Limus® (25% NPPT + 75% NBPT) was used at a dose of 0.12% (*w/w* in relation to urea) to fertilise winter wheat or maize in summer. The cumulative NH_3 losses after two weeks in the case of pure urea amounted to 11–25% of N, while only 0–6% losses were recorded when urea was supplemented with Limus®. Noteworthy, compared to urea alone, the addition of Limus® reduced NH_3 losses substantially by 74–100%, depending on the weather conditions prevailing after fertilisation (precipitation, temperature, wind speed, etc.) [57]. Studies [10] on the effect of the Limus® urease inhibitor showed that the total NH_3 loss within two weeks after application of urea without Limus® ranged from 9 to 108 kg N ha^{-1}, whereas the addition of Limus® significantly reduced the NH_3 loss (on average by 84%). Urea with Limus® did not significantly increase the yield of maize in comparison with the urea alone. The application of urea with Limus® resulted in 55–60% reduction in the dose of N, compared to farmers' practice, and/or further 20% N savings compared to application of an optimized N-urea dose (150 kg N ha^{-1}).

A study [58] on the effects of different doses of NBPT-coated vs. uncoated urea on maize cultivation showed that a lower dose of NBPT-coated urea (96 kg N ha^{-1}) was the most suitable amount for surface application to maize in tropical climates in comparison with the normal dose of 120 kg N ha^{-1} of urea (farmers' practice). The lower dose of NBPT-coated urea successfully delayed urea hydrolysis and concurrently enhanced nitrogen bioavailability to plants.

A field experiment [59] on urea with various urease inhibitors showed that the efficiency of N utilization in grain was increased by incorporation of urease inhibitors in the N fertiliser. Additionally, the time peak of soil nitrate-N was delayed by 15 days, compared to conventional fertilisation. These effects were accompanied by reduced abundance of N-cycling soil microbes. Temporal reduction in the level of bacterial ammonia monooxygenase was noted after application of DCD in an experiment on wheat grown on a sandy soil [40]. An incubation experiment on urease inhibitors showed that the action of NBPT reduced N losses through inhibition of the growth of ammonia-oxidizing bacteria and complete ammonia oxidation [46].

Direct analysis of physiological processes associated with N uptake by maize and *Arabidopsis* roots showed that NBPT limited plant ability to use urea as a nitrogen source [60]. Both influx and assimilation of urea were diminished by NBPT; even short-term exposure to NBPT resulted in alterations in plant metabolism ascribed to imbalance between C and N in plant cells [61]. The relatively short lifetime of NBPT in acid soils should be considered while predicting reduction of ammonia volatilization and a potential impact on crop metabolism [52,54]. According to the European Chemical Agency, the half-life time of NBPT varies strongly depending on environmental conditions: it is shorter in soil but may persist for a longer time in freshwater or freshwater sediments [54].

The studies [57–59] mentioned above confirm that the use of urease inhibitors in cultivation of maize for biofuel production offers a possibility to lower ammonia emissions by reducing nitrogen doses, thus improving the GHG production balance over the entire chain from fertiliser production to crop harvest.

The newly introduced requirements applicable to urea with urease inhibitors aim to reduce ammonia emission from soil urea by 70% and by 40% emission from liquid ammonia UAN [13]. The highly variable data from various experiments presented above indicate that the process of selecting inhibitors is not conclusive in relation to recommendations, depends on many variables such as climate, soil pH, soil properties, etc., and requires further research assessment. Regulations concerning ammonia emission from fertilisers (or practical guidance for use of urease inhibitors) should include N rates, or fertilisation intensity. The proportion of N losses due to ammonia emission is decreasing with decreasing N rates [62–64]. Moreover, decreased efficiency of urease inhibitors in acid soils [8,65] and cultivation of acid soil tolerant crops [66] is a potential challenge.

9. Analysis of other Available Solutions

Currently, given the small number of approved and available urease inhibitors and their complex interactions with fertilisers, soil, and climate, research on the selection of an effective urease inhibitor and its impact on the environment will obviously be continued. A review of the literature shows a wide spectrum of substances with properties of urease inhibitors (reducing nitrogen losses), e.g., phosphoramidates, hydroquinone, quinones, (di)substituted thioureas, benzothiazoles, coumarin and phenolic aldehyde derivatives, and vanadium hydrazine complexes, together with boron, copper, sulphur, zinc, ammonium thiosulfate, silver nanoparticles, oxidized charcoal, and others [8,53,67,68].

One of the potential urease inhibitors is ammonium thiosulfate (ATS, $(NH_4)_2S_2O_3)$). The first results on the application of ATS as a urease inhibitor were shown in 1990 [69,70]. ATS contains nitrogen and sulphur, compared to single-component fertilisers. Given its physicochemical properties (decomposition temperature 150 °C [71], which is substantially higher than the melting point of urea), it is technologically possible to produce stable granules of a mixed urea-ATS fertiliser, which can potentially have more favourable properties than ATS added separately to soils.

The doses of ATS could be beneficial especially for plants of very high to medium S requirements, like rape, cabbage, mustard, radish, turnip, onion, legumes, sugar beet, maize, and cotton [72].

Investigations of the application of ATS as a nitrogen-loss limiting substance have unfortunately been limited after the commercialization of the highly effective NBPT- and NPPT 2NPT-containing urease inhibitors. A granular fertiliser composed of a mixture of urea and ATS seems to have potential to reduce N losses considerably, especially in cultivation of plants with a high sulphur demand (including plants produced for the needs of biofuel production, i.e., rape, maize, sugar beet) on sandy soils [73]. The effectiveness of such a product may be higher than the separate application of urea and ATS.

The advantages of ATS as a urease inhibitor include its low cost, widespread availability, and compatibility with liquid fertiliser materials. The levels of inhibition of urea hydrolysis reported for ATS ranging from 10 to 50% [70] are significantly lower than the levels reported for NBPT. Four variants of experiments were conducted [74] with the use of soil treated with small fertiliser drops (0.05 mL), soil with large drops (0.5 mL), soil with 50% coverage of wheat straw and small drops, and soil with 50% coverage of wheat straw and large drops at the N dose of 100 kg N ha^{-1}. Ammonia loss was estimated at approximately 25% of urea in an unmodified urea ammonium nitrate solution (UAN). The effectiveness of ATS was about two times lower than that of the NBPT-containing product [74].

A study [75] carried out in the use of ATS showed that the average inhibition of urea hydrolysis was increasing with increase in temperature (29% at 20 °C and 37% at 30 °C). The results of the same research indicated that ATS efficiency was shown to depend on soil moisture, reducing urea hydrolysis by 28% in soil with optimal humidity (0.03 MPa) and 38% in drier soil (−0.1 MPa). Thiosulfate inhibited urea hydrolysis in clay- and organic C-poor soils most effectively [75]. However, results of field experiments performed on clay and fine-grained clay soils showed low urease inhibition efficiency of ATS mixed with UAN on straw and grain yield of spring wheat [76].

It was observed that the use of 25 ppm or 100 ppm of S-ATS in sandy loam soil (pH 7.8) reduced ammonium production and urease activity by 37% and 68%, respectively. The inhibition of urease activity in sandy soil (pH 8.3), where 70% was achieved at a lower S-ATS index and 88% at its higher value, was even more evident [77].

Comparison of the effect of different doses of ATS and NBPT on urea hydrolysis at 20 °C showed a similar level of urea hydrolysis was inhibited by NBPT applied at a dose of 1 and 10 μg g^{-1} of soil by 62% and by 33% and 63% at the ATS dose of 2500 and

5000 μg g^{-1} of soil, respectively, after three days at soil pH 6.1. After 10 days, the levels of urea hydrolysis inhibition were similar in the case of 5000 μg g^{-1} of ATS and 1 μg g^{-1} of NBPT. These results were obtained for soil with a pH value of 6.1. The ATS results were less favourable in the case of soils with a higher pH value [78]. The soil microbial biomass pool was not affected using ammonium thiosulfate (ATS), which decreases urease activity in some soils [77].

Additionally, it has been found that the soil fumigation agent 1,3-dichloropropene (1,3-D), which is emitted to the atmosphere and thus raises environmental concerns due to its toxicity and carcinogenicity, can be converted into less toxic non-volatile ions by thiosulfate fertilisers [79], an additional advantageous effect of using ATS.

The addition of ATS to urea as an inhibitor is unlikely to be as universal as NBPT and other modern and similarly highly effective inhibitors. Nevertheless, it may potentially be an effective product in certain (light) soils and may help to reduce N losses.

10. Summary

The global demand for food is growing rapidly as the world's population grows and diets change. As a result, intensified agricultural production and use of nitrogen fertilisers are observed.

Increasing agricultural production in the lowlands has serious long-term consequences for the environment. Preserving global biodiversity and minimizing the impact of ammonia and greenhouse gas emissions from agricultural production may depend on our future decisions. The EU set out in 2019 a course of action known as the Green Deal [80], which focuses on:

- more efficient use of resources through the transition to a clean and circular economy
- preventing loss of biodiversity and reducing the level of pollution

We recommend further research on dedicated solutions for the application of various types of urease inhibitors. We underline the importance of finding non-exclusive, multi-directional opportunities to reduce ammonia emissions worldwide, solutions that are cost effective, affordable for developing countries, suitable and efficient for a variety of climatic conditions and soil types.

Above all, agriculture should produce an adequate amount of raw material for food and fodder, and the rest of the agricultural land can be used for other purposes, such as the cultivation of energy crops. Currently, the production of biofuels (especially the first-generation liquid biofuels: bioethanol and biodiesel) is responsible for the conflict between food production and energy production and generates ammonia and greenhouse gas emissions. To alleviate this problem, it is necessary to implement new technologies of converting agricultural biomass into energy into production, in particular biomass obtained at the expense of food production. The use of new technologies to produce biofuels will reduce the consumption of nitrogen fertilisers and ammonia emissions to the atmosphere.

Mineral fertilisers are essential for increasing the efficiency of arable land use and ensuring global food safety. However, the management of fertilisation of crops in different climatic zones and soils with different properties, with nitrogen fertilisers containing a urease inhibitor, should be re-optimized. Such re-optimization should be directed at obtaining higher yields and reducing the impact on the environment. An analysis of the costs of fertilisation with a urease inhibitor would allow to evaluate the economic efficiency against the fertilisation without the urease inhibitors. This creates an opportunity to save natural lands, protect forests and meadows against their conversion into arable land, and conserve biodiversity.

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Appendix A

Table A1. Chemical composition and properties of urease inhibitors available on the market (composition and properties of formulations specified by manufacturers' MSDSs).

Name of Protease Inhibitor/Reference Boiling Point/ Flash Point	Composition	Proportion (%)	Classification of the Substance acc. to Regulation (WE) no. 1272/2008 (CLP)
NBPT 25% Yellow for Nexur [81] BP *- 189 °C (DMSO) FP **—87 (DMSO)	N-butyl thiophosphoric triamide (NBPT)	24–26	H318 Causes serious eye damage H361f Suspected of damaging fertility
	Dimethyl sulfonide	70–80	The substance is not classified as hazardous
	Tartrazine	<0.5	The substance is not classified as hazardous
LIMUS YELLOW [82] BP *—177 °C FP **—86 °C	Post-reaction mixture of compounds: N-butylthiophosphoric triamide (NBPT) and N-propylphosphorothioic triamide (NPPT)	25	H319 Causes serious eye irritation H302 Harmful if swallowed H317 May cause an allergic skin reaction H361f Suspected of damaging fertility H412 Harmful to aquatic life with long-lasting effects
	Polyethyleneimine	<25	H318 Causes serious eye damage H302 Harmful if swallowed H317 May cause an allergic skin reaction H412 Harmful to aquatic life with long-lasting effects
	Benzyl alcohol	<45	H302 Harmful if swallowed H332 Harmful if inhaled H319 Causes serious eye irritation H312 Harmful in contact with skin
AGROTAIN® DRI-MAXX [83]	N-n-butyl thiophosphoric triamide (NBPT)	40–70	H318 Causes serious eye damage H361 Suspected of damaging fertility or the unborn child H361f Suspected of damaging fertility
	Component registered by the manufacturer	30–60	Component declared as safe by the manufacturer
	Pigment registered by the manufacturer	<3	Pigment declared as safe by the manufacturer
StabilureN [84]	N-n-butyl thiophosphoric triamide (NBPT)	20–30	H318 Causes serious eye damage H361 Suspected of damaging fertility or the unborn child

* boiling point, ** flash point.

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