



FEDERAL UNIVERSITY OF SANTA CATARINA
TECHNOLOGICAL CENTER
DEPARTMENT OF CHEMICAL ENGINEERING AND FOOD ENGINEERING
GRADUATE PROGRAM IN CHEMICAL ENGINEERING

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**Bentonite-modified urea fertilizer for controlled release of nitrogen:
kinetics of ammonia volatilization**

Florianópolis

2024

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Bentonite-modified urea fertilizer for controlled release of nitrogen

Doctoral Thesis submitted to the Graduate Program in Chemical Engineering of the Federal University of Santa Catarina for obtaining the Doctor degree in Chemical Engineering.

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Florianópolis

2024

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Ribas, Marcela Mattus

Bentonite-modified urea fertilizer for controlled
release of nitrogen : kinetics of ammonia volatilization /
Marcela Mattus Ribas ; orientador, Dachamir Hotza,
coorientador, Agenor de Noni Júnior, 2024.

100 p.

Tese (doutorado) - Universidade Federal de Santa
Catarina, Centro Tecnológico, Programa de Pós-Graduação em
Engenharia Química, Florianópolis, 2024.

Inclui referências.

1. Engenharia Química. 2. Fertilizante nitrogenado. 3.
Bentonita. 4. Liberação controlada. 5. Volatilização de
amônia. I. Hotza, Dachamir. II. Júnior, Agenor de Noni.
III. Universidade Federal de Santa Catarina. Programa de
Pós-Graduação em Engenharia Química. IV. Título.

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Bentonite-modified urea fertilizer for controlled release of nitrogen

This work at doctoral degree in Chemical Engineering was evaluated and approved on October 27, 2023, by the examining board composed of the following members:

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Florianópolis, 2024

ACKNOWLEDGMENTS

First and foremost, I would like to praise and thank God, the Almighty, who has granted me countless blessings and knowledge so that I can pursue my dream and continue my academic journey.

I cannot find enough words to convey my deep gratitude, love, and respect to my parents, Silvio and Edna, and my siblings, Andressa and Thiago, for their love, help, and support. I am grateful and happy to always have my husband by my side, dreaming my dreams and being my support. I love you very much.

My sincere thanks must also go to my supervisors, Prof. Dachamir Hotza and Prof. Agenor De Noni Junior, who gave generously their time to share their knowledge and offer me valuable comments to improve my work. Thank you, Henrique Cislagui, Camila Rocha, Alan Carlos Batistão and Prof. Jucinei José Comin, for all contributions to this work. Your expertise and support are fundamental!

I thank the T-Minas company for funding, product supply, and for allowing me to be part of this social, environmental, and economic important project.

To PROCER, LINDEN, CA-EQA, and Soil, Water, and Plant Tissue Laboratory, thanks for providing essential equipment and analysis to develop this research. Special thanks to Fernanda Volpatto for always being willing to help.

I am grateful to UFSC for all the infrastructure, to all professors and staff to the Graduate Program in Chemical Engineering to make it all work.

To the CNPQ for the scholarship.

Finally, I sincerely thank my sister Andressa who lovingly and benevolently donated one of her kidneys, allowing me to experience all of this.

RESUMO

O Brasil é o quarto país em demanda global de fertilizantes com um consumo médio anual de 40 milhões de toneladas. Em torno de 85% da quantidade total de fertilizantes utilizados no país são importadas. Com o aumento nos preços e uma possível carência de ureia no Brasil, é importante o manejo consciente para evitar desperdícios. A falta de fertilizante encadeia uma série de problemas socioeconômicos, a começar pela elevação nos preços de alimentos básicos, como já foi constatado em 2021, diminuindo a segurança alimentar, aumentando a fome e a quantidade de pessoas abaixo da linha da pobreza. Fertilizantes de liberação controlada são grandes aliados visando uma menor necessidade em quantidade de fertilizante para se ter a mesma eficiência no plantio, diminuindo custos tanto de transporte quanto de compra. Com a liberação controlada de nitrogênio, a planta recebe a quantidade necessária desse mineral durante um tempo prolongado e não uma alta carga de imediato que vai se perdendo ao longo do tempo como é no caso da aplicação de ureia. Outro aspecto interessante do fertilizante de liberação controlada é a diminuição de perdas de nitrogênio por volatilização e lixiviação, levando a um menor risco de contaminação de solo e efluentes além da melhor gestão de recursos. O presente trabalho propõe analisar diversos aspectos sobre um fertilizante modificado a base de bentonita e ureia (BUF), visando obter dados sobre o mecanismo de interação entre estes dois compostos e analisar quais características que viabilizam a liberação controlada de nitrogênio. Cerca de 20% da ureia presente no BUF está intercalada nas camadas de bentonita, mostrando que a intercalação é eficaz, e a esfoliação obtida pelo processo de extrusão é importante para a obtenção de um fertilizante de liberação lenta. Além disso, foi possível concluir que as moléculas de ureia estão fortemente ligadas às camadas intermediárias de bentonita no fertilizante BUF, especialmente cerca de 20% do conteúdo total de ureia. Essa liberação mais lenta e sustentada de ureia confere ao BUF a importante característica de um eficiente fertilizante de nitrogênio de liberação lenta. A análise de volatilização de amônia no solo mostrou que a ureia perde nitrogênio por volatilização 60% mais rápido do que o BUF. Além disso, a metodologia do ácido bórico pôde ser validada em comparação com os testes do sensor de amônia. Foi possível concluir que a volatilização da amônia é 68% maior do que a do BUF no mesmo intervalo de tempo. Outro ponto a se observar é que a volatilização de amônia é mais rápida e elevada quando a ureia é usada como fertilizante do que quando a BUF é usada.

Palavras-chave: Fertilizante nitrogenado. Volatilização de amônia. Liberação controlada.

ABSTRACT

Brazil is the fourth country in global demand for fertilizers, with an average annual consumption of 40 million tons. Around 85% of the total fertilizers used in the country are imported. With the increase in prices and a possible shortage of urea in Brazil, it is essential to manage it consciously to avoid waste. The lack of fertilizer triggers a series of socioeconomic problems, starting with the rise in prices of basic foodstuffs, as has already been seen in 2021, decreasing food security, increasing hunger, and the number of people below the poverty line. Controlled-release fertilizers are great allies aiming at a lower need in fertilizer quantity to have the same efficiency in planting, reducing costs in transportation and purchase. With the controlled release of nitrogen, the plant receives the necessary amount of this mineral over a prolonged period and not a high immediate load lost over time, as is the case with the application of urea on the soil surface. Another exciting aspect of controlled-release fertilizer is the reduction of nitrogen losses by volatilization and leaching, leading to a lower risk of soil and effluent contamination, besides better resource management. The present work proposes to analyze several aspects of bentonite-modified urea fertilizer (BUF), aiming to obtain data on the interaction mechanism between these two compounds and analyze which characteristics enable the controlled release of nitrogen. Around 20% of the urea present in the BUF is intercalated in the bentonite layers, showing that intercalation is effective, and the exfoliation obtained by the extrusion process is important for obtaining a slow-release fertilizer. In addition, it was possible to conclude that the urea molecules are strongly bound to the intermediate bentonite layers in the BUF fertilizer, especially around 20% of the total urea content. This slower and more sustained release of urea gives BUF the important characteristic of an efficient slow-release nitrogen fertilizer. Analysis of ammonia volatilization in the soil showed that urea loses nitrogen through volatilization 60% faster than BUF. In addition, the boric acid methodology could be validated against the ammonia sensor tests. It was possible to conclude that the volatilization of ammonia is 68% higher than that of BUF in the same time interval. Another point to note is that ammonia volatilization is faster and higher when urea is used as a fertilizer than when BUF is used.

Keywords: Nitrogen fertilizer. Ammonia volatilization. Controlled release.

RESUMO EXPANDIDO

Introdução

O Brasil é o quarto país em demanda global de fertilizantes, com um consumo médio anual de 40 milhões de toneladas. Cerca de 85% do total de fertilizantes utilizados no país são importados. Com o aumento dos preços e uma possível escassez de ureia no Brasil, é essencial gerenciá-la de forma consciente para evitar desperdícios. A falta de fertilizantes desencadeia uma série de problemas socioeconômicos, a começar pelo aumento dos preços dos alimentos básicos, como já foi visto em 2021, diminuindo a segurança alimentar, aumentando a fome e o número de pessoas abaixo da linha da pobreza. Os fertilizantes de liberação lenta são grandes aliados visando a uma menor necessidade de quantidade de fertilizante para ter a mesma eficiência no plantio, reduzindo custos de transporte e compra. Com a liberação controlada de nitrogênio, a planta recebe a quantidade necessária desse mineral. Outro aspecto interessante do fertilizante de liberação lenta é a redução das perdas de nitrogênio por volatilização e lixiviação, levando a um menor risco de contaminação do solo e dos efluentes, além de uma melhor gestão dos recursos. O presente trabalho se propõe a analisar vários aspectos do fertilizante de ureia modificado com bentonita (BUF), com o objetivo de obter dados sobre o mecanismo de interação entre esses dois compostos e analisar quais características permitem a liberação lenta de nitrogênio. A primeira etapa foi quantificar a perda de volatilização de amônia de uma solução padrão de ureia e do fertilizante BUF na água e no solo. As perdas por volatilização de nitrogênio foram avaliadas usando câmaras estáticas equipadas com um eliminador de nitrogênio. Os resultados obtidos nos permitiram validar a metodologia e determinar a concentração máxima de nitrogênio liberada por volatilização para cada amostra. Os ensaios de volatilização de amônia do solo fertilizado foram realizados durante 30 dias. Foram realizados estudos dos efeitos das variações de pH e do tipo de solo sobre a estabilidade dos fertilizantes. O estudo final foi conduzido para obter a cinética de volatilização da amônia, os mecanismos de dessorção e a quantificação da amônia usando a metodologia Kjeldahl.

Objetivos

Este trabalho tem como objetivo analisar a cinética de volatilização de amônia de um fertilizante de ureia modificado com bentonita (BUF), conhecer os mecanismos de interação

entre o BUF e a ureia e quantificar a volatilização de amônia para comparar os dois fertilizantes e verificar a capacidade do BUF como um fertilizante de liberação controlada.

Metodologia

Para obter a volatilização de amônia dos fertilizantes no solo, foram preparadas câmaras de volatilização despejando 200 g de amostra de solo e 20 mL de água deionizada em cada câmara. Os fertilizantes foram adicionados a cada câmara para atingir uma concentração de nitrogênio equivalente a 200 kg ha⁻¹ de N. Um sensor de amônia (AKSO SGTP-NH₃) foi acoplado à câmara de volatilização para obter a concentração de amônia volatilizada dentro da câmara. Nas câmaras que realizaram a análise do indicador de ácido bórico, 50 mL de 2% desse sequestrante de amônia foram colocados em um recipiente cilíndrico no meio da câmara de volatilização. O nitrogênio amoniacal na solução de H₃BO₃ foi determinado por titulação com ácido sulfúrico 0,01 mol L⁻¹. FTIR e XRD foram realizados para obter grupos funcionais de ligação química grupos funcionais e para monitorar a esfoliação e a intercalação da ureia na bentonita para formar o BUF. Tanto o solo quanto os fertilizantes foram caracterizados segundo sua concentração em nitrogênio total. Ensaios de campo foram conduzidos na Fazenda Experimental da Universidade Federal de Santa Catarina durante 32 dias com o objetivo de verificar a volatilização de amônia dos fertilizantes aplicados ao solo, a partir da utilização de câmaras semiabertas equipadas de esponjas contendo sequestrante de amônia para a determinação pelo método de Kjeldahl.

Resultados e Discussão

Durante os estudos foi possível observar que já no estudo da liberação de fertilizantes na água, foi possível concluir que há uma quantidade de ureia intercalada nas folhas de bentonita e, além disso, na superfície da bentonita existem interações íon-dipolo entre essa nanoargila e a ureia. Essas interações entre a bentonita e a ureia no fertilizante BUF diminuem a possibilidade de volatilização da amônia. Os resultados foram confirmados pela análise de FTIR. Outra conclusão obtida pela taxa de liberação em água é que 20% da ureia apresentada no BUF está intercalada nas camadas de bentonita, mostrando que a intercalação é eficaz, e a esfoliação obtida pelo processo de extrusão é importante para a obtenção de um fertilizante de liberação lenta. Além disso, foi possível concluir que as moléculas de ureia estão fortemente ligadas às camadas intermediárias de bentonita no fertilizante BUF, especialmente cerca de

20% do conteúdo total de ureia. Essa liberação mais lenta e sustentada de ureia confere ao BUF a importante característica de um eficiente fertilizante de nitrogênio de liberação lenta. Os estudos de DRX confirmaram que as moléculas de ureia foram introduzidas nas folhas de bentonita, levando a uma expansão na distância entre as camadas, resultando em uma forte ligação de H com grupos hidrofílicos da bentonita. O aumento da distância entre camadas sugere uma esfoliação bem-sucedida da bentonita com ureia.

A análise de volatilização de amônia no solo mostrou que a ureia perde nitrogênio por volatilização 60% mais rápido do que o BUF. Além disso, a metodologia do ácido bórico pôde ser validada em comparação com os testes do sensor de amônia. Em resumo, uma descoberta importante de nossa pesquisa é que as moléculas de ureia são intercaladas em folhas octaédricas de bentonita, bem como quimicamente ligadas em sua superfície e poros, resultando em um comportamento de liberação lenta para a dissolução da ureia, tornando esse fertilizante modificado com ureia e bentonita útil para aumentar a eficácia do fertilizante em aplicações agrícolas.

Outro aspecto importante é o papel do pH do solo na regulação da volatilização da amônia, enfatizando sua importância em contextos agrícolas e ambientais. As análises demonstram que o pH do solo influencia significativamente a transformação e o destino da amônia no solo, sendo que as condições ácidas favorecem o aumento da volatilização da amônia. Os mecanismos subjacentes a essa relação envolvem o equilíbrio dependente do pH entre amônio e amônia, com níveis mais altos de pH promovendo a formação e perda de amônia por volatilização.

Os estudos cinéticos nos permitiram observar que, quando o BUF entra em contato com o solo, dependendo do valor do pH, a ureia é liberada da matriz de bentonita em uma difusão controlada, mas também dependente da esfoliação da bentonita. Além disso, foi possível concluir que a volatilização da amônia é 68% maior do que a do BUF no mesmo intervalo de tempo. Outro ponto a se observar é que a volatilização de amônia é mais rápida e elevada quando a ureia é usada como fertilizante do que quando a BUF é usada. Essa liberação mais lenta e sustentada da ureia presente no BUF, confere a este fertilizante modificado a base de bentonita a importante característica de um eficiente fertilizante de nitrogênio de liberação lenta.

Considerações Finais

Este trabalho examinou a eficácia comparativa de um novo fertilizante de liberação lenta (BUF) em relação à ureia pura, concentrando-se em seu impacto na volatilização da amônia. As descobertas apresentadas aqui ressaltam a superioridade do BUF em relação à ureia pura em aplicações agrícolas. Uma das principais vantagens do BUF é seu mecanismo de liberação controlada devido à intercalação da ureia nas lamelas de bentonita, minimiza efetivamente o problema de volatilização da amônia, garantindo que uma proporção maior do nitrogênio aplicado seja utilizada pelas culturas. A natureza do BUF permite uma liberação mais gradual e sustentada de nitrogênio, correspondendo à demanda de nutrientes das culturas ao longo do tempo. Isso resulta em maior eficiência dos nutrientes, pois as plantas podem acessar o nitrogênio quando necessário. A ureia pura, por outro lado, pode levar a desequilíbrios e desperdícios de nutrientes devido à sua rápida liberação. A redução das emissões de amônia contribui para melhorar a qualidade do ar e diminuir a poluição ambiental, o que é uma preocupação significativa na agricultura atualmente. A ureia pura normalmente exige aplicações mais frequentes para manter os níveis adequados de nutrientes, resultando em aumento dos custos de mão de obra e fertilizantes. Por outro lado, o BUF permite uma aplicação que leva a um longo período de liberação do nitrogênio. Embora o BUF possa ter um custo inicial um pouco mais alto em comparação com a ureia pura, seus benefícios em termos de melhor rendimento das culturas, frequência reduzida de aplicação de fertilizantes e menores perdas por volatilização de amônia fazem dele uma opção econômica para os agricultores no longo prazo.

Palavras-chave: Fertilizante nitrogenado; Volatilização de amônia; Liberação controlada.

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CONCEPTUAL DIAGRAM OF THIS STUDY

Bentonite-modified urea fertilizer for controlled release of nitrogen: kinetics of ammonia volatilization

The problem

- Brazil is the fourth largest world consumer of fertilizers, and importation exceed 80% of national consumption;
- Actual conflicts and political tensions between Russia and Ukraine directly affect the price and urea importation;
- The increase in the price of urea leads to an increase in the price of staple foods for human consumption, causing a socioeconomic problem;
- The excessive use of urea as a fertilizer damages the soil, groundwater, and the atmosphere.

Proposed solution

- A Bentonite-modified urea fertilizer (BUF) can be an alternative aiming at the controlled release of nitrogen;
- A controlled-release fertilizer (CRF) reduces the need for frequent soil fertilization, reducing waste of resources, volatilization losses, and harmful effects on the environment;
- Lower quantities use of fertilizers with the same efficiencies for agriculture minimizes socio-economic problems such as lack of food security.

Who already did this?

- There are just two papers about bentonite-urea fertilizer, and both studied just urea static release in water and characterizations (Hermida and Agustian, 2019; Xiaoyu et al., 2013).

Research hypotheses

- Is the proposed fertilizer more stable to environmental changes than pure urea?
- What are the physicochemical interactions between bentonite and urea?
- Is the BUF release of nitrogen significantly slower than pure urea?
- Is nitrogen loss by ammonia volatilization in BUF substantially lower than pure urea?

Methodologies

- Effects in urea release and ammonia volatilization of BUF and urea in water with different pH, temperature, and agitation characteristics;
- Effect of environmental changes on ammonia volatilization of BUF (soil type, pH, irrigation, and fertilization system);
- Study of urea desorption, ammonia volatilization kinetics, and nitrogen diffusion from BUF applied into water and soil;
- Comparison of BUF and urea nitrogen controlled release and ammonia volatilization.

Expected results

- Propose a modified fertilizer with higher efficiency compared to pure urea;
- Explore the interaction mechanisms between clay mineral and urea aiming the controlled release of nitrogen and reduced ammonia volatilization;
- Report the influence of environmental aspects on fertilizer efficiency.

1 INTRODUCTION

1.1 MOTIVATION

Brazil is the fourth country in global demand for nitrogen fertilizers, behind China, India, and the United States. Above all, Brazil's dependence on fertilizer imports is a major problem for the country's agronomic, economic, and social scenario. Around 85% of the total fertilizers used in the country are imported. Brazil consumes 40 million tons of fertilizers per year, 1/3 for each fertilizer group (NPK) (Table 1).

Table 1 Brazil's fertilizer consumption and importation needs.

Fertilizer Group (NPK)	Import percentage	Main suppliers
Nitrogenated (N)	95%	Russia, China, and Middle Eastern Countries
Phosphated (P)	75%	China, Morocco, and Russia
Potassium (K)	95%	Belarus, Canada, and Russia

Source: MAPA.

Nitrogen fertilizers are essential in all Brazilian agriculture, from commodity crops such as soybeans, corn, and sugarcane; to family farming such as rice, beans, and vegetables. Urea is the main fertilizer used due to the lowest cost per unit of nutrient among the nitrogen fertilizers available on the market, with about 45% nitrogen in its total mass. (EMBRAPA, 2022). Russia is the second-largest producer of nitrogen fertilizers globally. Until December 2021, Russia was the largest supplier of fertilizers to Brazil, which imported a monthly average of 7 million tons of urea. With the current war between Russia and Ukraine, the primary expected reaction for the fertilizer market is an increase in price and, in the worst case, the interruption of exports. In the first hours of the Russian attack on Ukraine, urea already showed a 42% increase in value (ALVES, 2022).

Fertilizers make up a significant part of the production costs, historically representing between 25% and 30% of crop investment. The ton of urea, for example, went from R\$ 1,940 (Dec/2020) to R\$ 5,355 (Dec/2021), according to Conab's Agricultural Inputs Report (ANTUNES, 2022; CONAB, 2022). According to Alexis Maxwell, an analyst at Green Markets, farmers may pass on the higher cost of fertilizers to consumers in lower crop yields

and subsequent higher food prices. There are already severe concerns regarding cultivating soybeans, corn, wheat, coffee, sugar, rice, beans, fruits, and other grains (MENDES, 2021a).

With rising prices and a possible shortage of urea in Brazil, conscious management to avoid waste is essential. The lack of fertilizer triggers a series of socioeconomic problems, starting with the increase in the prices of basic foodstuffs, as has already been seen in 2021, decreasing food security, increasing hunger, and the number of people below the poverty line.

Controlled release fertilizers are great allies in reducing the need for fertilizer to have the same efficiency in planting, reducing costs both in transportation and purchase. With the controlled release of nitrogen, the plant receives the necessary amount of this mineral over a prolonged period and not a high immediate load, as is the case with urea, which causes nitrogen losses. Another exciting aspect of controlled-release fertilizer is the reduction of nitrogen losses by volatilization and leaching, leading to a lower risk of soil and effluent contamination and better resource management. The production of controlled-release nitrogen fertilizers has been studied over the years. Polymers, urease inhibitors, or encapsulation are used in the formulation and increase the final cost. Bentonite is a nanostructured clay mineral that is low cost and environmentally friendly.

To the best of our knowledge, there are only two studies about bentonite-modified urea fertilizer (HERMIDA & AUGUSTIAN, 2019; XIAOYU et al., 2013). Furthermore, both works studied only the static release of urea in water. Thus, this study aims to analyze several aspects of bentonite-modified urea fertilizer (BUF) to obtain essential data on the interaction mechanism between bentonite and urea that allows the BUF to be classified as a controlled-release fertilizer (CEF). Urea desorption, nitrogen diffusion, and ammonia volatilization kinetics will also be studied. The main objective is to provide complete information about soil and fertilization characteristics, fertilizer stability, nitrogen release, and ammonia volatilization.

1.2 GENERAL OBJECTIVE

This work aims to analyze a bentonite-modified urea fertilizer (BUF) ammonia volatilization kinetics, know the interaction mechanisms between BUF and urea, and quantify ammonia volatilization to compare both fertilizers.

1.3 SPECIFIC OBJECTIVES

The specific objectives of this work are:

- a) Study the urea release, ammonia volatilization kinetics from BUF and urea in water and soil;
- b) Compare the effect of soil type and pH value on ammonia volatilization of BUF;
- c) Determine the main physicochemical aspects in bentonite-urea interaction that provide slow nitrogen release characteristics to BUF;

2 LITERATURE REVIEW

This chapter presents a brief literature review on the relevant topics to this work. Firstly, the fertilizer supply problems are due to high import requirements. Then, essential information about nitrogen-based controlled-release fertilizers, and clay minerals are presented. Finally, chemical interactions between urea and clay minerals are addressed. Lastly, a state of the art about ammonia volatilization measurement methods are presented, and some results are discussed highlighting ammonia volatilization from urea and controlled-release fertilizers.

2.1 FERTILIZER SUPPLY PROBLEMS

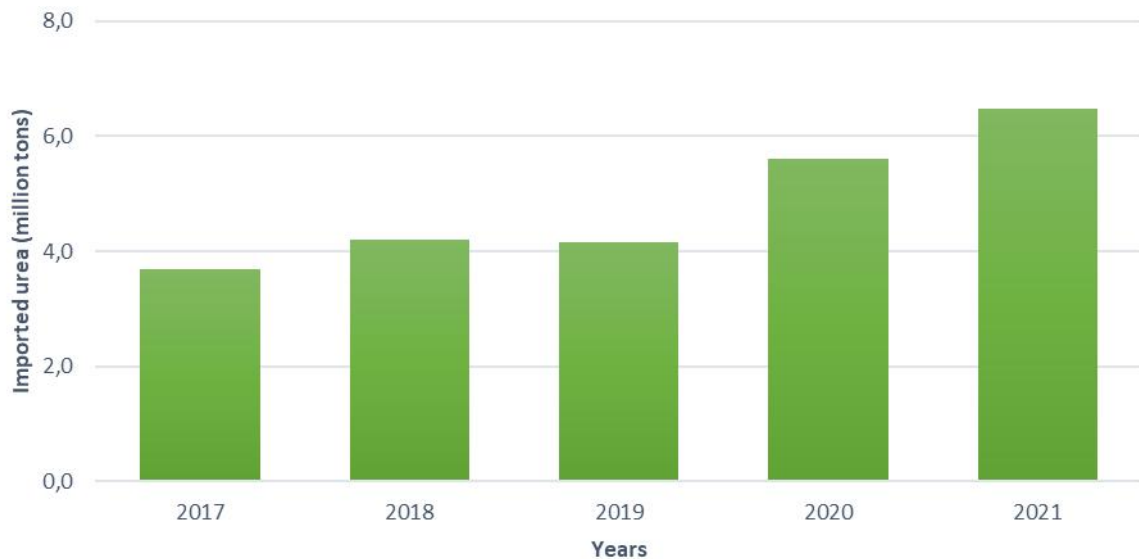
Brazilian dependence on fertilizer represents 85% of the total needed by the country. For this reason, any logistical, political, or economic problems around the world causes an impact on agriculture and the national economy.

Covid-19, which started in China in December 2019, quickly spread around the world, and on March 11, 2020, the World Health Organization (WHO) raised the contamination status to the pandemic. Many countries have enacted lockdowns, and hindered logistics, including delivery, exporting, and importing of fertilizers. The price of raw materials needed to produce agricultural inputs was also hampered, affecting mainly Urea and Monoammonium phosphate (MAP) (LOPES, 2021).

In 2021, the government of Belarus suffered trade sanctions from the European Union and the United States. As a result, the fertilizer supply was significantly reduced, which resulted in high prices due to high demand. In addition, a hurricane hit Florida in August 2021, disrupting fertilizer production and damaging ports in the United States, which limited transportation, making container costs very high (CONEXÃO CAMPO CIDADE, 2021).

As a consequence of the increase in fertilizer and production costs, the price of products that reach the end consumer undergoes significant inflation. The increase in the price of staple foods, such as potatoes, reflects the high cost of inputs, which have strong demand from other crops, such as soybeans and corn. What increases the price of fertilizers are the main grains because these represent the large volume of consumption. When wheat, rice, and corn go up in price, they are the great drivers of demand for fertilizer. When the fertilizer price goes up, it drives up the production costs of everything, triggering a chain price increase (CONEXÃO CAMPO CIDADE, 2021). Figure 1 shows the monthly average of urea imported over the last five years (AGRINVEST COMMODITIES, 2021).

Figure 1. Monthly average of urea imported by Brazil from 2017 to 2021.

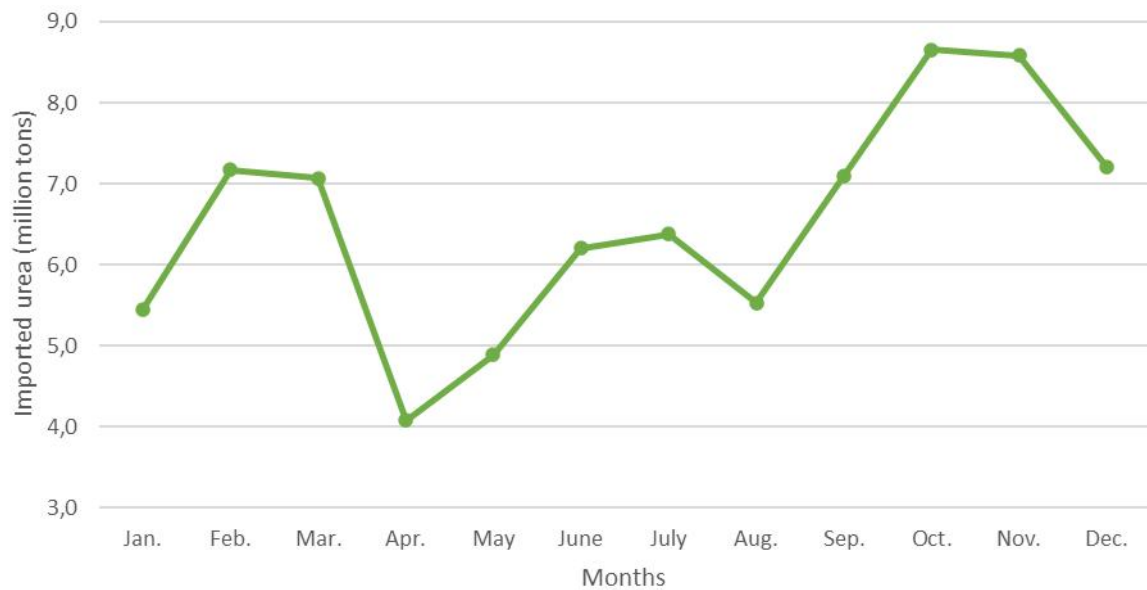


Source: Agrinvest Commodities (2021)

According to Bruno Lucchi (Technical Director of Confederation of Agriculture and Livestock of Brazil), from January to September 2021, urea prices rose 70.1% (LUCCHI, 2021). The sharp rise is due to a combination of high international prices, high demand, shortage of global supply, and logistical problems. And as these are vital components for the planting of crops, agricultural production costs went up (FREITAS, 2021).

In December 2021, Russia was the leading fertilizer supplier in Brazil, accounting for 23.5% of total imports from January to November, considering all fertilizers. Figure 2 shows the amount (in million tons) of urea imported from January to December 2021.

Figure 2. Urea imported by Brazil in 2021.

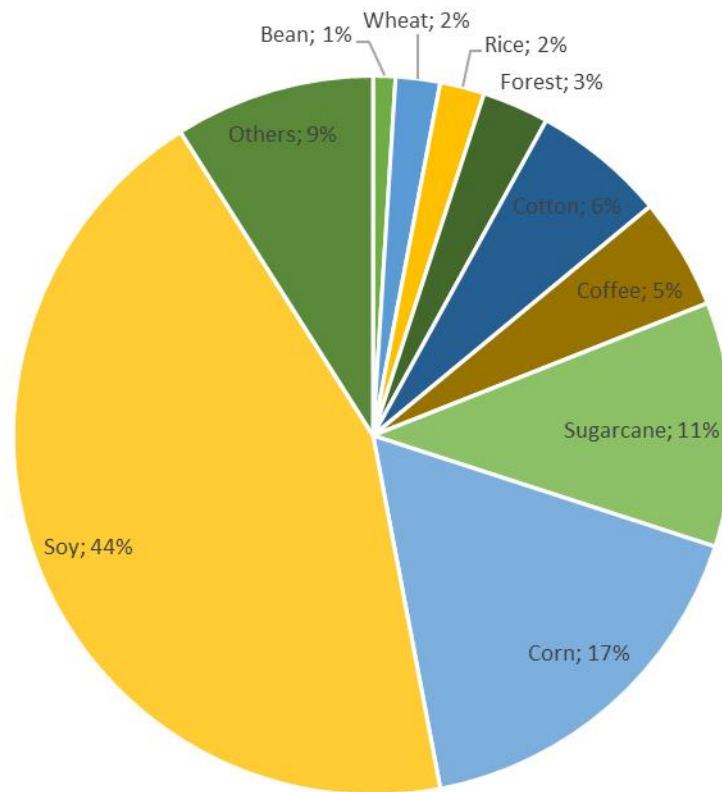


Source: Agrinvest Commodities (2021).

From January to December 2021, Brazil imported ~6 million tons of urea monthly, 14% more compared to 2020. Although the increase in Brazilian demand for fertilizers was the primary fuel for this increase in imports, the national production of fertilizers remained practically unchanged (MENDES(b), 2021; AGRINVEST COMMODITIES, 2021).

According to the data from the National Association for Fertilizer Diffusion (ANDA), in 2019, an estimated 4.7% of Brazilian fertilizer deliveries (about 1.6 million tons) were destined for coffee plantations, second only to soybeans, corn, sugarcane, and cotton (ROSSETTI et al., 2021) (Figure 3).

Figure 1. Use of fertilizers in Brazil per crop in 2019.



Source: Rossetti et al. (2021)

In 2021, among other factors, the strong appreciation of grain prices encouraged the growth of fertilizer consumption worldwide, justified by favorable exchange ratios for farmers in comparison with most crops. Thus, the global fertilizer market outlook has been reflecting the growing inability of supply to keep up with purchases by the leading consuming countries, resulting in input shortages in some regions and rising prices to the highest levels in years for the primary nutrients. In Brazil, the scenario of rising international prices still adds to the significant currency devaluation recorded in 2021, resulting in fertilizer prices significantly higher than in 2020. Urea prices increased by about 80% from 2020 to 2021 (ROSSETTI et al., 2021). In 2021, the price of rice, a staple food for half of humanity, has risen, among other factors, due to a rise in fertilizer costs for farmers in Asia (KNIGHT, 2021)

The preparations for the 2022/23 sugarcane harvest (April-March) in Brazil begin with many uncertainties during the global crisis of fertilizers, which have had a historical high since the beginning of the year and represent 50% of the costs of inputs in the crop. As a result,

average fees have already increased by about 20%. With prices at record levels, many producers started to substitute or ration some fertilizers (SIMIÃO, 2021).

In 2021, Russia limited its fertilizer quotas for exports of complex fertilizers to 5.35 million tons and nitrogenous fertilizers to 5.9 million tons.

All over the northern hemisphere, farmers are already showing that the shock in the supply of inputs has become a growing and more serious concern, in the face of the uncontrolled rise of fertilizers, but mainly in front of the lack of product.

The lack of nitrogenous products is severe and a determining point for defining the following crops in the 2022/23 season. The biggest shock should continue to be felt in the global food inflation numbers. Rising production costs are pushing up food prices of all kinds. Recently, wheat prices on the Chicago Mercantile Exchange hit their highest levels since 2012 (MENDES, 2021a).

The withdrawals among crops are the most diverse so far, with impacts of all kinds being expected. Soybeans, corn, wheat, coffee, sugar, rice, beans, fruits, and other grains are all food groups that are already signaling serious (MENDES, 2021b).

Geopolitical tensions in Russia (the second largest nitrogen producer) and Ukraine have escalated into a war, and uncertainties over product availability have already boosted prices. On the night of the first Russian attack on Ukraine, urea showed a 42% increase in value. Urea prices have increased by 214% (REUTERS, 2022).

About a quarter of the fertilizers imported by Brazil in 2021 came from Russia, 22% of the 41.6 million tons, totaling 15 billion dollars and 3.5 billion dollars spent in the Russian market. Russia is home to two of the largest fertilizer producers on the planet: PhosAgro and Uralkali. Both have Brazil as one of their main clients. (ANGELO, 2022). The substitution of fertilizers supplied by Russia is neither perfect nor cheap, especially when it comes to nitrogen fertilizers (SOUZA, 2022).

2.2 NITROGEN FERTILIZERS

Fertilizers are classified as any organic or inorganic material of natural or synthetic origin that can be added to soil to supply one or more essential nutrients for plant growth and development (SOIL SCIENCE SOCIETY OF AMERICA, 2008). According to the United Nations Organization, the world population will reach 9.7 billion people in 2050 (UNITED NATIONS, 2019); thus, food production will need to increase by 70% to achieve this food request (SANTOS et al., 2015).

Fertilizers are applied to the soil to increase agricultural productivity by providing essential elements for plant growth; however, between 40 and 70% of nutrients are lost through volatilization, erosion, and leaching (WU; LIU, 2008). The concentration of fertilizer lost varies according to soil characteristics, environmental factors, crop, and application method (AYOUB, 1999).

NPK fertilizers are composed of nitrogen, phosphorus, and potassium, and are expressed as elemental N, phosphorus peroxide (P_2O_5), and potassium oxide (K_2O), respectively (MARTINS, 2013). Plants use nitrogen for growth, protein formation, and chlorophyll; phosphorus promotes root, leaf, and fruit development; and potassium plays a vital role in stem and root growth and, like nitrogen, is used in protein synthesis (CORRADINI; DE MOURA; MATTOSO, 2010).

The primary source of nitrogen fertilizers is atmospheric N_2 , transformed into ammonia (NH_3) by the Haber-Bosch process. In this process, fossil fuels provide N_2 and H^+ subjected to high pressures and temperatures, resulting in NH_3 . Ammonia, in turn, serves as the raw material for the main nitrogen-based fertilizers, urea, and nitric acid. Nitric acid can rise to different nitrate fertilizers (CANTARELLA, 2007).

Nitrogen is an essential element for plants because it acts in the composition of ATP, NADH, NADPH, chlorophyll, proteins, and enzymes. This element presents high mobility in the soil, so it is of great interest to conduct studies to improve its absorption and metabolization within the plant. Nitrogen fertilizers are highly soluble, leaving no residue in the soil, increase soil acidity due to nitrification, cause a high salinity index, and generally do not have secondary macronutrients in their formula, except for ammonium sulfate (BREDEMEIER; MUNDSTOCK, 2000).

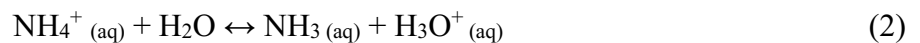
Ammonium sulfate presents the advantage of not suffering losses by volatilization even if applied to soils with a pH higher than 7. In the ammoniacal form, this fertilizer has 20% nitrogen and 24% sulfur, an attractive characteristic for soils lacking in S, as is the case in several regions of Brazil (ANTONIO, 2012), due to the higher price per unit of nitrogen and lower availability of this nutrient than urea and ammonium nitrate (CANTARELLA, 2007).

Ammonium nitrate has 33% nitrogen, half in nitric (NO_3) and half in ammoniacal form (NH_4). Despite the high nitrogen concentration, this fertilizer can be used to manufacture explosives, so its use is restricted and controlled by authorities worldwide (CANTARELLA, 2007; MALAVOLTA, 2006).

Ammonia (NH_3) is generated as a result of nitrogen (N) degradation by ammonium ion (NH_4^+) deprotonation, especially in alkaline soils (Equation 1).

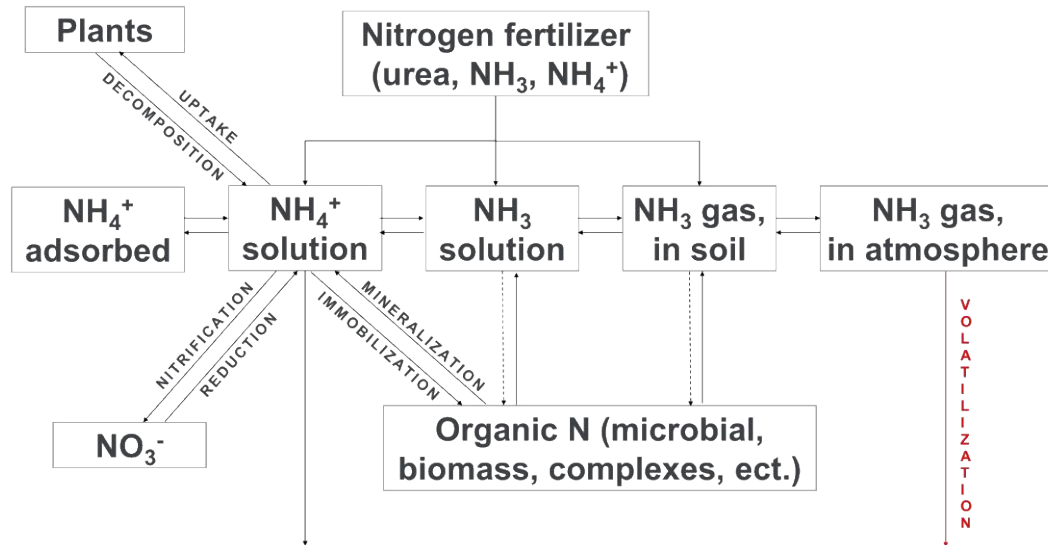


Ammonium can react with sulfate aerosols to form ammonium sulfate in the atmosphere and soil. Ammonia and ammonium sulfate increases acidification and eutrophication, causing negative economic and environmental impacts (SHAH; WESTERMAN; AROGO, 2006). In the absence of water, only mineral and non-volatile ammonium are present. In solution, ammonium is dissociated into NH_4^+ and NH_3 . The main factors that affect ammonia volatilization are the ammoniacal nitrogen concentration in solution (soil, plant, and effluent) and its pH, the resistance to gas diffusion into the atmosphere, the soil type, and the temperature (SOMMER et al., 2003). Air temperature is critical because both equilibrium constant (K_d) and Henry's law constant (K_H) depend on it. Ammonia and ammonium ion are derived from urea hydrolysis obtained from ionization (Equation 2) and liquid-gas equilibrium (Equation 3).



Urea is the most employed nitrogen fertilizer because of its high concentration of nitrogen ($460 \text{ g}\cdot\text{kg}^{-1}\cdot\text{N}$), the restriction of ammonium nitrate as fertilizer, and the higher cost of ammonium sulfate (CHIEN; PROCHNOW; CANTARELLA, 2009). Volatilization is accentuated in alkaline soils and acidic and alkaline soils when urea is applied to the surface, especially in flooded soils and at the early stage of plant growth. Urea $[(\text{NH}_2)_2\text{CO}]$ hydrolysis to ammonium bicarbonate $[(\text{NH}_4)\text{HCO}_3]$ causes an increase in soil pH that induces ammonia (NH_3) volatilization (CHIEN; PROCHNOW; CANTARELLA, 2009; SOARES; CANTARELLA; MENEGALE, 2012). Under the influence of physicochemical processes and at the origin of ammonia volatilization, ammoniacal nitrogen (NH_4^+ and NH_3) is generally transformed into nitrate by nitrification (Figure 4). Nitrate can be denitrified to nitrous oxide (N_2O) and nitrogen (N_2). Mineralization and denitrification are microbial facilitated processes accompanied by emissions of nitrous oxide and nitric oxide (NO) (CELLIER et al., 2013).

Figure 2. Chemical and biological reactions that affect ammonia volatilization.



Source: Freney and Simpson (1983).

High pH in solution favors the formation of aqueous ammonia and hydrogen ion (right-hand side of Equation 3), increasing NH_3 concentration in solution and the gaseous phase. If the soil has pH values below 7, the main ammoniacal-N form will be NH_4^+ and the potential for volatilization will be small. In contrast, if the soil presents higher pH values, the main structure will be NH_3 , and the potential for volatilization will be more significant (DASGUPTA; DONG, 1986).

The effect of initial soil pH can be overlaid by a strong interaction between the fertilizer, like urea, and the soil solution that induces hydrolysis and precipitation reactions. In this case, the soil cation exchange capacity (CEC) is essential, if the soil presents a large CEC, with high NH_4^+ retention, the volatilization potential of NH_3 tends to reduce because of the adsorption of NH_4^+ on the exchange site and consequent reduction on NH_4^+ concentration in soil solution (EMEP/EEA, 2019).

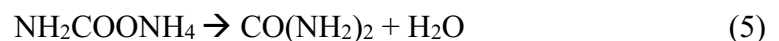
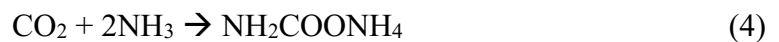
Ammonia losses are also dependent on wind speed, soil buffering capacity, soil moisture content, and low or high plant canopy. The presence of plant residues can increase urease activity and, consequently, increase NH_3 emission. Ammonia losses are higher in countries with tropical and subtropical climates with average volatilization of 20 – 60% of the applied nitrogen (BOUWMAN; BOUMANS, 2002; CANTARELLA et al., 2003, 2008; CHIEN; PROCHNOW; CANTARELLA, 2009; LARA CABEZAS; KORNDORFER; MOTTA, 1997). The choice of fertilizer and the application technique greatly influence volatilization. Depending on the fertilizer used, once it is applied to the soil surface, there is a consequential loss due to the

volatilization that occurs in the first hours after fertilization (CELLIER et al., 2013; GENERMONT et al., 1998; HUIJSMANS; HOL; VERMEULEN, 2003; SOMMER et al., 2003).

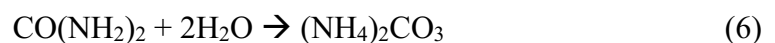
Nitrogen loss measurements are essential to correct fertilization, avoiding excess or lack of this nutrient, economic losses, and negative environmental impacts. Nitrogen flow measurement methods can be experimental, which allows the direct determination of emissions of gaseous nitrogen compounds, or the use of models that are generally proposed to carry out integrated assessments for long periods and large areas or to analyze evolutionary scenarios (CELLIER et al., 2013).

2.2.1 Urea

Urea ($\text{CO}(\text{NH}_2)_2$), also called carbamide, is a nitrogenous compound containing a carbonyl group attached to two amine groups. In vivo, urea is formed in the liver via the urea cycle from ammonia and is the end product of protein metabolism. Industrially, urea is obtained through the reaction between ammonia (NH_3) and carbon dioxide (CO_2), under high pressure, forming ammonium carbamate ($\text{NH}_2\text{COONH}_4$) (Equation 4), which is then dehydrated to give rise to urea (Equation 5) (PEREIRA, 2014):

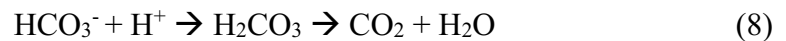


When pure, urea presents around 47% nitrogen in its composition, being then the nitrogen fertilizer with the lowest cost per unit of nitrogen and, consequently, the most used molecule for supplementation of this mineral in the soil (DAL MOLIN, 2016). Urea can be absorbed through both the leaves and the roots. As a fertilizer, it can be taken up directly or after hydrolysis. The enzyme urease catalyzes the hydrolysis of urea, resulting in ammonium carbonate (Equation 6); ammonium carbonate is highly unstable, breaking down into ammonium, bicarbonate, and hydroxyl (Equation 7):



Ammonium, in turn, can be readily taken up by the plant, and converted into ammonium, or, in aerated soils, nitrified by bacteria of the genus *Nitrobacter* and *Nitrosomonas*, originating nitrate (NO_3^-) up to 40 days after soil fertilization (DAL MOLIN, 2016; ROGERI et al., 2015). The effectiveness of urea as a fertilizer can be reduced due to ammonia volatilization and nitrate leaching (AARNIO, 1995).

Ammonium can be converted to ammonia and lost to the atmosphere, depending on the cation exchange capacity, clay content (texture), pH, and soil temperature (BYRNES, 2000). Due to the predominance of acidic soils in Brazil, the volatilization of nitrogen in the form of ammonia is minimal when ammonia fertilizers are incorporated into the soil. However, when nitrogen is added by applying urea to the soil surface, NH_3 volatilization can be enhanced. The increased susceptibility to volatilization occurs because the hydrolysis process of urea promotes the elevation of soil pH around the granules due to the reactions of bicarbonate and hydroxyl with hydrogen present in the soil (Equation 8) (CANTARELLA, 2007; ERNANI, 2008; YAMADA; ABDALLA, 2006):



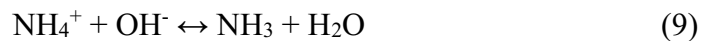
This elevation in soil pH can lead to losses of between 8 and 77% of the applied nitrogen (FARIA et al., 2014; LARA CABEZAS; SOUZA, 2009). In tropical countries, such as Brazil, crops absorb between 50 and 70% of the nitrogen; therefore, about 40% of the N is lost to the environment, resulting in a low return on the investment made in fertilization (FINK, 1992). Besides the high cost of frequent fertilization, this still causes environmental damage because the excess nutrients can contaminate the atmosphere and the soil, besides groundwater and rivers (PEREIRA, 2014). The ecological damage due to excess ammonium and oxidized nitrogen compounds can cause algae blooms that, in turn, cause oxygen depletion. In the case of blue and green algae, substances toxic to animals and humans are produced during blooming. Another problem of excessive use of fertilizers is the toxicity of nitrate (NO_3^-) and nitrite (NO_2^-), ions related to various diseases. Moreover, the excess of nitrogen compounds is also associated with acid rain and the release of N_2O and NO gases, which contribute to the greenhouse effect and reduction of the ozone layer (RESENDE, 2002; SERRANO-SILVA et al., 2011; SNYDER et al., 2009). Thus, the efficient use of fertilizers is essential for greater productivity, economic return, and minimization of nutrient losses to the environment.

2.2.2 Nitrogen losses

Several factors influence the availability of nitrogen for plants, such as climatic factors, soil characteristics, type of crop, a form of sowing, and fertilization. Besides this, nitrogen is susceptible to volatilization, leaching, and denitrification, which cause a loss in concentration in the soil, leading to a deficiency of this nutrient for the plant.

What determines the predominance of one form of loss, or another, is the form in which the nitrogen is found in the soil. If it is present in larger quantities in the ammonium form, the loss by volatilization will be more pronounced; in the nitrate form, leaching and denitrification will be predominant (DAL MOLIN, 2016).

Nitrogen present in the ammonium form is subject to deprotonation when the ground around the molecule is elevated, giving rise to ammonia (NH₃), a volatile gas under natural conditions and can be lost to the atmosphere. The equilibrium reaction between ammonium and ammonia is shown in Equation 9:



The most influential factors in transforming ammonium into ammonia are the soil pH and the type of fertilization. Volatilization is enhanced in alkaline soils with the use of ammonia fertilizers, as well as in acidic soils with the application of urea on the soil surface (ERNANI, 2008). Ammonia volatilization is still pronounced when applied at high doses, in places of high temperatures, on soils with medium humidity, on sandy soils, and when the application is made on the surface (TASCA et al., 2011).

The nitrate form shows predominant loss by leaching. The anionic behavior of nitrate prevents it from making specific bonds to the soil colloids, only electrostatic bonds occurring. Thus, all nitrate is in the soil solution and susceptible to leaching by percolating water (ARAÚJO et al., 2004; LORENSINI et al., 2012).

Denitrification also leads to nitrate loss in environments with little oxygen input, such as rice in flooded cultivation. The low availability of O₂ makes nitrate the first molecule to receive electrons due to the activity of anaerobic microorganisms. Thus, denitrification occurs from the reduction of nitrate (NO₃⁻) to nitrous oxide (N₂O), a gas that in turn is lost to the atmosphere (DAL MOLIN, 2016).

2.3 CONTROLLED-RELEASE FERTILIZERS

The use of fertilizers is of great importance for the growth and quality of plants. Still, there are many losses of minerals to the environment, reducing their absorption by the plants and causing economic losses to the farmer. Nitrogen losses to the environment are around 40 to 70%, phosphorus losses are between 80 and 90%, and potassium losses are between 50 and 70%. (COSTA; VITTI; CANTARELLA, 2003; LARA CABEZAS et al., 1999; TRIVELIN et al., 2002; WU; LIU, 2008b).

Due to the high loss of minerals contained in fertilizers, and in particular nitrogen losses, the study and use of fertilizers with increased efficiency have been of great importance for increasing agricultural production, as well as for minimizing environmental pollution and economic losses (DU et al., 2008; MACHADO et al., 2011; TANG; KWON; LECKIE, 2009). Stabilized fertilizers can be defined as ones that present one or more stabilizing mechanisms that provide nutrient conservation in the applied form (TRENKEL, 2010). These fertilizers are produced so that losses to the soil and atmosphere are reduced, thus increasing the nutrient uptake by the crop. Fertilizers with increased efficiency are slow-release, controlled-release fertilizers, or stabilized fertilizers (CANTARELLA, 2007). Although not officially distinguished, slow-release fertilizers are usually products of microbial degradation, such as urea-formaldehyde or urea-aldehyde, while controlled-release fertilizers are mostly coated with sulfur films or polymers (TRENKEL, 2010).

Controlled release is applied in several areas to reduce the overdosage of drugs or agrochemicals and keep the concentration of active ingredients constant in the medium and according to need. Controlled release fertilizers contain nutrients required by the crop so that their availability is prolonged, increasing the intervals of application of the fertilizer in the soil (TRENKEL, 2010). The term "controlled-release fertilizer" is correct when the rate, pattern, and duration of the minerals release are known and adjustable during fertilizer production. However, the use of the term "slow-release fertilizer" requires the observation of a slower rate of release than usual but does not require the exact definition of the rate, pattern, and duration of release. The European Committee for Standardization has established three criteria that slow-release products must meet, these being: a maximum of 15% of the components can be released within 24 h, the release rate of these components cannot exceed 75% within 28 days, and at least 75% must be released within the time indicated (CEN, 2001; SHAVIV, 2001).

Slow or controlled release fertilizers present a gradual availability of the minerals they contain. Thus, the availability of nutrients can be adapted to the needs of specific crops or even

to the characteristics of the soil, allowing greater use of the fertilizer and consequently a lower cost to the producer. This gradual availability of minerals can be presented by fertilizers through coatings with polymers or proteins, making it semi-permeable; through the use of water-soluble compounds of low molecular weight, which are hydrolyzed slowly; or means that are still being studied (TRENKEL, 2010).

The use of these fertilizers has increased due to the constant need to increase productivity, decrease environmental damage, and reduce costs (SANTOS et al., 2015). These materials also have soil conditioning properties, improving water availability for the plants. Controlled release fertilizers present as advantages the regular supply of nutrients to the crop, a lower frequency of fertilization, reduction of losses, and reduction of root damage due to high salt content, among others (MESSA et al., 2016).

Thus, several materials have been studied to find solutions for a controlled release of nitrogen and other macronutrients and reduce losses by volatilization, leaching, and denitrification. The coating of urea granules with polymers, with sulfur, as well as the use of urease inhibitors, have been widely studied, but they have low adherence to service due to the high final cost of the product (GAGNON; ZIADI; GRANT, 2012; NASCIMENTO et al., 2013; SINGH et al., 2013). Other studies are being carried out to develop fertilizers with greater efficiency and lower costs, such as the incorporation of nutrients in composites or nanocomposites.

2.3.1 Composite materials

To produce controlled-release fertilizers, composite materials are formed, which have a continuous phase as a matrix and a dispersed phase as reinforcement or modifier, which combine in a hybrid structure. The final product presents the properties of interest of two initial constituents. If the dispersed phase has a nanometric order dimension, this material will be called a nanocomposite (WANG et al., 2001). The combination of a polymeric material with a clay mineral can, for example, confer differentiated mechanical, thermal, and diffusion properties of great interest (REN et al., 2008).

Many studies have been carried out to develop composite fertilizer materials for controlled or slow-release, most of which are nitrogen compounds (PEREIRA, 2014). These materials can decrease nitrogen loss by leaching and volatilization and increase the soil's water-holding capacity (YANG et al., 2013). The intercalation of urea complexed with magnesium into montmorillonite was studied by Kim et al. (2011) significant considerable suppression of

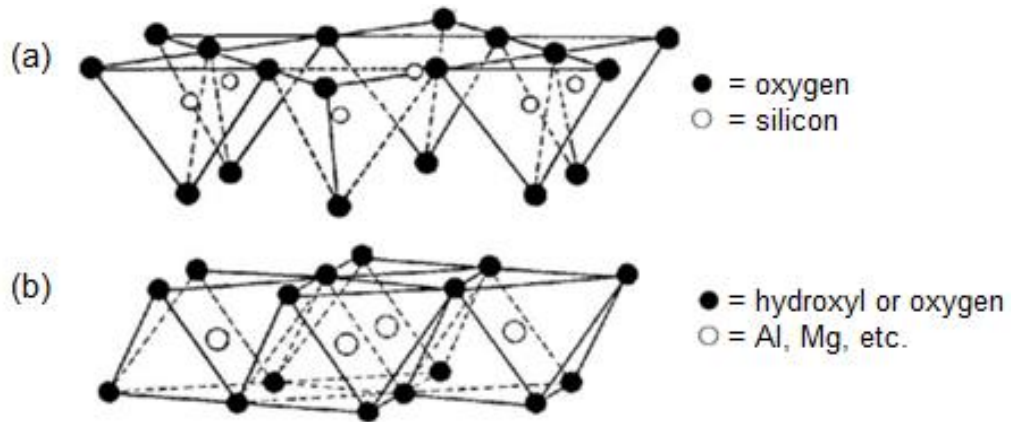
NH_3 and N_2O emission and greater N uptake by the crops as a consequent higher yield. Bortolin et al. (2013) have demonstrated that a hydrogel formed from polyacrylamide, methylcellulose, and montmorillonite shows a 200 times slower release of urea than pure urea. These studies indicate that clay minerals, especially montmorillonite, have attractive bases for slow or controlled release fertilizers.

2.3.2 Clay minerals

Clays are natural, earthy materials composed of fine minerals, which acquire plasticity when moistened, and are formed essentially by hydrated silicates of aluminum, iron, and magnesium (SANTOS, 1989). Clays are composed mainly of clay minerals and may contain, in smaller concentrations, organic matter, soluble salts, oxides, hydroxides, quartz, calcite, dolomite, feldspar, and amorphous minerals. The clay minerals, such as montmorillonite, correspond to the majority crystalline phase of the clays (GUGGENHEIM; MARTIN, 1995; SANTOS, 1989). Clay minerals can be defined as hydrated silicates with a layered crystalline network or fibrous structure (KÄMPF; CURI, 2003; SANTOS, 1989) or as phyllosilicate minerals and other minerals that render the clay plastic and harden by drying or calcination (GUGGENHEIM; MARTIN, 1995).

Clay minerals consist of fitted tetrahedral sheets and octahedral sheets that form stacked layers of varying numbers. The tetrahedral sheets are composed of individual tetrahedrons (ZO_4 coordination groups, where $Z = \text{Si}$ or Al) that are linked together by basal oxygen (Figure 5a). Octahedral sheets consist of individual octahedrons (coordination group YO_6 , where $Y = \text{Al}$, Fe or Mg and $\text{O} = \text{O}$ or OH) joined together laterally by sharing octahedral edges (Figure 5b) (KÄMPF; CURI, 2003; LEE; TIWARI, 2012). When a tetrahedron and an octahedron are joined, a 1:1 layer is formed. When two tetrahedral layers overlap a central octahedron layer, a 2:1 layer is formed.

Figure 3. (a) Tetrahedra of ZO_4 (where $Z = \text{Si}$ or Al) joined by sharing basal oxygen; (b) octahedra of YO_6 (where $Y = \text{Al}$, Mg or Fe , and $O = \text{O}$ or OH) joined by sharing edges.



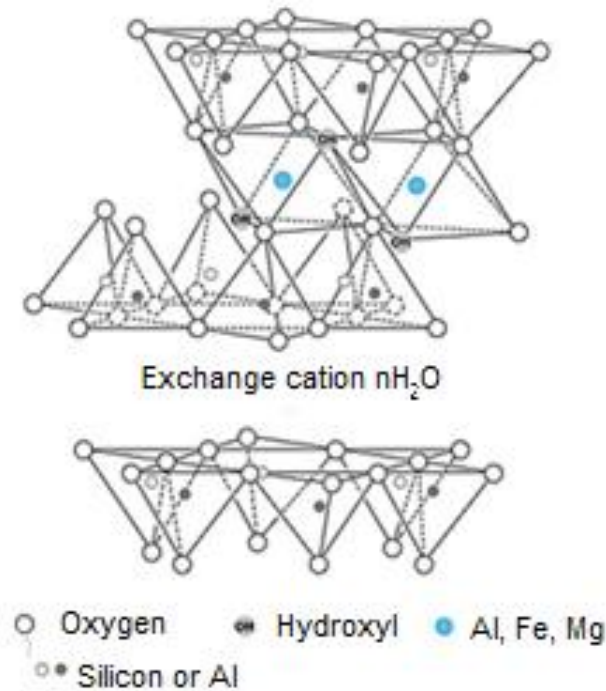
Source: Pereira (2014).

Smectites correspond to one of the most important groups of clay minerals present in soils and sediments, with a 2:1 structure. This group includes the montmorillonite, nontronite, saponite, hectorite, saunonite, beidellite, and volconscoite. (BORCHARDT, 1989; SANTOS, 1989).

2.3.3 Montmorillonite

Montmorillonite, the most common clay mineral of the smectite group, has the two leaves of the tetrahedral sites occupied by Si^{4+} ions and two-thirds of the octahedral sites filled by Al^{3+} and Mg^{2+} (Figure 6). Its general formula is $M_x(\text{Al}_4\text{-Mg}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$, its particles present sizes that can vary from $2 \mu\text{m}$ to $0.1 \mu\text{m}$ and are blade-shaped (SINHA RAY; OKAMOTO, 2003).

Figure 4. 2:1 structure of montmorillonite.



Source: Pereira (2014).

The isomorphous substitutions that occur inside the crystals are related to the presence of Mg^{2+} . Isomorphous substitutions are exchanges between cations of similar size and different charges at the site of crystal lattice formation. These substitutions within the layers generate an imbalance of charges on the external surfaces and in the interlayer regions, causing an excess of a negative charge, which is then compensated by the adsorption of hydrated cations (K^+ , Na^+ , and Ca^{2+}) in the interlamellar spaces, which can be exchanged for others of the same charge. Thus, the montmorillonite lamellae are essentially hydrophilic (BIDADI; SCHROEDER; PINNAVAIA, 1988; SARIER; ONDER; ERSOY, 2010). The type of montmorillonite is defined by the predominant exchangeable cation, if this cation is Na^+ , it is sodium montmorillonite, and if the predominant cation is Ca^{2+} , it is said to be calcium montmorillonite (MALLA et al., 1993; SANTOS, 1989).

When anhydrous montmorillonite, especially sodium montmorillonite, comes into contact with moist environments, the exchangeable cations become hydrated, and the basal spacing increases due to water entry. With water entry, the interlamellar cations become susceptible to being exchanged, stoichiometrically, for other charge-balancing cations. This property of montmorillonite clay minerals is called cation exchange capacity (CEC) (MALLA et al., 1993; SANTOS, 1989).

Montmorillonite presents interesting dispersion properties, besides its structure being composed of lamellae with a thickness of around 1 nm, resulting in a high specific area (PEREIRA, 2014). The most exciting properties of montmorillonite are high cation exchange capacity (CEC), high surface area, high adsorption capacity, and high plasticity. The high plasticity of this clay mineral results from the attraction forces between its particles and the lubricating action of the water present in the interlamellar spaces (MURRAY, 2000). An exciting feature of its properties is the reduced permeability to gases and liquids. The montmorillonite nanolayers have barrier properties, increasing the tortuosity of the diffusion path of water and oxygen molecules, for example (MA et al., 2013).

Montmorillonite is the main component of bentonite clay, and this is an abundant mineral in Brazil, where reserves are geographically distributed as 44.2% in Paraná, 24.1% in São Paulo, 21.2% in Paraíba, 8.5% in Bahia, and 2.0% in Rio Grande do Sul (SILVA, 2012).

2.4 BENTONITE- UREA INTERACTIONS

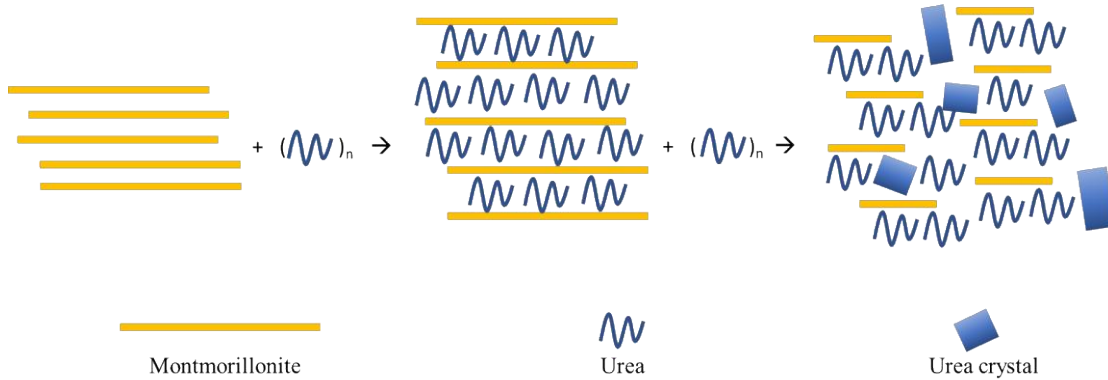
Little is known about what interactions occur between bentonite and urea. Therefore, one of the objectives of this work is to study the aspects related to this possible interaction. It is already known that bentonite can trap some liquids such as animal urine in its interior without releasing an odor, which in most cases is due to the volatilization of ammonia.

Bentonite is a low-cost product that is widely found in nature, is environmentally friendly, presents high cation exchange capacity (CEC), and promotes an increase in the efficiency of urea as fertilizer. Clay minerals are lamellar or fibrous nanostructures and are chemically composed of alum, iron, or magnesium metasilicates. When in contact with water, bentonite acquires some plasticity and becomes rigid after drying. Its high cation exchange capacity, large surface area, strong absorption, and swelling power have made bentonite a high-interest product for new technologies (ZOU et al., 2009).

An extruded material made of urea and montmorillonite (Mt) shows intercalation in interlamellar spaces (DJOUANI, 2011). A composition of 1:1 urea-montmorillonite presents a reduced urea crystallinity, indicating an interaction between urea and Mt, which does not occur if a higher concentration of urea is used in the formulation. The urea fraction in urea-Mt is crystalline, even if the interaction between both products can reduce it. This crystallinity of urea supports the hypothesis that Mt is a disperse phase, resulting in interlamellar displacement because of the insertion of urea (PEREIRA et al., 2012).

In extrusion, the solubilized urea intercalates in clay lamellar spaces, forming a correctly composite. If urea additions are made, they will not interfere in Mt interlamellar spaces but will crystallize independently, forming tiny urea crystals (Figure 7).

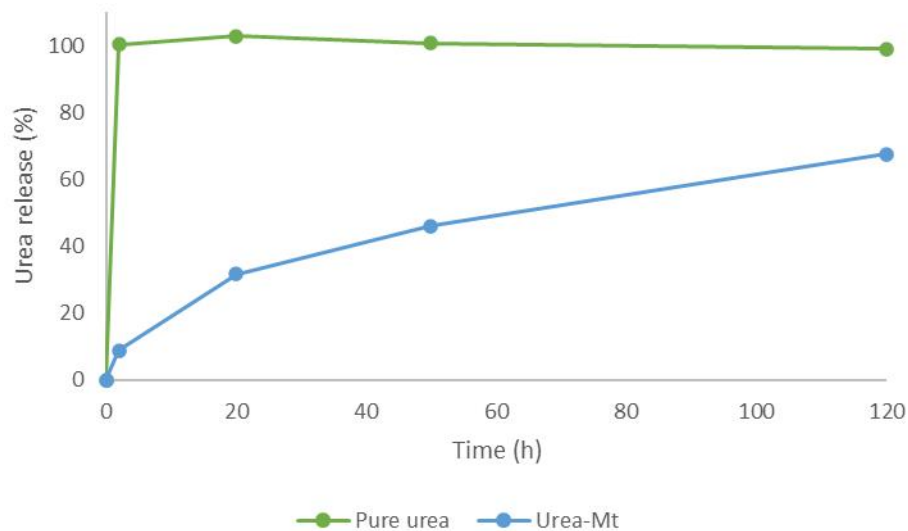
Figure 5. Urea intercalation in montmorillonite by extrusion process.



Source: Pereira et al. (2012)

In some experiments, Pereira et al. (2012) noted that urea and montmorillonite not extruded do not show any difference in urea release, proving that any interaction between urea and Mt occurs without previous processing as the extrusion. On the other hand, extruded 1:1 urea-Mt material retarded the urea release in water for up to 120 h (Figure 8).

Figure 6. Urea released from pure urea and urea-Mt extruded material.



Source: Pereira et al. (2012).

As stated at the beginning of this section, little is known about the interactions between bentonite and urea, but the work proposed by Pereira et al. (2012) presents exciting findings. These results clearly show that the intercalation of montmorillonite by urea is effective and is the central aspect of urea-Mt interaction. Despite this, more can be done to deeply understand the interactions between urea and bentonite, mainly considering the chemical element rather than the physical only.

2.5 AMMONIA VOLATILIZATION MEASUREMENT METHODS

2.5.1 Enclosure methods

The enclosure method is based on the insertion of the fertilized soil system into a closed-static chamber, which restricts air exchange, or a semi-open chamber that allows diffusive exchange. Ammonia mass recovered on a trapping medium, and the volatilization chamber area are the base for ammonia flux (ϕ) determination. In a close-dynamic chamber, ammonia flux ($\text{mg}/\text{m}^2\cdot\text{s}$) is determined as shown in Equation 10 (SHAH et al., 2012).

$$\phi = (C_{\text{out}} - C_{\text{in}}) \frac{Q}{A} \quad (10)$$

where C_{in} and C_{out} are the measured aerial ammonia concentration C_g (mg/m^3) in the inlet and exhaust airstreams, respectively; Q is the airflow rate (m^3/s) provided by a fan or compressed air; and A is the surface area (m^2).

Depending on how C_g is calculated, ammonia flux can be in real-time or as an average time. Ammonia flux can also be estimated from Equation 1 by wind tunnel experiments, an enclosure method. In this case, the tunnel is open at one end and has a fan at the other end, through which the ambient air is pulled over (SHAH et al., 2012).

2.5.2 Nitrogen recovery method

The method of nitrogen recovery is based on an N balance that includes all nitrogen addition and loss pathways, allowing the determination of total N recovered and the relative ammonia losses. This method may induce some errors in ammonia flux estimation because

volatilization and denitrification can simultaneously result in ammonia and other N gaseous species loss. In this case, the loss of gaseous nitrogen species can be underestimated (JAMBERT; SER; DELMAS, 1997; SHAH et al., 2012).

2.5.3 Efficiency study of volatilization measurement methods

Svensson (1994) developed an equilibrium concentration technique using a dynamic chamber. The chamber was composed of plastic coverture (0.4 m × 0.3 m × 0.18 m) and equipped with a battery fan (Figure 9). Ammonia flux was determined by the meteorological law of resistance (Equations 11, 12, and 13):

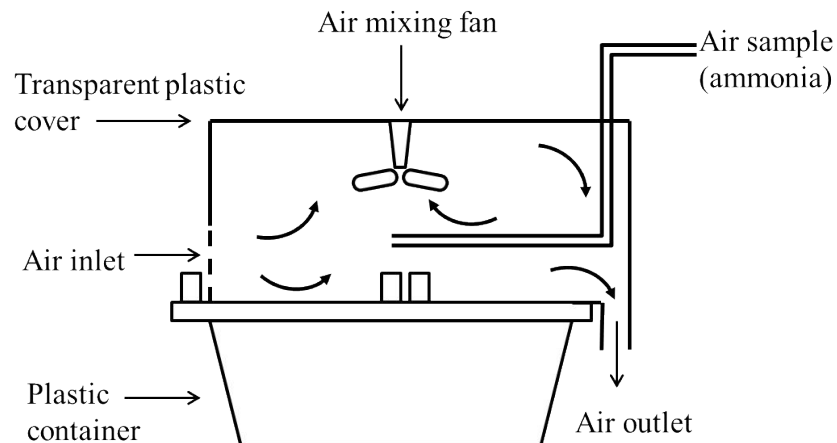
$$\phi = (C_{eq} - C_{a,z}) K_{z,a} \quad (11)$$

$$\phi_{ch} = (C_{ch} - C_a) \frac{Q}{A} \quad (12)$$

$$\phi_{ch} = (C_{eq} - C_{ch}) K_{z,ch} \quad (13)$$

where C_{eq} is C_g (mg/m^3) at the soil-air interface and $C_{a,z}$ is C_g at external ambient air; C_{ch} and C_a are C_g values leaving and entering the chamber; $K_{z,a}$ and $K_{z,ch}$ are mass transfer coefficient (m/s) outside and inside the chamber; and ϕ_{ch} is the ammonia flux at the chamber. Equations 12 and 10 are identical in an adequately vented chamber (SVENSSON, 1994).

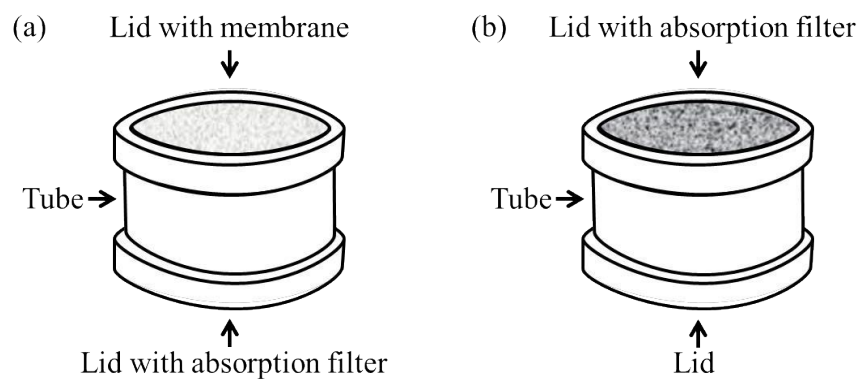
Figure 7. Dynamic chamber equipped with a battery fan to airflow.



Source: Svensson (1994).

Two ammonia traps of acid-soaked filters were placed into the volatilization chamber. One sampler has the filter exposed to the ambient air responsible for the molecular and turbulent ammonia flux and the other to the bottom, responsible only for molecular flux (Figure 10). The values of trapped ammonia, molecular diffusivity of ammonia in the air, and the physical dimensions of the samplers, C_{ch} and C_a , be obtained. Therefore, C_{eq} combines 11 and 12 equations, and the ammonia flux can be calculated. (SVENSSON, 1994).

Figure 8. Passive diffusion samplers for measuring NH_3 in the air (a) for concentration measurements and (b) for determining the laminar boundary layer.



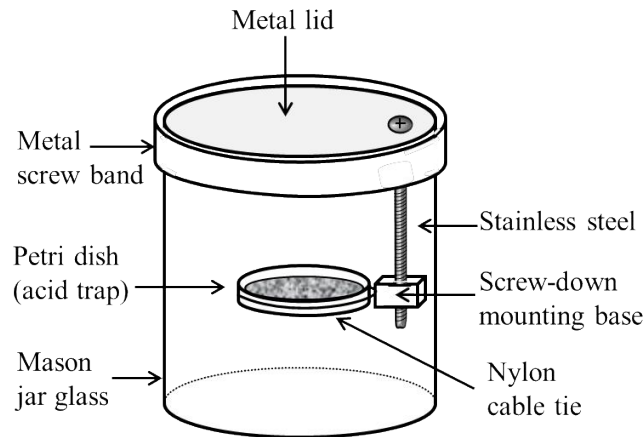
Source: Svensson (1994)

Mulvaney et al. (1997) developed an efficient and cost-efficient enclosure chamber using a Mason-jar for routine chemical extraction in the laboratory for inorganic nitrogen volatilization analysis of soil, water, and Kjeldahl digests. Some authors also applied this diffusion chamber to study ammonia volatilization and analyze t. Franzen et al. (FRANZEN et al., 2011) tested commercial ammonia volatilization inhibitors. In turn, Stiegler et al. (2011) performed a trapping efficiency study with ammonium sulfate enriched with a known amount of ^{15}N to trace the fate of the NH_3 applied to a turfgrass-based system.

Rogers et al. (2017) investigate the efficiency of a static diffusion chamber constructed as described by Mulvaney et al. (MULVANEY et al., 1997) in which the enclosure can be opened and closed to remove and replace the acid trap (Figure 11). To achieve an NH_3 conducive environment while minimizing N mineralization, immobilization, and nitrification, the soil pH was maintained at 7.8. To conduct the efficiency analyses, ammonium chloride (NH_4Cl) was applied at two rates of NH_4-N applied to the chambers, 45 mg and 90 mg. Volatilized NH_4 and NH_3 were captured with boric acid and disposed into the chamber in a Petri dish. Chambers were sampled in time intervals in which Petri dishes trap were removed

and replaced for subsequent sampling. Two methods were applied to determine ammonia volatilization: a mass balance measured by the difference in inorganic-N used and inorganic-N recovered and comparing the amount of nitrogen collected in the trap to the amount of nitrogen used.

Figure 9. Diffusion chamber made of Mason-jar.



Source: Mulvaney et al. (1997); Rogers et al. (2017); Stiegler et al. (2011).

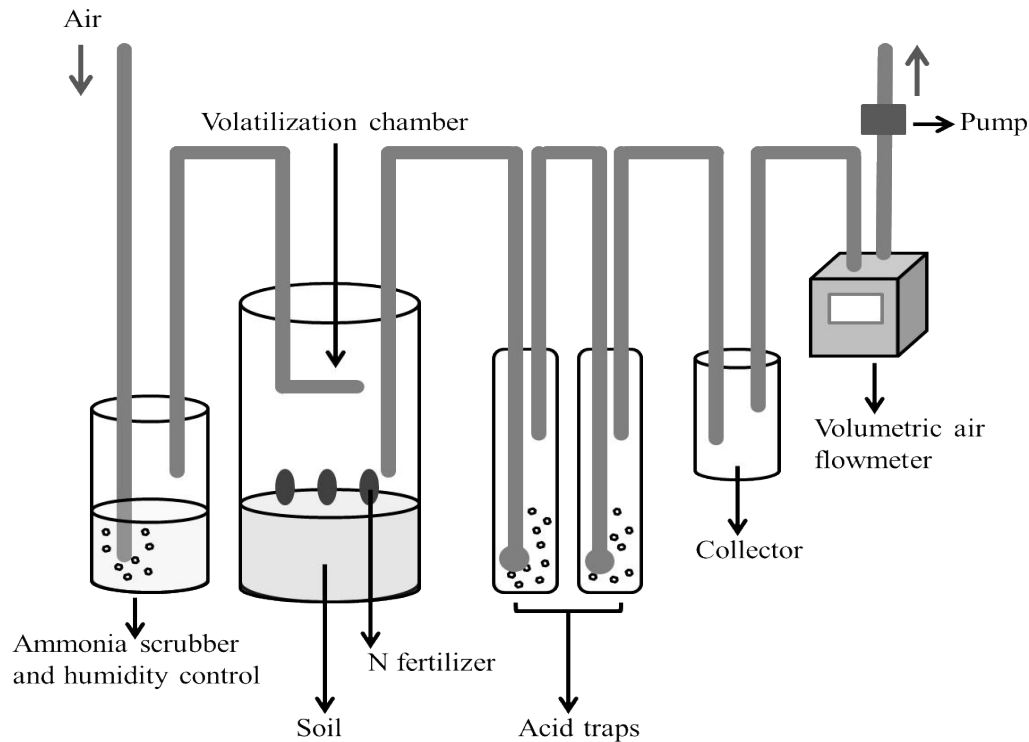
Marchal and Debell (1980) studied and compared four methods to measure ammonia flux from urea-based fertilizers applied on forest soils: closed-static, semi-open, closed-dynamic, and N recovery (^{15}N) methods. For chamber methods, the data were collected for 24 days and 41 days for N recovery experiments. The experiments were conducted with forest-grade urea (220 kg N/ha) on forest soil with vegetation cut on the surface. The experimental apparatus was made of Plexiglas and two ammonia traps composed of polyfoam disks soaked in H_2SO_4 .

Black et al. (1985) compared closed-dynamic chamber and N recovery methods in a 6-day study with urea (100 kg N/ha) applied on a 10 mm high pasture. The enclosure chamber was made of a 23 cm diameter PVC pipe inserted 7 cm into the soil. Urea was broadcast into the pipes sealed with clear Perspex covers. Acid traps (H_2SO_4) were placed into the chambers and were replaced daily for volatilized ammonia quantification.

Cadre et al. (2005) proposed an improvement on a laboratory system to estimate ammonia volatilization of low ammonia flux over a short timescale. The volatilization chamber was composed of a cylindrical glass (8.4 cm in diameter and 14.7 cm in high) equipped with two polyethylene tubes in the lid, one for the air inlet and the other for the air outlet (Figure 12). A pump provided the air flux through the chamber, and the airflow rate was monitored by

one volumetric airflow meter. The chamber was connected with an acid trap (H_2SO_4) to capture the volatilized ammonia. Air humidity and NH_3 content were controlled by a purifier containing H_2SO_4 and water. The efficiency of this method was determined by the ammonia volatilization of an ammonium chloride solution.

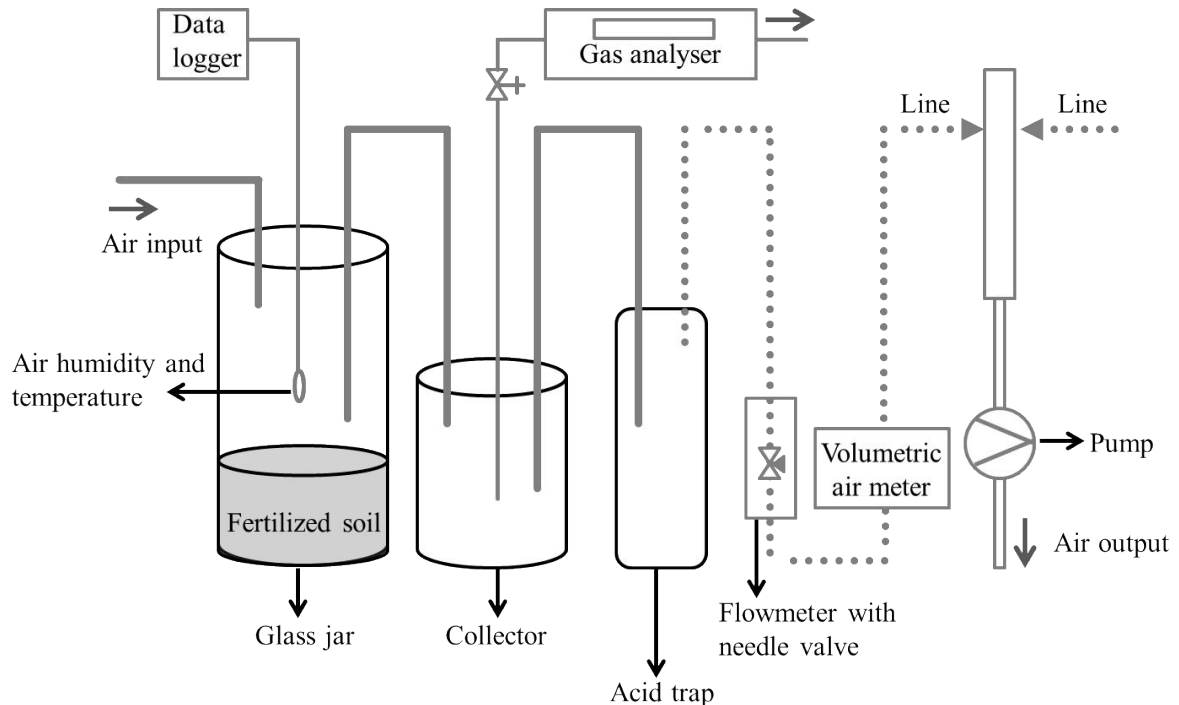
Figure 10. Volatilization chamber.



Source: Cadre et al.(2005).

Monaco et al. (2020) experimented with a similar Cadre et al. (2005) apparatus (Figure 13). An essential difference between these studies is placing a photoacoustic trace gas analyzer (P-TGA) system into the glass jar collector proposed m by Monaco et al. (2020). The authors conducted simultaneously an acid trap method to compare the results obtained by P-TGA.

Figure 11. Volatilization measurement system. Unbroken and dotted lines refer to Teflon and nylon tubes, respectively.



Source: Monaco et al. (2020).

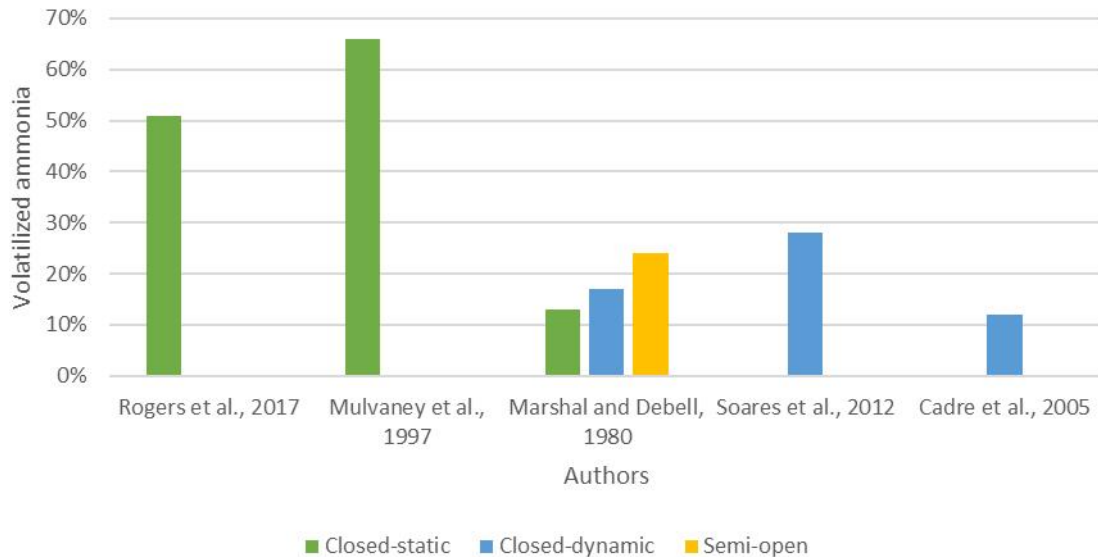
Soares et al. (2012) conducted experiments in volatilization chambers under controlled laboratory conditions. The chambers were made of cylindrical glass vessels with a capacity of 1.5 L and fed with air by a compressor. These chambers are closed at the top but with two holes of 0.5 cm in diameter and 5 cm below the lid. The experiments were conducted with surface-applied urea (300 kg N/ha) on cultivated soil classified as Red Latosol by EMBRAPA (2006). Volatilized ammonia was trapped into glass flasks containing boric acid and pH indicators (methyl red plus and bromocresol green). The boric acid solution was replaced daily until ammonia volatilization. Ammonia was determined by procedures presented by Cantarella and Trivelin (2001).

2.5.4 Summary of results – efficiency of methods

The studies presented by some authors showed the efficiency and applicability of laboratory apparatus and methodologies to determine ammonia volatilization. A summary of

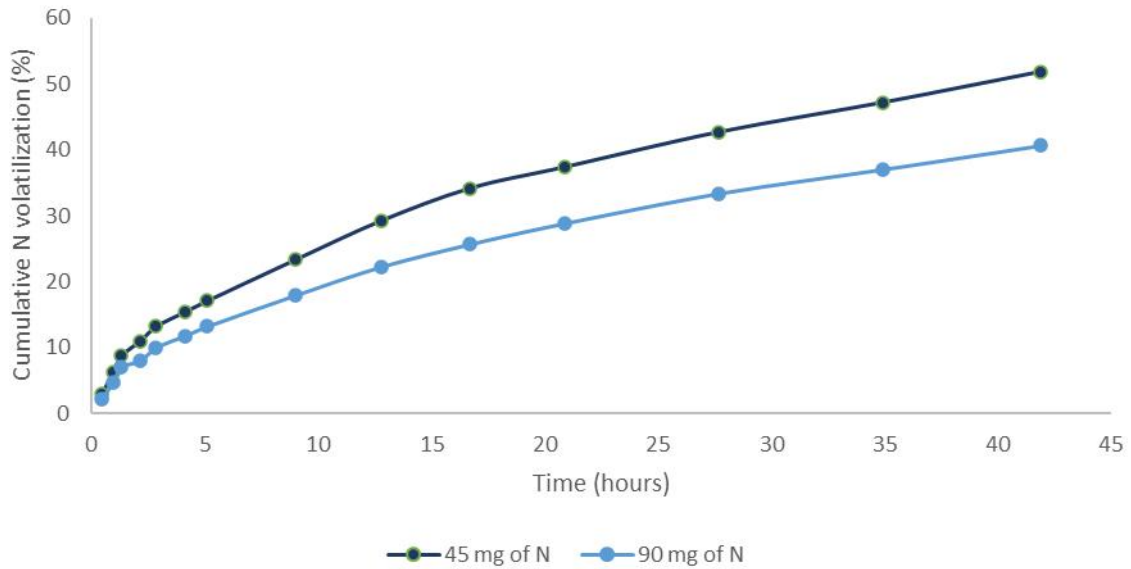
these studies' ammonia losses after soil fertilization results is presented in Figure 14. The results will be discussed next.

Figure 12. Nitrogen recovery as volatilized ammonia from fertilized soil.



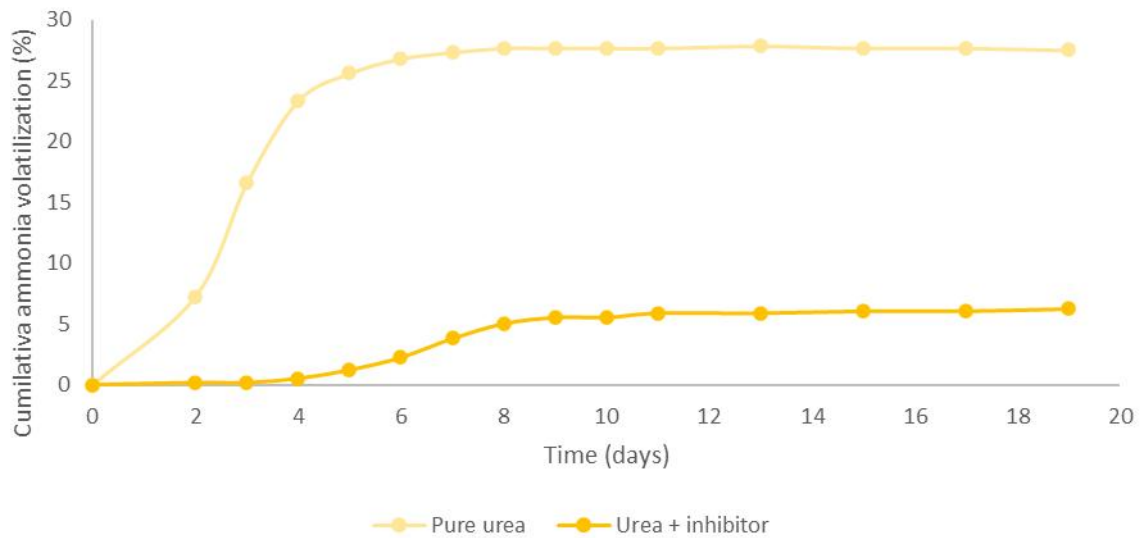
Rogers et al. (2017) studied NH_3 volatilization from 45 and 90 mg of initial nitrogen concentration in a closed-static chamber. This study was performed using artificial soil (sand and CaCO_3) to avoid other N transformations than NH_3 . After 40 h of analysis, cumulative ammonia volatilization reached 51% and 40% of total applied N for 45 mg and 90 mg of N used, respectively (Figure 15). The authors observed that nitrogen determinations obtained by the acid trap and mass balance method showed no significant difference. The authors concluded that questions remained concerning the system's efficiency due to the chamber's opening and closing to remove and replace the acid trap.

Figure 13. Cumulative percentage of N volatilized from 45 and 90 mg of applied N. Adapted from Rogers et al. (2017).



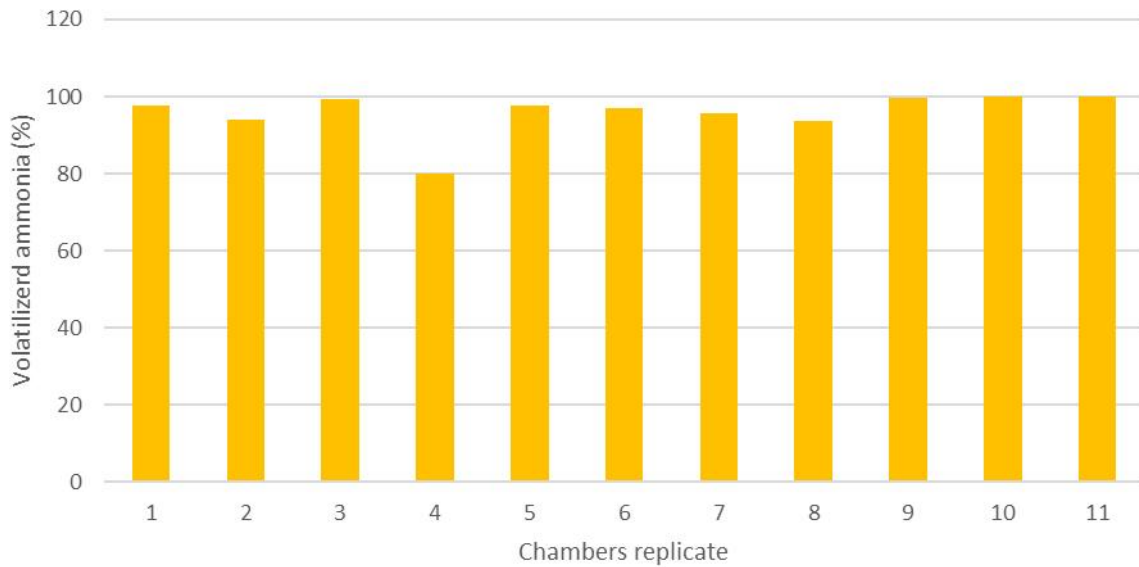
Soares et al. (2012) studied the volatilization of pure urea applied on the soil surface with or without urease and nitrification inhibitors. For pure urea applied to the soil surface, there was a recovery of 80% total nitrogen and 37% volatilized ammonia (Figure 16). This method was less effective than other studies' results. However, this result remains a good recovery percentage because it is not an efficient technique study. It is conducted with urea applied on the soil surface and not a pure solution with a known amount of nitrogen.

Figure 14. Cumulative ammonia volatilization of pure urea and urea with an inhibitor of urease. Adapted from Soares et al. (2012).



Cadre et al. (2005) studied the efficiency and application of a closed-dynamic system with two acid traps. The efficiency study was conducted only by analyzing NH_3 volatilization from an ammonium chloride solution pH 8.0. The authors also studied ammonia volatilization from soil samples treated with solubilized fertilizer pellets. With water as a medium, the closed-dynamic chamber allowed 98% of total N recovery in the first acid trap, proving its efficiency (Figure 17). Ammonia volatilization from treated soil reached 12% of total N applied, 39% lower than other studies for the same method, probably due to airflow, fertilization type, and soil difference. The authors concluded that it is necessary to control air humidity and avoid deposition on walls because it is a strong sink for ammonia, inducing a considerable underestimation.

Figure 15. Efficiency of ammonia volatilization chambers (%). Adapted from Cadre et al. (2005).



Mulvaney et al. (1997) also studied the efficiency of a closed-static chamber method by applying a standard solution prepared with $(\text{NH}_4)_2\text{SO}_4$, KNO_3 , and NaNO_2 , allowing the recovery of a known amount of applied nitrogen. Without soil, the total N recovery was 97%. The analysis conducted with soil resulted in 66% recovery. The volume and concentration of H_3SO_4 , as well as the concentration of N (mg), applied) were studied to recover 97% of N, and the results are presented in Table 2. The authors concluded that this method is efficient. Still, before routine use in the laboratory, the analysis should be done to check complete recovery from a known amount of N applied.

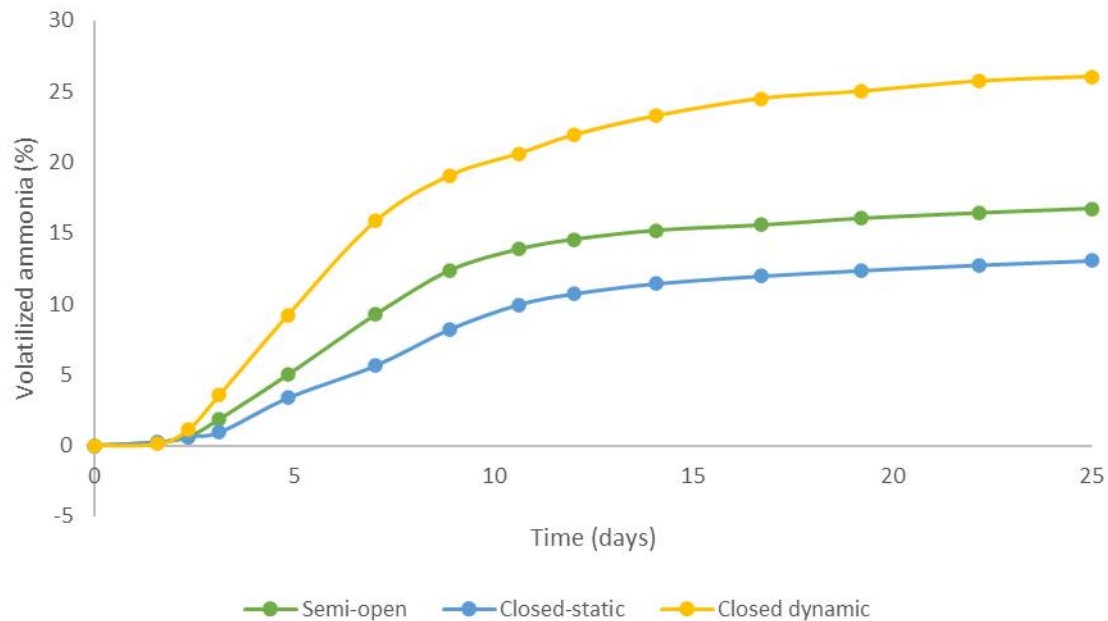
Table 2. Conditions for 97% N recovery from different concentrations and volumes of H_3BO_3 . Adapted from Mulvaney et al. (1997).

H_3BO_3 concentration (g/L)	H_3BO_3 volume (mL)	Maximum amount of N (mg)	Time (h)
20	3	0.3	28
20	7	2.0	72
40	4	4.0	30

Marshall and Debell (1980) showed that the restricted airflow reduced ammonia flux in the closed-static chamber, resulting in lower ammonia volatilization, reaching 14% of volatilization before 25 days of analysis. The semi-open chamber showed final volatilization of

17%, while the closed-dynamic chamber allowed volatilization of 24%. The higher ammonia flux, and consequently higher volatilization, was obtained from the closed-dynamic chamber method, and it was assigned to the airflow (Figure 18).

Figure 16. Ammonia volatilization (%) from semi-open, closed-static, and closed-dynamic chambers. Adapted from Marshall and Debell (1980).



It isn't easy to compare all works mainly because of the time of analysis of each research. Although, it is possible to conclude that analyzing the method's efficiency is more effective to do experiments in a water medium with a standard solution made of ammonium chloride, for example, as seen in Cadre et al. (2055) Mulvaney et al. (1997) works.

Close findings are presented by Rogers et al. (2017) and Mulvaney et al. (1997), who studied ammonia volatilization by standard solutions applied to the soil. Rogers et al. (2017) observed 40% volatilization from the 90 mg/N standard solutions, slightly less than the 66% obtained by Mulvaney et al. (1997). Some factors that may have provided this difference are the artificial soil used by Rogers et al. (2017) to reduce volatilization and the time. While Rogers et al. assays were performed over two days, Mulvaney et al. assays were carried out over three days.

Unlike Rogers et al. (2017), Cadre et al. (2005), and Mulvaney et al. (1997), the other researchers were not looking for validation of a methodology but rather volatilization tests by the same methods.

Finally, it is possible to conclude that closed-static, closed-dynamic, and semi-open methodologies are reproducible, with a particular eye for closed-static chambers. This volatilization chamber is less expensive, easier to build and handle, can be adapted to be kept closed during the entire experiment to avoid underestimations, and is widely cited in the literature as an efficient apparatus to measure ammonia volatilization under laboratory conditions. A summary of the general aspects of each cited paper can be seen in Table 3.

Table 3. Comparison of ammonia losses obtained by enclosure methods and total N recovery (as % applied N) for different studies.

Author	Method	Days of analysis	Chamber type	The efficiency of N recovery (%)	Cited by (selected)
Rogers et al., 2017	45 and 90 mg of N of ammonium chloride solution applied in artificial soil and ammonia acid trap.	2	Closed-static	45 mg/N: 51% 90 mg/N: 40%	Kira et al. 2019; Loomis et al., 2020; Rogers et al., 2019
Soares et al., 2012	Urea applied on the soil surface with or without urease and nitrification inhibitors	20	Closed-dynamic	Pure urea: 28% Urea + inhibitors 6%	Pan et al., 2016; Timilsena et al., 2005; Bordonal et al., 2018; Linquist et al, 2013; Cantarella et al., 2018; Zaman et al., 2012.
Cadre et al., 2005	Ammonium chloride solution and fertilizer pellets were applied to soil samples. Acid traps are used.	10	Closed-dynamic	Water: 98% Soil: 12%	Ruijter et al., 2010; Vaio et al., 2008; Monaco et al., 2012; Bertora et al., 2010; Vaillant, 2007; Smit et al., 2008; Stratton, 2014; Abeed et al.,2021.
Mulvaney et al., 1997	Use standard solutions a known amount of applied nitrogen in water and soil.	3	Closed-static	Water: 97% Soil: 66%	Khan et al., 2001; Stevens et al., 2005; Jacinthe et al., 1998; Adesemoye et al., 2010; Adams et al., 2011.
Marshal and Debell, 1980	Urea applied on soil.	42	Closed -static, closed-dynamic, and semi-open chambers	Closed-static: 13% Closed-dynamic: 24% Semi-open: 17%	Bouwman et al., 1997; Schlesinger and Hartley, 1992; Fenn and Hossner, 1995; Gioacchini et al., 2002; Barbanti et al., 2006; Goud et al., 2011; Johansson, 1984.

2.6 OPPORTUNITY AND INNOVATION

The main problem of Brazilian agriculture is the high need for fertilizer imports. Brazil is the only country in the world with large-scale agricultural production without autonomy in fertilizer supply. Brazil has large capacities for fertilizer production, but between 2016 and 2020 four Petrobras fertilizers plants were closed, instead of building new factories. The last plant to close was the Paraná Nitrogenated Fertilizer Plant (Fafen-PR), in 2020 (CHAPOLLA, 2022). Petrobras sold in February 2022 the Nitrogen Fertilizer Unit in Três Lagoas, Mato Grosso do Sul, to the Russian Group ACRON (Figure 19). This plant is estimated to be in operation by 2027 with a daily production of 3,600 tons of urea (BARROS, 2022).

Figure 17. Nitrogen Fertilizer Unit in Três Lagoas, Mato Grosso do Sul.



Source: Barros (2022).

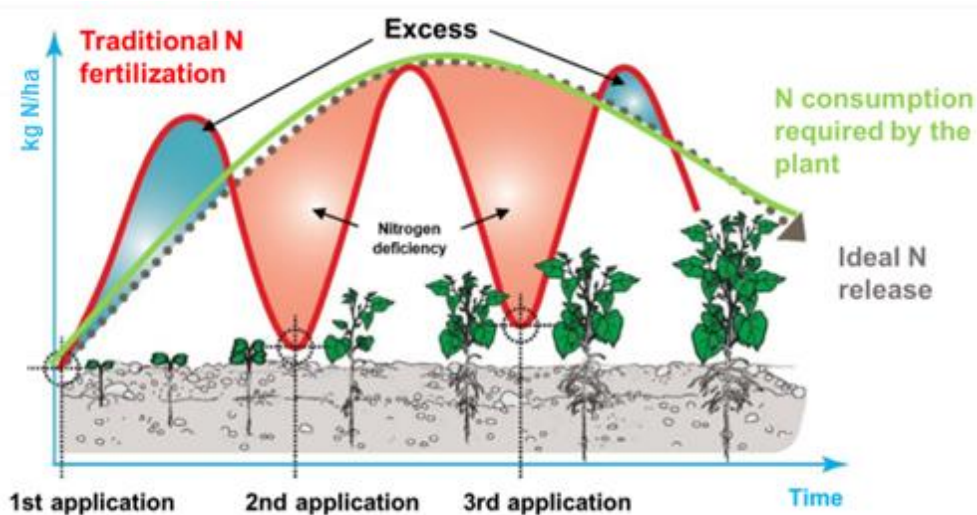
The federal government intended to launch a national fertilizer plan in December 2021, but there was a delay. Currently, 85% of the fertilizer used by farmers is imported from Russia. With the plan, the President estimates to bring this rate down to about 60% (CHAPOLLA, 2022). The new planned plant will have easy access to natural gas since the Brazil-Bolivia gas pipeline passes close to the site. Other plants that had been leased by Petrobras, in Bahia and Sergipe, need to bring natural gas by ship (BARROS, 2022).

Even decreasing the import requirement to 60%, this is still a high value. Also, pandemics and geopolitical conflicts will continue to occur, and farmers need to be increasingly prepared for a shortage in fertilizer supply. The use of alternative technologies and new knowledge can help the producer increase production efficiency without increasing the cost.

Urea is usually applied directly to the soil resulting in high ammonia losses by volatilization. With the increase in prices and a possible shortage of urea in Brazil, it is crucial to manage it consciously to avoid waste. The need for fertilizer triggers a series of socioeconomic problems, starting with the rise in prices of basic foodstuffs and biofuel, as has already been seen in 2021, decreasing food security and increasing the hunger and the number of people below the poverty line.

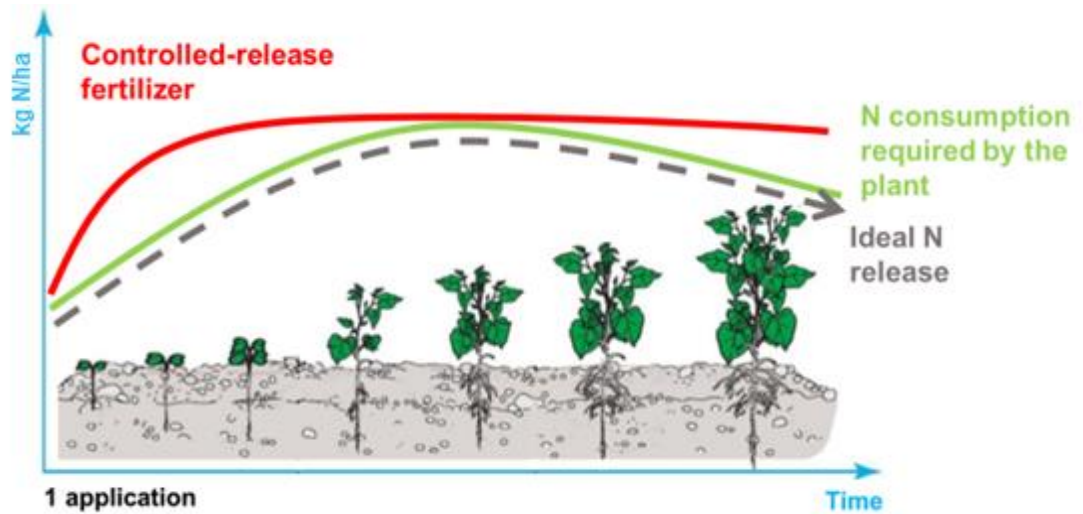
The ideal fertilizer releases nutrients synchronously with the crop's nutritional needs. In traditional N fertilization with urea, this ideal fertilization can be achieved doing consecutive applications as N availability decreases (Figure 20).

Figure 18. Ideal fertilization in a traditional system.



The use of controlled-release fertilizers (CEF) is an excellent alternative to applying urea directly to the soil because these fertilizers promote a release of nitrogen according to the plant's needs. This more prolonged release period allows the acquisition of smaller quantities of fertilizer, leading to a lower impact of the purchase cost of these fertilizers on the final consumer. Also, the use of CEF allows for only one application and avoids both the excess nitrogen in the soil and the lack of N in the plant (Figure 21).

Figure 19. Ideal fertilization with controlled-release fertilizer.



Another exciting aspect of controlled-release fertilizer is the reduction of nitrogen losses by volatilization and leaching, leading to a lower risk of soil and effluent contamination and better resource management. The production of controlled-release nitrogen fertilizers has been studied over the years, but generally, polymers, urease inhibitors, or encapsulation increases the cost of the final product. Bentonite is a low-cost nanostructured clay mineral widely found in Brazil. The fertilizer production based on bentonite and urea allows us to combine the high concentration of nitrogen in urea and the positive characteristics of bentonite.

The development and application study of a controlled-release fertilizer made of bentonite and urea can be an efficient, cost-effective, and environmentally friendly alternative to replace pure urea fertilizer. The bentonite-modified urea fertilizer (BUF) can improve the agricultural performance in fertilizer/crop, reducing the urea amount needed. Decreasing the Brazilian need for urea importation is essential in this critical moment and in the future. A lower urea use results in higher socioeconomic and environmental security, maintaining basic food prices, and reducing soil, atmosphere, and water damages.

However, to be used at an agricultural level, controlled-release fertilizer technology requires a breakthrough, mainly related to reducing costs and increasing knowledge about physicochemical interactions, nutrient desorption kinetics, and efficiency to field applications. As discussed, urea can be successfully inserted into bentonite interlamellar space by extrusion. This material can present exciting properties such as controlled-release nitrogen and lower ammonia volatilization than pure urea. Different methodologies are applied to study fertilizer efficiency, as shown in this section. A successful nitrogen release protocol must guarantee good fertilizer stability over the process conditions and reuse the analysis chamber for several cycles. Thus, the sample characterization and measurement of release kinetics and ammonia

volatilization using acceptable methods can be a potential solution to consecrating a new and controlled-release fertilizer to be applied in agricultural fields.

3 EXPLORING THE INTERACTION OF BENTONITE AND UREA FOR IMPROVED NITROGEN RELEASE IN FERTILIZERS

3.1 INTRODUCTION

Fertilizers are defined as any organic or inorganic material of natural or synthetic origin that can be added to soil to supply one or more essential nutrients for plant growth and development (VAIO et al., 2008). According to the United Nations Organization, the world population will reach 9.7 billion people in 2050 (DEPARTMENT OF ECONOMIC AND SOCIAL AFFAIRS, 2022). To meet the demand for food, there is a need to increase food production by 70% (SANTOS et al., 2015). Fertilizers are applied to the soil to increase agricultural productivity by providing essential elements for plant growth. However, between 40% and 70% of nutrients are lost through volatilization, erosion, and leaching (WU; LIU, 2008a). The amount of fertilizer loss varies based on factors such as soil characteristics, environmental conditions, crop type, and method of application (AYOUB, 1999).

The primary source of synthetic nitrogen fertilizers is atmospheric N_2 , transformed into ammonia (NH_3) by the Haber-Bosch process. In this process, fossil fuels provide nitrogen and hydrogen, which are subjected to high pressures and temperatures, resulting in NH_3 . Ammonia is the primary raw material for producing nitrogen-based fertilizers such as urea and various nitrate fertilizers (CANTARELLA, 2007).

Nitrogen is an essential element for plants because it acts in the composition of ATP, NADH, NADPH, chlorophyll, proteins, and enzymes. Due to its high mobility in soil, conducting studies to enhance the absorption and metabolism of nitrogen within the plant is of significant interest. Nitrogen fertilizers are highly soluble and do not leave any residue in the soil. They can increase soil acidity due to nitrification and have a high salinity index. Typically, nitrogen fertilizers do not contain secondary macronutrients in their formula, except for ammonium sulfate (BREDEMEIER; MUNDSTOCK, 2000).

Ammonia is generated as a result of nitrogen degradation by ammonium ion (NH_4^+) deprotonation, especially in alkaline soils. Ammonium can react with sulfate aerosols to form ammonium sulfate in the atmosphere and soil. Ammonia and ammonium sulfate increase acidification and eutrophication, causing negative economic and environmental impacts (SHAH; WESTERMAN; AROGO, 2006). In the absence of water, only mineral and non-volatile ammonium are present. In solution, ammonium is dissociated into NH_4^+ and NH_3 . The main factors that affect ammonia volatilization are the ammoniacal nitrogen concentration in

solution (soil, plant, and effluent) and its pH, the resistance to gas diffusion into the atmosphere, the soil type, and the temperature (SOMMER et al., 2003).

Urea $[(\text{NH}_2)_2\text{CO}]$ is the most employed nitrogen fertilizer because of its high concentration of nitrogen ($460 \text{ g}\cdot\text{kg}^{-1}\cdot\text{N}$) and presents the lowest cost per unit of nitrogen (CHIEN; PROCHNOW; CANTARELLA, 2009; DAL MOLIN, 2016). The volatilization of urea is more pronounced in alkaline soils, where the pH is above 7.5. In these soils, the urea is rapidly converted into ammonia gas by the enzyme urease, which is active under high pH conditions. Urea hydrolysis to ammonium bicarbonate $[(\text{NH}_4)\text{HCO}_3]$ causes an increase in soil pH that induces ammonia volatilization (CHIEN; PROCHNOW; CANTARELLA, 2009; SOARES; CANTARELLA; MENEGALE, 2012).

High pH in solution favors the formation of aqueous ammonia and H^+ , increasing NH_3 concentration in the solution and the gaseous phase. If the soil has pH values below 7, the main ammoniacal-N form will be NH_4^+ , and the potential for volatilization will be small. In contrast, if the soil presents higher pH values, the main structure will be NH_3 , and the potential for volatilization will be more significant (DASGUPTA; DONG, 1986).

The effect of initial soil pH can be overlaid by a strong interaction between the fertilizer, like urea, and the soil solution that induces hydrolysis and precipitation reactions. In this case, the soil cation exchange capacity (CEC) is essential. If the soil presents a large CEC, with high NH_4^+ retention, the volatilization potential of NH_3 tends to reduce because of the adsorption of NH_4^+ on the exchange site and consequent reduction of NH_4^+ concentration in soil solution (EMEP/EEA, 2019).

Ammonia losses are also dependent on wind speed, soil buffering capacity, soil moisture content, and low or high plant canopy. The presence of plant residues can increase urease activity and, consequently, increase NH_3 emission. Ammonia losses are higher in countries with tropical and subtropical climates with average volatilization of 20% – 60% of the applied nitrogen (BOUWMAN; BOUMANS, 2002; CANTARELLA et al., 2008; CHIEN; PROCHNOW; CANTARELLA, 2009; LARA CABEZAS; KORNDORFER; MOTTA, 1997).

Due to the high loss of minerals contained in fertilizers, and in particular nitrogen losses, the study and use of fertilizers with higher efficiency have been of great importance for increasing agricultural production, as well as for minimizing environmental pollution and economic losses (DU et al., 2008; MACHADO et al., 2011; TANG; KWON; LECKIE, 2009).

Slow or controlled-release fertilizers present a gradual availability of the minerals they contain. Thus, the availability of nutrients can be adapted to the needs of specific crops or even to the characteristics of the soil, allowing greater use of the fertilizer and consequently a lower

cost to the producer. Fertilizers can achieve a controlled release of minerals by employing different techniques. One approach involves coating the fertilizers with polymers or proteins, creating a semi-permeable layer. Another technique utilizes water-soluble compounds with a low molecular weight that undergo gradual hydrolysis. Additionally, research is ongoing to identify novel methods for achieving controlled release of minerals through fertilizers. (TRENKEL, 2010).

The use of these fertilizers has increased due to the constant need to increase productivity, decrease environmental damage, and reduce costs (SANTOS et al., 2015). These materials also have soil conditioning properties, improving water availability for the plants. Controlled-release fertilizers offer several advantages over traditional fertilizers. They provide a steady and consistent supply of nutrients to the crops, which leads to better plant growth and higher yields. Additionally, they require less frequent application, which can result in cost savings and less labor. Controlled-release fertilizers also reduce nutrient losses due to leaching and volatilization, which is beneficial for the environment. Furthermore, they can help reduce root damage caused by high salt concentrations in the soil, promoting healthier and more robust plants. (MESSA et al., 2016).

Several materials have been investigated to address the challenge of achieving a controlled release of macronutrients like nitrogen while minimizing losses due to leaching, denitrification, and volatilization. Coating urea granules with polymers or sulfur, as well as using urease inhibitors, has been extensively researched. However, these methods have limited practical application due to their high cost. To overcome this challenge, researchers are exploring alternative approaches such as developing fertilizers with increased efficiency and lower costs. For instance, the integration of nutrients into composites or nanocomposites is a promising area of investigation. (GAGNON; ZIADI; GRANT, 2012; NASCIMENTO et al., 2013; SINGH et al., 2013). Nanocomposites based in bentonite clay and organic molecules are a low-cost effective option, compared to the others cited composites, to obtain slow-release fertilizers once bentonite occurs naturally in mines worldwide, and it has a nonexpensive and large-scale extraction (HELAL et al., 2023). The development of novel slow-release fertilizers based on clay minerals are a promising area of research that has gained increasing attention from scientists and academics due to their unique properties as nanomaterials.

This paper proposes the study of a slow-release nitrogen fertilizer based on a montmorillonite matrix. Montmorillonite is the main component of bentonite, a nanostructured clay mineral formed essentially by aluminosilicates with high hydro plasticity, and and ability to exchange ions in aqueous solution (SANTOS, 1989). Montmorillonite presents suitable

dispersion properties, besides its structure being composed of lamellae with a thickness of around 1 nm, resulting in a high specific area (PEREIRA, 2014). Important features of montmorillonite are high CEC, high surface area, and high adsorption capacity, besides remarkable plasticity. Moreover, it presents reduced permeability to gases and liquids, because the nanolayers have barrier properties, increasing the tortuosity of the diffusion path of water and oxygen molecules, for example (MA et al., 2013).

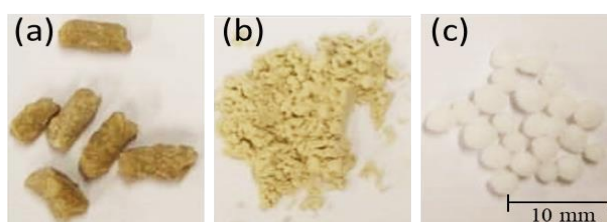
The present study provides a detailed characterization of a slow-release urea nanocomposite based on intercalation into montmorillonite obtained by an extrusion process. This process is based on the intercalation of urea molecules in the interlayer spaces of montmorillonite to form a bentonite-modified urea fertilizer (BUF).

3.2 MATERIAL AND METHODS

3.2.1 Materials

Bentonite, bentonite-urea fertilizer pellets (Figures 1a and 1b), Red Latosol, and Quartzenit Neosol were provided by T-Minas (Quatro Barras, PR, Brazil). Urea ($[(\text{NH}_2)_2\text{CO}]$), was obtained from Neon (Figure 20c).

Figure 20. Visual aspects of: (a) bentonite-urea fertilizer (BUF); (b) pure bentonite; (c) pure urea.



The following chemicals (purchased from Neon) were used: magnesium oxide (MgO 97%), sulfamic acid (H_3NSO_3 98%), sulfuric acid (H_2SO_4 0.1 N), boric acid (H_3BO_3 99.8%), bromocresol green ($\text{C}_{21}\text{H}_{14}\text{Br}_4\text{O}_5\text{S}$ 99%), methyl red (as a water-soluble salt) ($\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2$ 99%), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$ 99%), sodium nitrite (NaNO_2 99%), sodium sulfate anhydrous (Na_2SO_4 99%), pentahydrate copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 98%), phenolphthalein in solution ($\text{C}_{20}\text{H}_{14}\text{O}_4$ 1%), hydrochloric acid (HCl 0.1 N) and ethanol ($\text{C}_2\text{H}_6\text{O}$ 95%) were used as well. All chemicals were of analytical grade and used without further purification.

3.2.2 Characterization methods

Soil active acidity was determined by the pH in water with a ratio of soil/water of 1:1 in volume. Soil samples (10 cm³) were placed into a beaker, and 10 mL of water was added. After 30 min, the mixture was stirred, and the pH was measured.

Total nitrogen was determined by the Kjeldahl method (BREMNER. J. M., 1965). In this method, N in the sample is reduced into NH₄⁺ by H₂SO₄ digestion with salts and catalysts to accelerate the reaction.

Powdered samples of bentonite, urea, and BUF blended with potassium bromide (1 mg of sample to 200 mg of KBr) were analyzed by Fourier-Transform Infrared (FTIR) spectroscopy. The objective was to identify chemical bonds and consequently, the functional groups presented in urea, T-Minas bentonite (Bentonite), and T-Minas fertilizer (BUF). For spectrum integration of each sample, 24 times scan at 4 cm⁻¹ scanning resolution was done. Samples were scanned in the region of 4000-400 cm⁻¹ IR spectra.

Powdered samples of bentonite, urea, and bentonite-urea fertilizer (BUF) were analyzed by X-Ray Diffraction (XRD) to access their crystallinity. The samples were scanned between 5° to 60° (2θ) in an X-ray diffractometer with monochromatic Cu Kα radiation (λ = 0.1546 nm), continuous scanning at 0.05° scanning speed, and a measuring time of 0.8 s per step, operating at 40 kV and 40 mA. The interplanar spacing (*d*) was obtained from Bragg's Law diffraction equation (Equation 14).

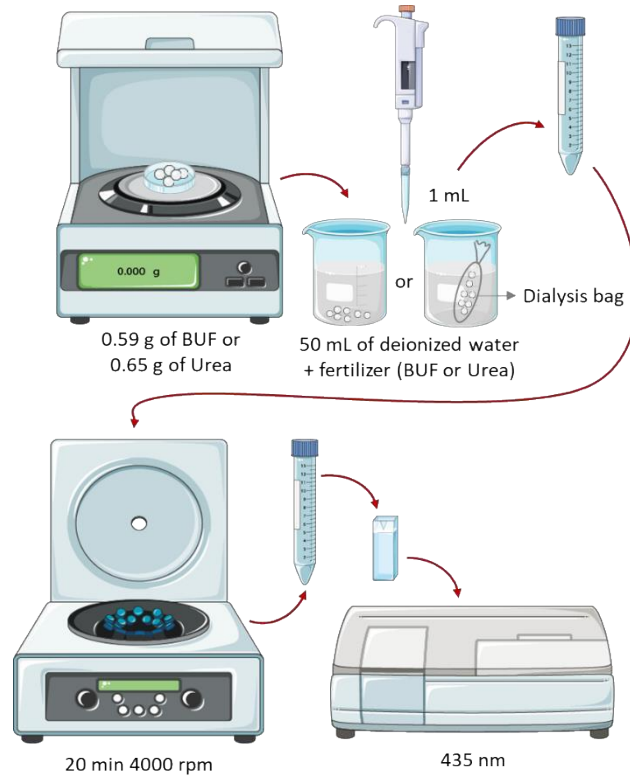
$$2d \sin \theta = n\lambda \quad (14)$$

where *n* is the order of reflection (*n*=1), and θ is the refraction angle.

3.2.3 Release rate of urea in water

To investigate the urea release of BUF and pure urea in the function of time, 0.45 g corresponding nitrogen was placed in a beaker with 50 mL of deionized water. The beakers were sealed to reduce evaporation losses. Aliquots of 1 mL were collected at different intervals over 10 days and centrifuged for 20 min at 4000 rpm (KASVI, K14-0815C) (Figure 21).

Figure 21. Scheme of the methodology for measuring the release rate of urea.



Another release rate analysis was conducted, over 24 h, by separating the sample from the water with a dialysis tube cellulose membrane (avg. flat width 43 mm, Sigma-Aldrich), permeable to water and urea, to protect the samples avoiding the dispersion of the particles and to maintain a low urea concentration around urea and BUF, for example. In this case, as urea is released, it continuously diffuses out of the membrane because of the concentration gradient, reflecting the acceleration of the release of urea out of the system (membrane) as shown in Figure 22. The determination of released urea concentration in an aqueous solution was based on measuring the absorbance of the sample using a UV-vis spectrophotometer (Hitachi U-1900 UV-Vis) at 435 nm, according to the method of Petersen & Petersen (1961).

To investigate the urea release kinetics from water BUF and pure urea dissolution, different mathematical models were assessed (BRUSCHI, 2015). The kinetics were determined by the best fit of experimental data versus time. The kinetic models are fitted with the first-order release model (Eq. 15). The semiempirical power law model of Korsmeyer-Peppas was also used to determine the diffusion type (Eq. 16). (KORSMEYER; PEPPAS, 1981)

$$\text{Log } Q_t = \text{Log } Q_0 - K_1 t/2.303 \quad (15)$$

$$Q_t = K_{KP} t^n \quad (16)$$

where Q_t is the fraction of urea released (%) at each time point (t); Q_0 is the initial percentage of urea (%); K_1 is the first-order release kinetic constant (h^{-1}); K_{KP} is the release kinetic constant according to the Korsmeyer-Peppas' model (h^{-1}); n is the diffusion exponent.

The value of the diffusion exponent n in the Korsmeyer-Peppas' model indicates the urea release mechanism. The type of release correlated with the n value is shown and described in Table 1. Higuchi's release model corresponds to an $n = 0.5$ (HIGUCHI T., 1963).

Table 4. Type of diffusion related to the diffusion exponent value.

Diffusion exponent value	Type of diffusion
$0 < n < 0.45$	Hindered Fickian diffusion (diffusive release and non-swellable matrix)
$n = 0.45$	Fickian diffusion (diffusion is the main release mechanism)
$0.45 < n < 1.0$	Non-Fickian diffusion (release follows both diffusion and erosion-controlled mechanisms)
$n = 1.0$	Zero-order diffusion (kinetics governed by degradation and relaxation or degradation of monolithic systems)

3.2.4 Ammonia determination in air

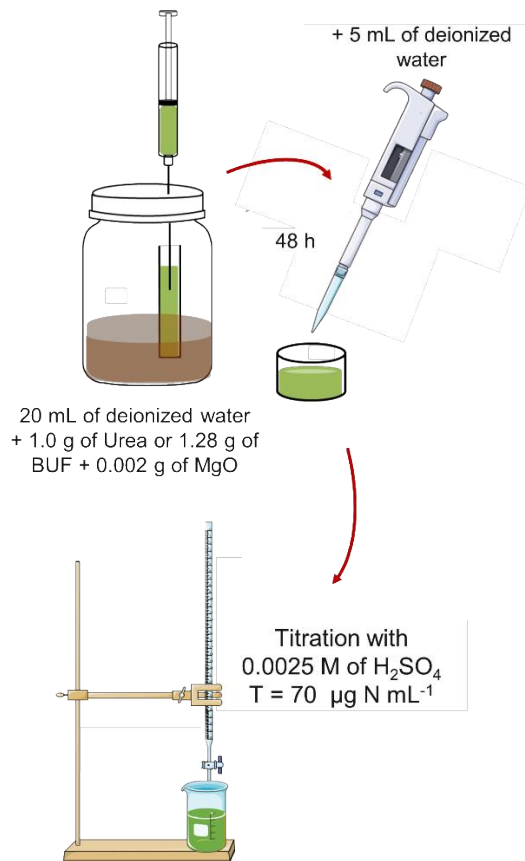
3.2.4.1 Ammonia volatilization of fertilizer in water

To determine NH_4^+ losses by volatilization, the mass of 1.0 g of urea and 1.28 mg of BUF were poured into the volatilization chambers with an aliquot of 20 ml of deionized water and mixed with 0.2 mg of MgO. As a control, water was also added into the volatilization chamber and mixed with 0.2 mg of MgO. A Petri dish with a boric acid indicator was attached to the jar lid, and the chamber was closed. The volatilization chamber was maintained at 25 °C for diffusion. After 48 h of complete diffusion of NH_3 into the H_3BO_3 solution, the petri dish was removed from the chamber, and 5 ml of deionized water was added to the plate. Ammonium-nitrogen in the H_3BO_3 solution was determined by titration with 0.0025 M H_2SO_4 from a micro burette (Figure 22). The N amount liberated by air diffusion was calculated from Equation 17.

$$[N] = (S - C) * T \quad (17)$$

where $[N]$ is the concentration of N in $\mu\text{g mL}^{-1}$; S (mL) is the volume of H_2SO_4 used in the titration of the sample; C (mL) is the volume of H_2SO_4 used in the titration of control; and T is the titer of titrant (for $0.0025 \text{ M H}_2\text{SO}_4$, $T = 70 \mu\text{g N mL}^{-1}$).

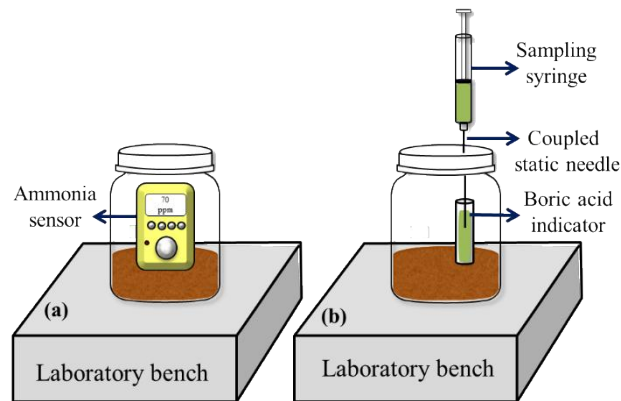
Figure 22. Scheme of the methodology for measuring the ammonia volatilization of the fertilizers in water.



3.2.4.2 Ammonia volatilization of fertilizer in soil

To obtain ammonia volatilization of fertilizers in the soil, volatilization chambers (Figure 4) were prepared by pouring 200 g of soil sample and 20 mL of deionized water into each chamber. Pure soil and soil with bentonite were the control reference in each experiment (MULVANEY et al., 1997; ROGERS et al., 2017; STIEGLER et al., 2011). The fertilizers were added to each chamber to achieve a nitrogen concentration equivalent to 200 kg ha^{-1} of N.

Figure 23. Closed static volatilization chamber with soil + fertilizer equipped with: (a) an ammonia sensor; (b) a boric acid indicator.



An ammonia sensor (AKSO SGTP-NH₃) was coupled to the volatilization chamber to obtain the concentration of volatilized ammonia inside the chamber (Figure 23a). In chambers that conducted boric acid indicator analysis, 50 mL of 2% of this ammonia sequestrant was placed into a cylinder container in the middle of the volatilization chamber (Figure 23b). Ammonium-nitrogen in the H₃BO₃ solution was determined by titration with 0.01 mol/L sulfuric acid was carried out on days 0, 2, 3, 12, and 30. For this analysis, 1 mL of the boric acid indicator was extracted from the container, and the same volume was replaced with a new boric acid solution. The experiment was conducted in triplicate for each fertilizer and control. Ammonia was adsorbed by a 2% boric acid solution with bromocresol green and methyl red. A comparison between both methods to measure the ammonia concentration was done to validate the sensor use, once it simplifies the overall procedure with less intervention in the volatilization chamber.

Volatilized ammonia was determined by titration with 0.01 mol/L sulfuric acid standard solution on various days of incubation. The cumulative volatilized ammonia was determined using Equation 18 (FERTAHİ et al., 2020).

$$Q_t = \frac{V_e \sum C_t + V_0 C_f}{C m_o} \quad (18)$$

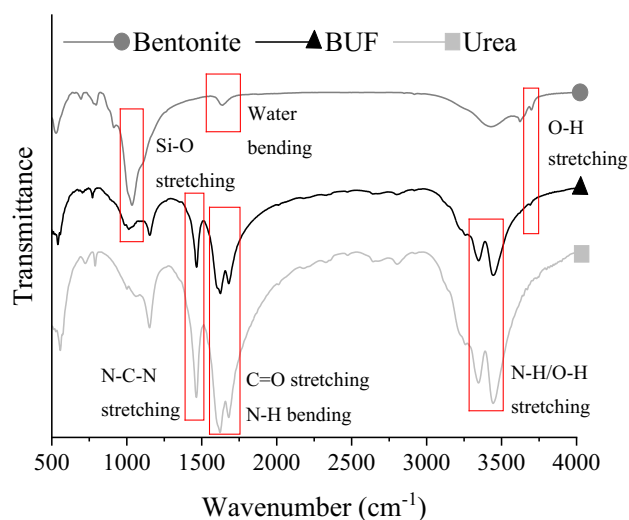
where Q_t is the cumulative amount of volatilized ammonia (ppm); V_e (mL) is the sampling volume; V_0 (mL) is the initial volume of the experimental medium; C_t (g) and C_f (g) are the correspondingly representative concentrations of N at sampling time t and at the last sampling time; $C m_o$ (g) is the total weight of nitrogen in the fertilizer.

3.3 RESULTS AND DISCUSSION

3.3.1 Identification of functional groups

Figure 5 shows the FTIR spectra of bentonite, urea, and BUF. BUF has identical spectra as urea but with lower signals. These less marked signals can be seen as physical interaction between urea and bentonite. As is marked in Figure 24, it is possible to see that BUF has a signal at the 1035 cm^{-1} wavenumber due to a Si-O-Al bending, corresponding to the octahedral layers of the aluminosilicate characteristic of montmorillonite clays (DE OLIVEIRA et al., 2016). The absorption band at 1620 cm^{-1} is attributed to the angular vibration of the OH group related to the adsorbed water in bentonite and C=O from the amide group (CONH_2) of urea, as well as the N-H bending (DE OLIVEIRA et al., 2016). With the results of FTIR spectra, it is seen that bentonite and urea have some interaction as Van der Waals and electrostatic attraction (Figure 25).

Figure 24. FTIR spectra of bentonite, bentonite-urea fertilizer (BUF), and pure urea.



The FTIR spectra of BUF displayed peaks due to bentonite and urea, confirming the presence of urea in the bentonite matrix. Evidence of successful exfoliation of bentonite and interaction between bentonite and urea are provided by the N-H bending vibrations (1640 cm^{-1} and 3450 cm^{-1}), O-H stretching vibration (3698 cm^{-1}), and carbonyl stretching vibrations of urea (1700 cm^{-1}). The wavenumber shift in silicon–oxygen bond from 1035 cm^{-1} in the bentonite FTIR pattern to 1029 cm^{-1} in the BUF pattern is due to electron density changes in the bentonite layers as a result of intercalation with urea molecules. This shift in Si-O stretching

frequency suggests that there are important interactions between bentonite and urea to form BUF (Figure 25). Similar results were found by Mdusanka et al. (2017) for encapsulated urea in hydroxyapatite and montmorillonite (MADUSANKA et al., 2017).

Figure 25. Zoom in FTIR spectra of bentonite and bentonite-urea fertilizer (BUF) to show Si-O and O-H stretching shifts after bentonite-urea extrusion.

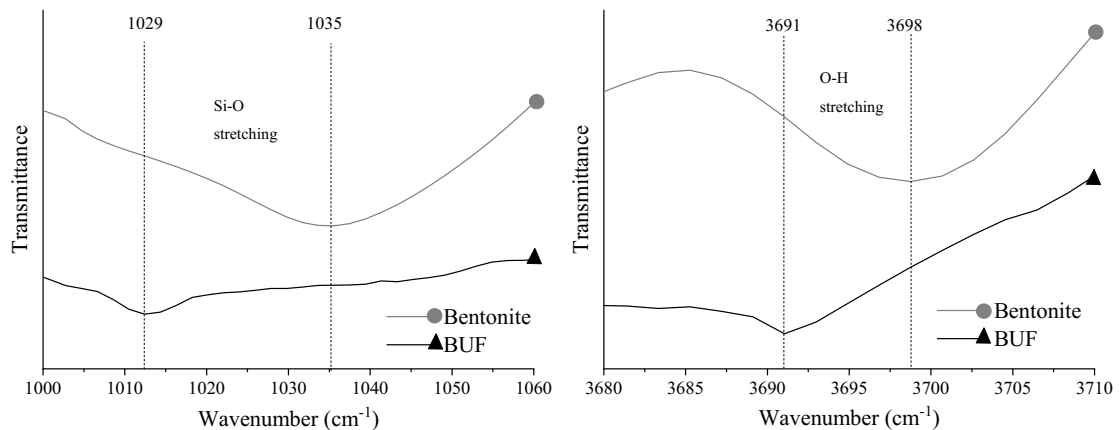
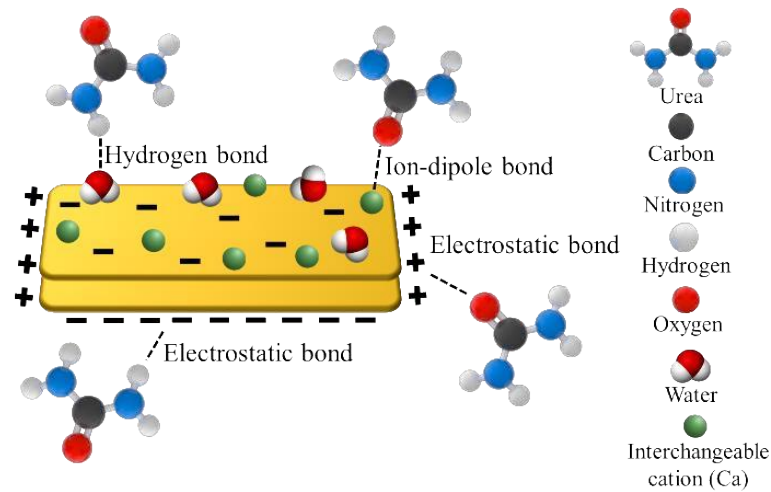


Figure 26 presents a schematic diagram of the proposed binding mechanism of urea with bentonite. Where is possible to note the hydrogen bond with the H present in urea molecule and the oxygen of the bentonite adsorbed water as seen in 3600 cm⁻¹ vibration of Figure 5. This reaction forms ammonium carbonate ((NH₄)₂CO₃), which in contact with water, forms ammonium that is available to plants, avoiding volatilization in the form of ammonia. Another important interaction between urea and bentonite is the ion-dipole bond between the Ca²⁺ and the oxygen from the reaction of the urea, in this case O²⁻. Electrostatic bonds are also present in the bentonite-urea interaction as N-C=O of urea and functional groups containing O of bentonite, which can prevent N loss through ammonia volatilization. Also, we have electrostatic attraction between NH₄⁺ and negatively charged surfaces.

Figure 26. Schematic diagram of the proposed binding mechanism of urea with bentonite.

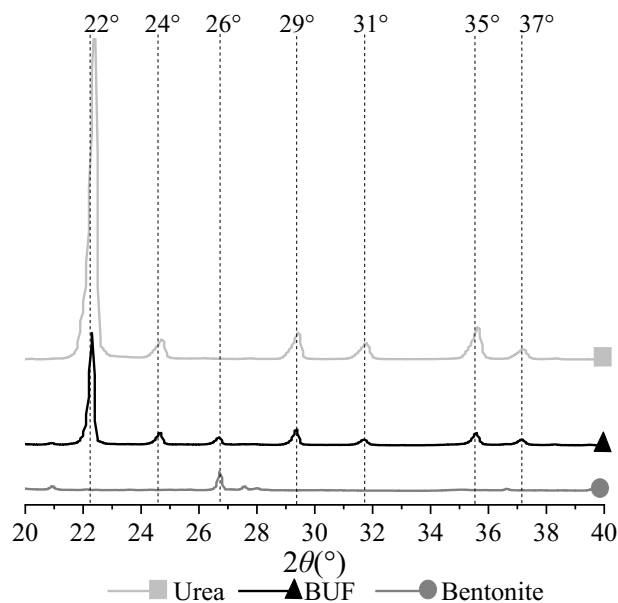


3.3.2 Exfoliation and intercalation of urea in bentonite

X-ray diffraction analysis proceeded to monitor the exfoliation and intercalation of urea into bentonite to form bentonite-urea fertilizer (Figure 27).

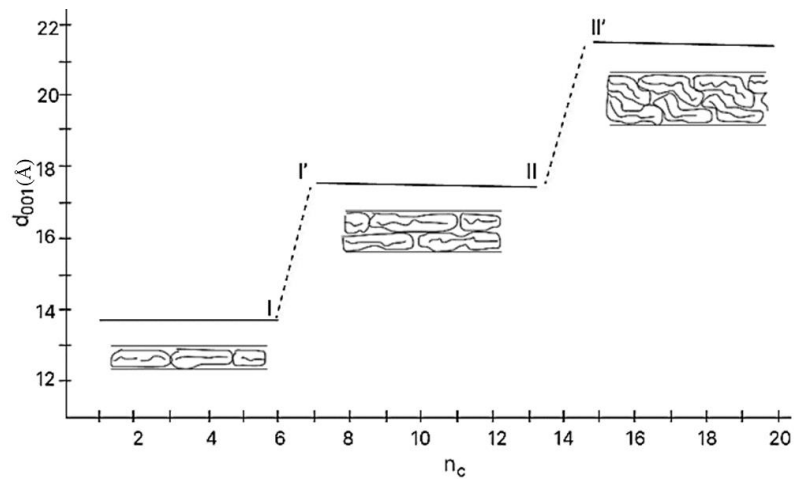
The interlamellar distance is calculated by Bragg's law, presented in Equation 14. In this case, to determine the distance d , the wavelength, λ , is given by 0.1542 nm, referring to the wavelength of Cu radiation; the n is given by 1, and the angle θ is observed in the graph.

Figure 27. X-ray diffraction (XRD) patterns of bentonite, bentonite-urea fertilizer (BUF), and pure urea.



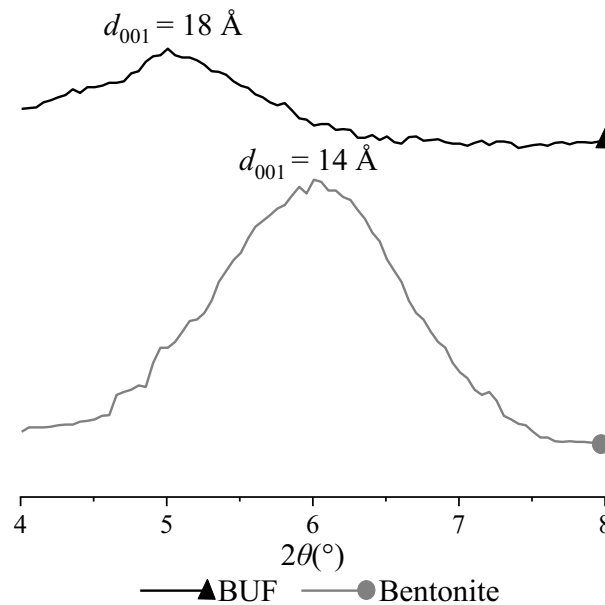
Most of the diffraction angle signals present in urea also appear in the BUF pattern (22° , 24° , 26° , 29° , 31° , 35° , and 39°), but with less intensity due to a decrease in crystallinity of the urea compared to the BUF. It occurs because of the extrusion process between bentonite and urea.

Figure 28. Graph adapted from Lagaly, Fernandes & Weiss (1976) showing the increase in the basal space (d_{001}) of montmorillonite clays as a function of the chain size of quaternary salt cations, n_c (number of carbon per chain), which influences the formation of monolayers (I), bilayers (I'-II), and pseudo trilayers (II') between the lamellae (LAGALY; FERNANDEZ GONZALEZ; WEISS, 1976).



Furthermore, the XRD pattern of bentonite allowed studying the interlamellar distance that is a characteristic of basal separation on montmorillonites, observed by the displacement of the diffraction angle. To obtain this displacement, Bragg's law is applied, in which the diffraction angle theta (θ) is proportionally inverse to the interplanar distance d . If there is a decrease in the diffraction angle, consequently there is an increase in the interplanar distance. Figure 28 shows the increase in basal space (d_{001}) from I and I', and II and II'. Figure 29 shows an important shift in the position of the d_{001} peak ($2\theta = 5^\circ$), to a low angle ($2\theta = 6^\circ$) suggesting an interplanar spacing change in the bentonite matrix (SHUKLA; THAKUR, 2010). The interplanar expansion between bentonite ($d=14 \text{ \AA}$) and BUF ($d=18 \text{ \AA}$) was 4 \AA (Figure 28). According to Djouani et al. (2011) and Pereira et al. (2012), this interplanar displacement confirms the intercalation of urea in the interlamellar spaces (DJOUANI et al., 2011; PEREIRA et al., 2012).

Figure 29. Basal space shift in X-ray diffraction (XRD) patterns of bentonite-urea fertilizer (BUF) and bentonite.



The diffraction angle θ is inversely proportional to the interplanar distance d . Therefore, the decrease in the diffraction angle occurs due to the increase in the interplanar distance.

The introduction of urea molecules into bentonite sheets increases the interlayer spacing. Bentonite has a hydrophilic interlayer space that allows the migration of urea molecules through strong H bonding with hydrophilic groups. Urea organic molecules migration led to an expansion in the interlayer distance.

The increase in the interlayer distance suggests a successful exfoliation of bentonite with urea as well as shows that are different bending sites of interaction (MADUSANKA et al., 2017).

3.3.3 Ammonia volatilization of fertilizer extract

Urea presents 45% of total nitrogen and BUF presents 35%, a 10% difference in the concentration of this nutrient. To know the maximum of ammonia that would volatilize from BUF and Urea, extracts of the same mass of these two fertilizers were analyzed and the total amount of ammonia volatilized was obtained in a 48 h essay. Pure distilled water was taken as a control reference to both fertilizer and BUF (Table 5).

Table 5. Ammonia volatilization from urea and BUF extracts.

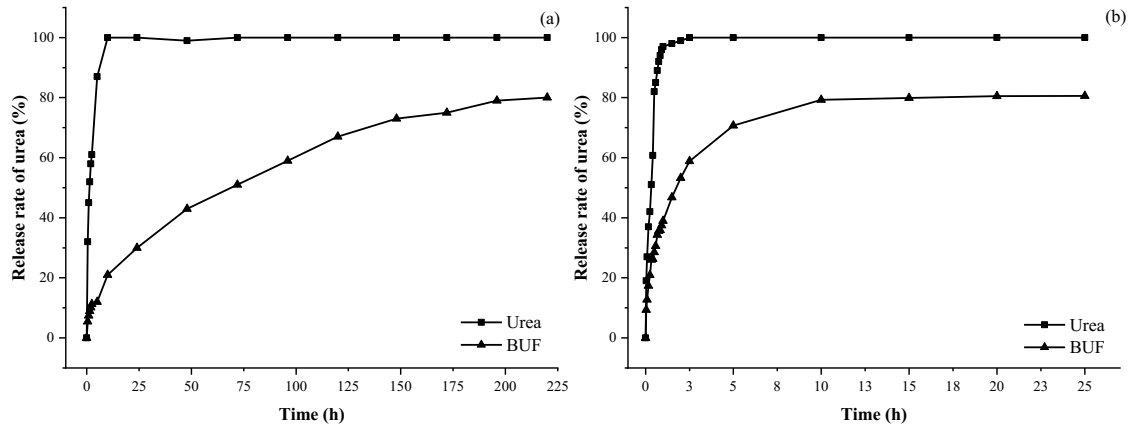
Fertilizer	Fertilizer concentration (mg/mL)	Total N content (ppm)	Ammonia volatilized (ppm)
Urea	5.0	2250	1402 ± 60
BUF	6.4	2250	721 ± 60

The fertilizers extract study showed that BUF released around 50% less ammonia than the same concentration of urea. Even in the liquid medium condition, it was possible to conclude that there is an amount of urea that is interlayered into bentonite sheets and that there are ion-dipole interactions between bentonite and urea that occurs in the negative surface of bentonite. These interactions decrease the amount of nitrogen species available for volatilization to occur, showing less nitrogen loss in the form of ammonia for BUF than for pure urea.

3.3.4 Urea release rate in water

The urea release rate analysis in deionized water was conducted to compare the release of pure urea and bentonite-urea fertilizer (BUF), as well as to observe if there are some interactions between urea and bentonite (Figure 30a). Urea achieved 100% dissolution after 25 h of the experiment. BUF showed a slow urea release in the water medium, reaching a release of 80% after 225 h. A second study (Figure 30b) was conducted using a cellulose dialysis membrane to keep the aqueous medium with virtually zero urea concentration and increasing the chemical potential for urea release. In other words, avoiding the effect of urea diffusivity in a bulk aqueous medium once no stirring was applied in any cases. This effect is evidenced by the reduction in the slow-release potential of BUF and the faster dissolution of urea because of the osmotic pressure between the inner and outer parts of the membrane (BORTOLIN et al., 2013; PEREIRA et al., 2012; TOMASZEWSKA; JAROSIEWICZ, 2002). Urea presented 100% of dissolution after 2 h of exposition. BUF showed a slower dissolution compared to pure urea, reaching 78% of dissolution after 10 h of analysis. These results, similar to the unprotected experiments, prove that there is an important intercalation of urea in bentonite sheets.

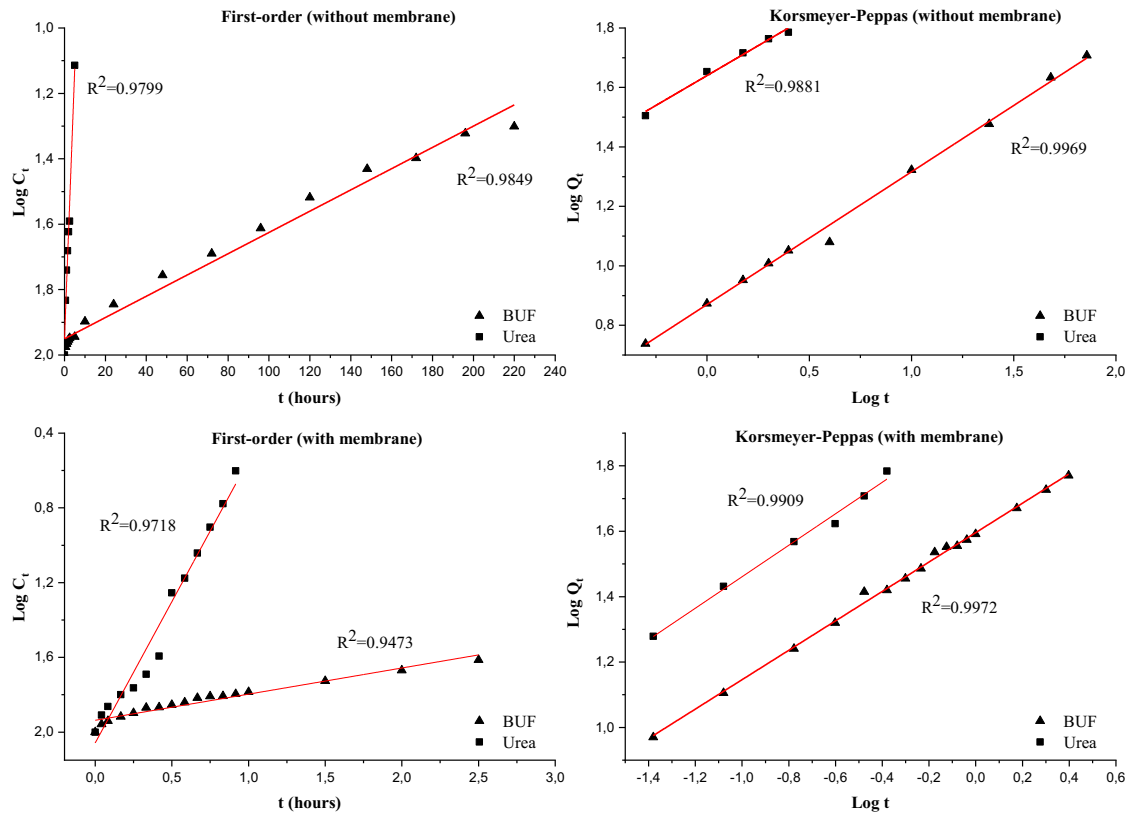
Figure 30. Release rate of urea, in water, as a function of time for pure urea and bentonite-urea fertilizer at pH 7 and $25 \pm 2^\circ\text{C}$: (a) directly in water, and (b) with the fertilizers protected by a dialysis membrane.



After 10 h or 225 h of analysis with or without dialysis membrane, a plateau begins to form in the BUF urea release rate. At this point, around 20% of nitrogen was not released, and it is possible to conclude that this 20% is the amount of urea that is intercalated into the bentonite layers, which requires more time to release or the plant extraction. The remain fertilizer has mass fraction 60/40, bentonite/urea. This result clearly shows that the intercalation of bentonite by urea is effective. About 80% of urea dissolved in water (from 0 to 200 h) from BUF, probably the released nitrogen specie had a bond with the bentonite surface and pores. It occurs because, during the extrusion process, the exchangeable cation Ca^{2+} present on the bentonite surface and pores is replaced by NH_4^+ . These results are similar to those found by Pereira et al. (2012) in which the authors noted a fast total dissolution of urea and around 80% of release by different bentonite-urea ratio modified fertilizers.

Figure 31 shows the experimental data fitted by Eq 15 as well as the linearized form of Eq. 16. It is possible to observe the Kornmeyer-Peppas model presented the best fit. This model is generally used to analyze the release of an active compound from a matrix when the diffusion mode is not well known or when one or more types of phenomena are involved.

Figure 31. Comparison of release kinetics of BUF and urea in water, without and with dialysis membrane, using first-order kinetics and the diffusion behavior with the Korsmeyer-Peppas model.



BUF has a Fickian diffusion according to the KP model, which presented an n value was 0.45 indicating diffusion is the main release mechanism. The Fickian model of BUF indicates that the diffusion rate of urea decreases when the concentration in the medium increases. This diffusion-controlled mechanism, as in the case of a water-soluble active compound, comes from a homogeneous matrix with a slow-release behavior (MADUSANKA et al., 2017). Thus, it can be deduced that when BUF contacts soil, depending on pH value and moisture level, urea will be released from the bentonite matrix in a slow and controlled diffusion. For urea, the diffusion behavior was a Hindered Fickian with a n value of 0.40. This diffusion mechanism indicates that there is a release of a non-swelling matrix.

The release kinetics of urea and BUF protected by a dialysis membrane are shown in Figure 30. The best fitting was also obtained for both fertilizers with KP model. In this study, BUF fertilizer presented an n value of 0.45, showing a Fickian release, that follows a diffusion mechanism, as well as in the analysis without membrane. Urea shows an n value of 0.47, when the release mechanism is controlled mainly by diffusion but also by erosion. The value of the

release constant of the KP model (K_{KP}) was 8 h^{-1} for BUF and 44 h^{-1} for urea, showing a urea release from BUF around 6 times slower than pure urea.

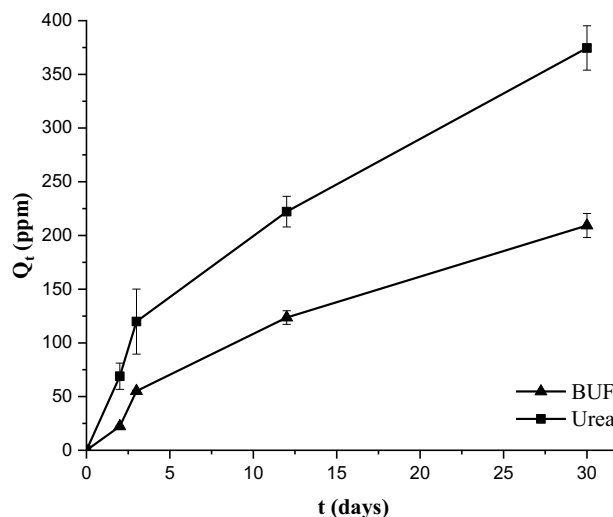
If the value of n is 0.5, is a particular case that represents the Higuchi model, and in this case, there is a diffusion-controlled mode, similar to what is presented for BUF. In the case of n value is 1, the kinetics governed by degradation and relaxation or degradation of monolithic systems, and also is a particular case that represents a zero-order model. The gradual release of urea present in BUF is shown in Figure 30, in which the release of urea is slow and gradual as identified in the literature for slow-release fertilizer (MADUSANKA et al., 2017; PEREIRA et al., 2012). In this case, it is possible to conclude that urea molecules are tightly bonded to bentonite interlayers, especially about 20% of their total content. This slower and sustained urea release gives BUF the important characteristic of an efficient slow-release nitrogen fertilizer.

3.3.5 Ammonia volatilization of fertilizer in soil

To study ammonia volatilization of fertilizers in the soil, neosol was limed until reach a pH of 7.0. The loss of nitrogen as volatilized ammonia was studied in a 30-day essay with BUF and urea as fertilizers. Bentonite and pure soil were taken as control.

Figure 32 shows the cumulative results obtained of volatilized ammonia in ppm. Since day two, it was possible to see a difference between urea and BUF volatilization. While BUF released 22 ± 1 ppm of ammonia, urea released 69 ± 4 ppm. After fertilization, nitrogen loss by ammonia's volatilization in urea is 150% higher than BUF.

Figure 32. Cumulative volatilized ammonia from BUF and urea was applied to neosol (pH 7) for 30 days of analysis, by boric acid methodology.

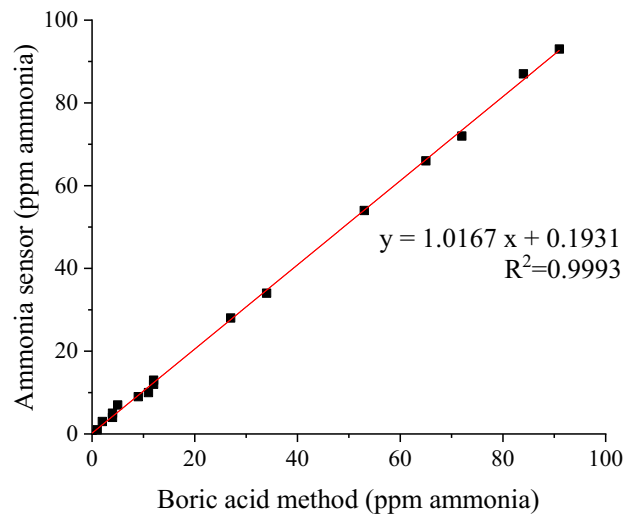


As shown in Figure 32, it is possible to conclude that urea ammonia volatilization is 60% faster than BUF since BUF took 30 days to reach volatilization of around 222 ppm. In contrast, urea needed only 12 days to get the same point.

3.3.6 Boric acid methodology validation

To investigate the methodology based on boric acid as an ammonia sequestrant in air, studies with volatilization chambers equipped with boric acid were compared with volatilization chambers equipped with the ammonia sensor. The results are shown in Figure 33.

Figure 33. Comparative data regarding the cumulative release rate of ammonia (ppm) obtained by the methodologies of boric acid and ammonia sensor.



With this study, the boric acid methodology could be validated, due to its similarity of results when compared to the use of the ammonia sensor (Figure 33). With the experimental results, we could compare both methodologies and obtain a linear fit with an R^2 of 0.9993, showing the validation of the boric acid methodology to ammonia volatilization studies.

3.4 CONCLUSIONS

In essence, our study presents a straightforward and efficient approach for creating nanocomposites by intercalating bentonite clay into urea. Even in extreme conditions such as the release rate of fertilizers in water, it was possible to conclude that there is an amount of urea that is interlayered into bentonite sheets and that there are ion-dipole interactions between bentonite and urea that occurs in the negative surface of bentonite. These interactions between bentonite and urea in BUF fertilizer decrease the possibility of ammonia volatilization. The results were confirmed by FTIR analysis. Another conclusion obtained by the release rate in water is that 20% of urea presented in BUF is intercalated into the bentonite layers, showing that the intercalation is effective, and the exfoliation gotten by the extrusion process is important to obtain a slow-release fertilizer.

The kinetic studies allowed us to deduce that when BUF contacts soil, depending on pH value and moisture level, urea will be released from the bentonite matrix in a slow and controlled diffusion. Furthermore, it was possible to conclude that urea molecules are tightly bonded to bentonite interlayers in BUF fertilizer, especially about 20% of the urea total content. This slower and sustained urea release gives BUF the important characteristic of an efficient slow-release nitrogen fertilizer. XRD studies confirmed that urea molecules were introduced into bentonite sheets leading to an expansion in the interlayer distance, resulting in strong H bonding with hydrophilic groups of bentonite. The increase in the interlayer distance suggests a successful exfoliation of bentonite with urea.

Ammonia volatilization analysis in soil showed that urea loses nitrogen by volatilization 60% faster than BUF. In addition, the boric acid methodology could be validated in comparison to ammonia sensor tests.

In summary, an important finding from our research is that urea molecules are intercalated into octahedral sheets of bentonite as well as chemically bonded in its surface and pores, resulting in slow-release behavior for urea dissolution, making this bentonite-urea-modified fertilizer useful for enhancing fertilizer efficacy within agricultural applications.

4 AMMONIA VOLATILIZATION KINETICS FROM BENTONITE-UREA FERTILIZER IN SOIL

4.1 INTRODUCTION

Ammonia volatilization, characterized by the conversion of ammonium (NH_4^+) to ammonia (NH_3) gas and subsequent release into the atmosphere, is a key pathway of N loss from fertilizers. Traditional fertilizers, such as urea, are particularly susceptible to rapid volatilization, necessitating innovative approaches like bentonite-urea fertilizers to reduce N losses. This paper delves into the kinetics of ammonia volatilization from such fertilizers, aiming to shed light on their potential benefits and application strategies. Apart from the economic implications, ammonia volatilization can lead to environmental issues such as air pollution by the elevated NH_3 levels, affecting human health; soil and water acidification because of NH_3 deposition; and NH_3 emissions may contribute to eutrophication of nearby water bodies, harming aquatic ecosystems. Fertilizers are applied to the soil to increase agricultural productivity by providing essential elements for plant growth; however, between 40 and 70% of nutrients are lost through volatilization, erosion, and leaching (WU; LIU, 2008a). The concentration of fertilizer lost varies according to soil characteristics, environmental factors, crop, and application methods (AYOUB, 1999).

Urea ($\text{CO}(\text{NH}_2)_2$), also called carbamide, is a nitrogenous compound containing a carbonyl group attached to two amine groups. In vivo, urea is formed in the liver via the urea cycle from ammonia and is the end product of protein metabolism. Industrially, urea is obtained through the reaction between ammonia (NH_3) and carbon dioxide (CO_2), under high pressure, forming ammonium carbamate ($\text{NH}_2\text{COONH}_4$), which is then dehydrated to give rise to urea (PEREIRA, 2014). When pure, urea presents around 47% nitrogen in its composition, being then the nitrogen fertilizer with the lowest cost per unit of nitrogen and, consequently, the most used molecule for supplementation of this mineral in the soil (DAL MOLIN, 2016). Urea can be absorbed through both the leaves and the roots. As a fertilizer, it can be taken up directly or after hydrolysis. The enzyme urease catalyzes the hydrolysis of urea, resulting in ammonium carbonate; ammonium carbonate is highly unstable, breaking down into ammonium, bicarbonate, and hydroxyl. Ammonium can be converted to ammonia and lost to the atmosphere, depending on the cation exchange capacity, clay content (texture), pH, and soil temperature (BYRNES, 2000). The increased susceptibility to volatilization occurs because the hydrolysis process of urea promotes the elevation of soil pH around the granules due to the

reactions of bicarbonate and hydroxyl with hydrogen present in the soil (CANTARELLA, 2007; ERNANI, 2008; YAMADA; ABDALLA, 2006). This elevation in soil pH can lead to losses of between 8 and 77% of the applied nitrogen (FARIA et al., 2014; LARA CABEZAS; SOUZA, 2009). In tropical countries, such as Brazil, crops absorb between 50 and 70% of the nitrogen; therefore, about 40% of the N is lost to the environment, resulting in a low return on the investment made in fertilization (FINK, 1992). Besides the high cost of frequent fertilization, this still causes environmental damage because the excess nutrients can contaminate the atmosphere and the soil, besides groundwater and rivers (PEREIRA, 2014). The ecological damage due to excess ammonium and oxidized nitrogen compounds can cause algae blooms that, in turn, cause oxygen depletion. In the case of blue and green algae, substances toxic to animals and humans are produced during blooming. Another problem of excessive use of fertilizers is the toxicity of nitrate (NO_3^-) and nitrite (NO_2^-), ions related to various diseases. Moreover, the excess of nitrogen compounds is also associated with acid rain and the release of N_2O and NO gases, which contribute to the greenhouse effect and reduction of the ozone layer (RESENDE, 2002; SERRANO-SILVA et al., 2011; SNYDER et al., 2009). Thus, the efficient use of fertilizers is essential for greater productivity, economic return, and minimization of nutrient losses to the environment.

Urea is the most employed nitrogen fertilizer because of its high concentration of nitrogen ($460 \text{ g}\cdot\text{kg}^{-1}\cdot\text{N}$), the restriction of ammonium nitrate as fertilizer, and the higher cost of ammonium sulfate (CHIEN; PROCHNOW; CANTARELLA, 2009). Volatilization is accentuated in alkaline soils and acidic and alkaline soils when urea is applied to the surface, especially in flooded soils and at the early stage of plant growth. Urea $[(\text{NH}_2)_2\text{CO}]$ hydrolysis to ammonium bicarbonate $[(\text{NH}_4)\text{HCO}_3]$ causes an increase in soil pH that induces ammonia (NH_3) volatilization (CHIEN; PROCHNOW; CANTARELLA, 2009; SOARES; CANTARELLA; MENEGALE, 2012).

High pH in solution favors the formation of aqueous ammonia and hydrogen ion, increasing NH_3 concentration in solution and in gaseous phase. If the soil has pH values below 7, the main ammoniacal-N form will be NH_4^+ and the potential for volatilization will be small. In contrast, if the soil presents higher pH values, the main form will be NH_3 and the potential for volatilization will be greater (DASGUPTA; DONG, 1986).

The effect of initial soil pH can be overlaid by a strong interaction between the fertilizer, as urea, and the soil solution that induces hydrolysis and precipitation reactions. In this case, the soil cation exchange capacity (CEC) is important, if the soil presents a large CEC, with high NH_4^+ retention, the volatilization potential of NH_3 tends to reduce because of the

adsorption of NH_4^+ on the exchange site and consequent reduction on NH_4^+ concentration in soil solution (EMEP/EEA, 2019).

Ammonia losses are also dependent on wind speed, soil buffering capacity, soil moisture content, and low or high plant canopy. The presence of plant residues can increase urease activity and, consequently, increase NH_3 emission. Ammonia losses are higher in countries with tropical and subtropical climates with average volatilization of 20 – 60% of the applied nitrogen (BOUWMAN; BOUMANS, 2002; CANTARELLA et al., 2003, 2008; CHIEN; PROCHNOW; CANTARELLA, 2009; LARA CABEZAS; KORNDORFER; MOTTA, 1997). The choice of fertilizer and the application technique greatly influence volatilization. Depending on the fertilizer used, once it is applied to the soil surface, there is a consequential loss due to the volatilization that occurs in the first hours after fertilization (CELLIER et al., 2013; GENERMONT et al., 1998; HUIJSMANS; HOL; VERMEULEN, 2003; SOMMER et al., 2003).

Nitrogen loss measurements are essential to correct fertilization, avoiding excess or lack of this nutrient, economic losses, and negative environmental impacts. Nitrogen flow measurement methods can be experimental, which allows the direct determination of emissions of gaseous nitrogen compounds, or the use of models that are generally proposed to carry out integrated assessments for long periods and large areas or to analyze evolutionary scenarios (CELLIER et al., 2013).

Hence, the objective of this paper is to review and summarize laboratory measurement methods of ammonia emission, pointing the efficiency and the weaknesses of each method presented.

The process of ammonia volatilization can be understood through a series of chemical and physical mechanisms such as urea hydrolysis through the action of urease enzymes, producing NH_4^+ ions and bicarbonate ions (HCO_3^-); transformation of NH_4^+ ions, that are subject to soil adsorption, ion exchange, and microbial activity, influencing their fate; and volatilization, mainly in alkaline conditions. Bentonite-urea fertilizers modulate these mechanisms by delaying urea hydrolysis, potentially reducing NH_3 volatilization.

Several factors can impact the kinetics of ammonia volatilization from bentonite-urea fertilizer as the soil pH, because alkaline soils favor volatilization; temperature that affects the activity of urease enzymes; the adequate soil moisture, because moist soils retain NH_4^+ ions; and the proportion of bentonite in the fertilizer formulation.

Red Latosols, with their inherent low nutrient content and high weathering intensity, present unique challenges for agriculture. To enhance crop productivity, farmers often resort to

nitrogen-based fertilizers, including controlled-release fertilizers (CRFs). However, a significant fraction of the applied N can be lost to the atmosphere through ammonia volatilization, leading to economic losses and environmental problems.

Understanding the kinetics of ammonia volatilization from bentonite-urea fertilizer in soil is critical for modern agriculture. This knowledge empowers farmers and researchers to develop effective strategies for optimizing nutrient use efficiency, protecting the environment, and enhancing crop productivity. Ongoing research and practical applications are essential for addressing this complex issue and ensuring sustainable nutrient management in agriculture.

4.2 MATERIAL AND METHODS

4.2.1 Materials

4.2.1.1 Bentonite and soil

Bentonite and bentonite-urea fertilizer pellet (BUF) were provided by T-Minas. Red Latosol was collected from Palma Sola, Santa Catarina, Brazil. Quartzarenic Neosol was collected from Florianópolis, Santa Catarina, Brazil.

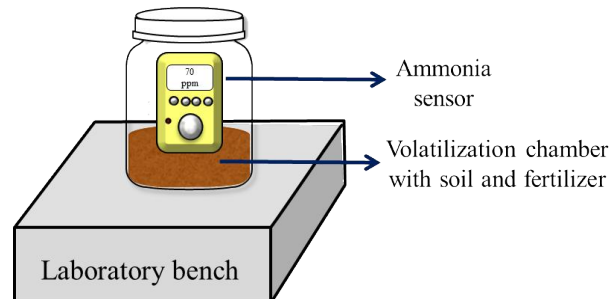
4.2.1.2 Chemicals

The following chemicals were used: urea (100%, Neon), magnesium oxide (98%, Neon), sulfamic acid (98%, Neon), sulfuric acid (0.1 N, Neon), boric acid (99.8%, Neon), bromocresol green (99% Neon), methyl red (as a water-soluble salt) (99% Neon), ammonium sulfate (99%, Neon), sodium nitrite (99%, Neon), sodium sulfate anhydrous (99%, Neon), pentahydrate copper sulfate (98%, Neon), phenolphthalein in solution (1%, Neon), Nessler's reagent, hydrochloric acid (0.1 N, Neon) and ethanol (95%, Neon) were used as well. All chemicals were of analytical grade and used without further purification.

4.2.2 Laboratory experimental unities

Experimental closed-static unities were built according to Mulvaney et al. (1997), Rogers et al. (2017), and Stiegler et al. (2011) propositions with adaptations (Figure 34). Volatilization chambers were prepared by pouring 200 g of soil sample into each chamber. Pure soil and soil with Bentonite were the control in each experiment. Fertilizer was added to each chamber to achieve an N concentration equivalent to 3 g of N. In chambers that were conducted boric acid indicator analysis, 50 mL of 2% of this ammonia sequestrant was placed into a cylinder container in the middle of the volatilization chamber. An ammonia sensor (AKSO SGTP-NH₃) was coupled to the volatilization chamber to obtain the concentration of volatilized ammonia inside the chamber. The soil pH was corrected to reach pHs between 5 and 7.

Figure 34. Closed static volatilization chamber with an ammonia sensor.



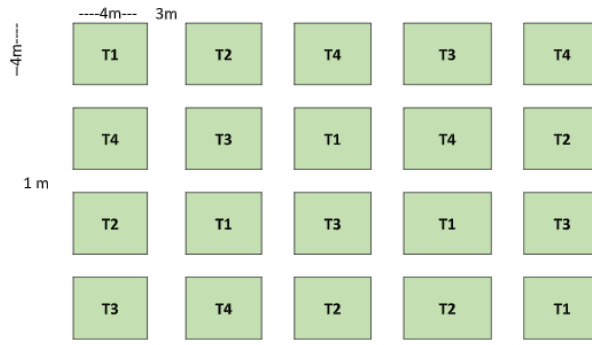
4.2.3 Field experiments

The work was carried out at the Experimental Farm of the Federal University of Santa Catarina, located in Florianópolis, state of Santa Catarina, in southern Brazil. According to the Köppen climate classification, the farm is located in a sub-region with a constantly humid subtropical climate, with no dry season and a hot summer. Normal rainfall ranges from 1270 to 1600 mm per year. The average annual relative humidity is around 82%, with total annual sunshine from 2021 to 2166 hours (ALVARES et al., 2013). The experiment was carried out in March and April 2023. Typical Hydromorphic Quartzarenic Neosol according to the Brazilian Soil Classification System (EMBRAPA, 2018). It is therefore a predominantly sandy soil, with a dark color due to the high content of organic matter present and the common presence of water in the soil, due to the high water table.

The soil analysis of the tillage area showed the following chemical characteristics determined on samples taken from the 0-20 cm layer: pH in water 5.8; Al 0.0 mmolc dm⁻³; Ca 5.3 mmolc dm⁻³; Mg 3.7 mmolc dm⁻³; K 22.0 mg dm⁻³; P 3 mg dm⁻³; MO 4.8 g dm⁻³.

The experimental plots (4x4m each) were established with soil preparation corrected with lime, potassium, and phosphorus in a total area of 1250 m² (Figure 35). The experimental design was completely randomized with 5 replications per treatment, giving a total of 20 experimental plots (1 species x 4 treatments x 5 replications).

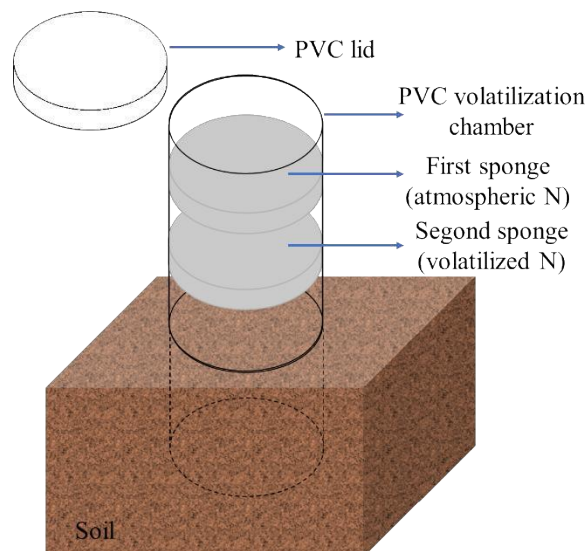
Figure 35. Experimental design where T1 are the control; T2 are pure urea; T3 are BUF; and T4 are soil with bentonite.



The experiments were settled up using a tropical grass forage specie, *Brachiaria brizanth* (Piatã) which was subjected to different sources of nitrogen fertilizer: control without nitrogen, conventional nitrogen fertilizer (urea), BUF and Bentonite also as a control.

Ammonia volatilization from the treatments was assessed using semi-open chambers (Figure 36), like the model described by Nommik (1976), which were in each of the trays before the application of the fertilizers. After installing the chambers, the fertilizers were distributed evenly over the bare soil, according to the over the bare soil, depending on the treatment and at a standard dose equivalent to $125 \text{ kg ha}^{-1} \text{ N}$.

Figure 36. PVC volatilization chamber with two ammonia sequestrant sponges.



The system consisted of a PVC pipe base inserted into the soil, and two polyurethane foam disks (with a density of 0.23 g cm^{-3} , 2 cm thick and an area of 314 cm^2) soaked in 45 ml of

a 0.5 N phosphoric acid + glycerin solution (5% v/v) were placed inside the pipe, in 45 ml of a 0.5 N phosphoric acid + glycerin (5% v/v) solution. The disk positioned in the upper part of the chamber acts as a trap for potential contamination with NH₃ present in the air, while the disk positioned at 10 cm has the function of capturing NH₃ volatilized from the area under the chamber.

Ammonia volatilization was assessed over a period of 32 days, with quantifications (trap changes). In each of the evaluations, both disks (bottom and top) were replaced with new ones with new ones, also soaked in acid+glycerin solution. The replaced lower disk was placed in a plastic bag and stored in a refrigerator for later quantification of the of the captured NH₃. The quantification process begins by extracting/washing each foam in 400 ml of a 0.0005 N solution of sulfuric acid. The concentration of NH₃ in the extracted aliquots was determined in duplicate by distillation (Kjeldahl distiller) followed by titration. The sampling frequency was as follows: 4, 8, 12, 16, 20, 24, 28 and 32 days after the treatments were applied.

4.2.4 Volatilized ammonia

Volatilized ammonia was determined by the Kjeldahl method (BREMNER; MULVANEY, 2015). In this method, N in the sample is reduced in NH₄⁺ by H₂SO₄ digestion with salts and catalysts to accelerate the reaction.

4.2.5 Volatilized ammonia in volatilization chamber

Ammonia was adsorbed by a 2% boric acid solution with bromocresol green and methyl red. Volatilized ammonia was determined by titration with 0.01 mol/L sulfuric acid standard solution on days 0, 2, 3, 15, and 30 of incubation. The cumulative volatilized ammonia was determined using Equation 18 (FERTAHY et al., 2020). where Cum.Re is the cumulative amount of release N; V_e is the sampling volume; V₀ is the initial volume of the experimental medium; C_t and C_f are the correspondingly representative concentrations of N at sampling time t and at the last sampling time; C_{m₀} is the total weight of nitrogen in the fertilizer.

$$Cum. R_e = \frac{V_e \sum C_t + V_0 C_f}{C_{m_0}} \quad (18)$$

In addition to the boric acid indicator methodology, we also tested the volatilization only with an ammonia sensor (AKSO SGTP-NH₃) into the volatilization chamber to obtain the concentration of volatilized ammonia inside the chamber.

4.2.6 Urea release and ammonia volatilization kinetics

The kinetics were determined by the best fit of experimental data versus time. The ammonia volatilization kinetic was fitted with the first-order release model (Eq. 15). The semiempirical power law model of Korsmeyer-Peppas was used to determine the diffusion type for urea release kinetics (Eq. 16). (KORSMEYER; PEPPAS, 1981)

$$\text{Log } Q_t = \text{Log } Q_0 - K_1 t/2.303 \quad (15)$$

$$Q_t = K_{KP} t^n \quad (16)$$

where Q_t is the fraction of urea released (%) at each time point (t); Q_0 is the initial percentage of urea (%); K_1 is the first-order release kinetic constant (h^{-1}); K_{KP} is the release kinetic constant according to the Korsmeyer-Peppas' model (h^{-1}); n is the diffusion exponent.

The value of the diffusion exponent n in the Korsmeyer-Peppas' model indicates the urea release mechanism. The type of release correlated with the n value is shown and described in Table 6.

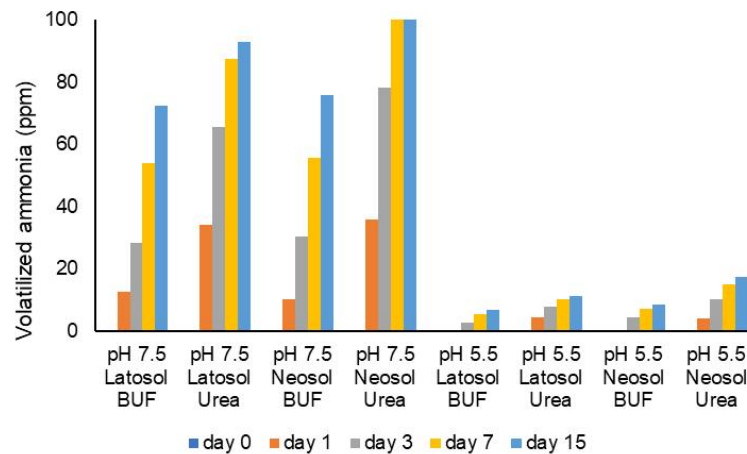
Table 6. Type of diffusion related to the diffusion exponent value.

Diffusion exponent value	Type of diffusion
$0 < n < 0.45$	Hindered Fickian diffusion (diffusive release and non-swelling matrix)
$n = 0.45$	Fickian diffusion (diffusion is the main release mechanism)
$0.45 < n < 1.0$	Non-Fickian diffusion (release follows both diffusion and erosion-controlled mechanisms)
$n = 1.0$	Zero-order diffusion (kinetics governed by degradation and relaxation or degradation of monolithic systems)

4.3 RESULTS AND DISCUSSION

The cumulative release rate of ammonia was obtained for urea and BUF in latosol and neosol, at pH 5.5 and 7.5, in order to notice the influence of the soil type and the pH in ammonia volatilization (Figure 37). The volatilized ammonia measurement was done by boric acid method and ammonia sensor. The ammonia sensor was used in order to validate the boric acid method.

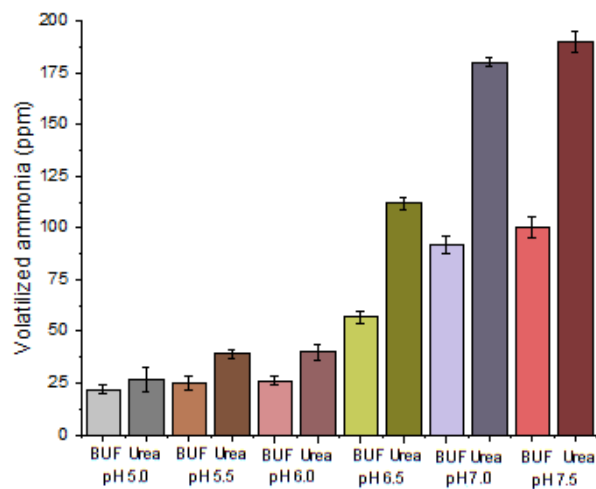
Figure 37. Cumulative release rate of ammonia at $25\text{ }^{\circ}\text{C} \pm 2^{\circ}\text{C}$ in Red Latosol and Quartzarenic Neosol at pH 5.5 and 7.5; with ammonia sensor.



A lower ammonia volatilization was observed in pH 5.5 compared to both Neosol and Latosol at pH 7.5. The pH is the most important variable that affects ammonia volatilization. In both Neosol and Latosol, pure urea presented about 20% more ammonia volatilization than BUF. After 15 days of analysis, the soils with pH 7.5 showed an ammonia volatilization about 80% higher than the soils with pH set to 5.5.

In order to better understand the effect of pH on ammonia volatilization, another experiment was conducted by fertilizing soils with corrected pHs between 5 and 7.5 (Figure 38).

Figure 38. Cumulative release rate of ammonia from Urea and BUF at 25 °C ± 2°C in Red Latosol at pH 5.0, 5.5, 6.0, 6.5, 7.0, and 7.5.

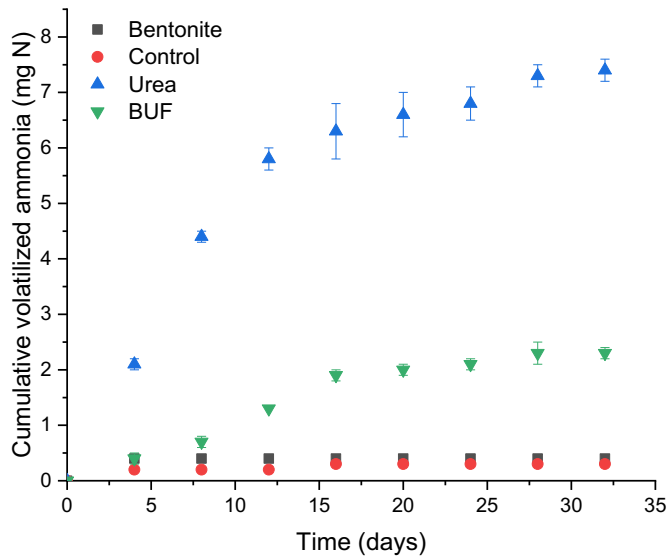


The tests were conducted for pure urea and BUF in triplicate for each pH during 60 days of incubation. We can see from the graph that at pHs above 7.0 volatilization is more pronounced, while at pHs below 6.0 the loss is less. From the data obtained, it can be concluded that the critical pH for volatilization is 6.5, and that below this pH there is less loss. So, it is visible that in soils with a pH below 6.5 the loss of nitrogen through volatilization is similar for both fertilizers, both pure urea and the BUF protected fertilizer. It is important to highlight that in Brazil, soil pH is commonly adjusted to between 6.0 and 6.5.

With regard to the accumulated loss of N-NH₃, there were differences between the treatments in all the evaluation period. The N loss from BUF amounted to 26.4 kg N ha⁻¹ at the end of 32 days, equivalent to 19.6% of the N applied. The total accumulated loss of N-NH₃ in pH 7.5 was 50% lower when BUF were used instead urea. inhibitors. And that's when we consider the entire 32-day period.

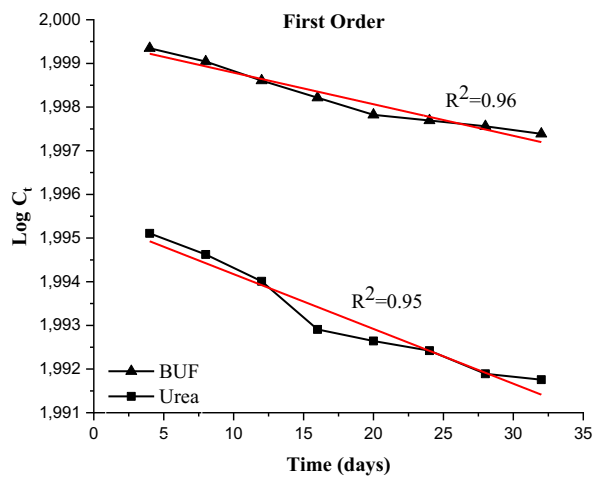
The lower loss of N in BUF compared with pure urea is shown in Figure 39. So, it is possible to conclude that urea molecules are tightly bonded to bentonite interlayers. This slower N loss gives BUF the important characteristic of an efficient fertilizer for minimizing ammonia volatilization.

Figure 39. Cumulative volatilization of ammonia from Bentonite, Control (pure soil), Urea and BUF in Neosol on days 0 to 32.



The reduction in cumulative loss of N when using BUF were about 71% compared to ordinary urea. It is important to note that the accumulated losses of N-NH₃ from the BUF (2 mg) after day 15 were statistically similar throughout the final evaluation period.

Figure 40. Comparison of ammonia volatilization kinetics from BUF and urea in Neosol, using First Order model.

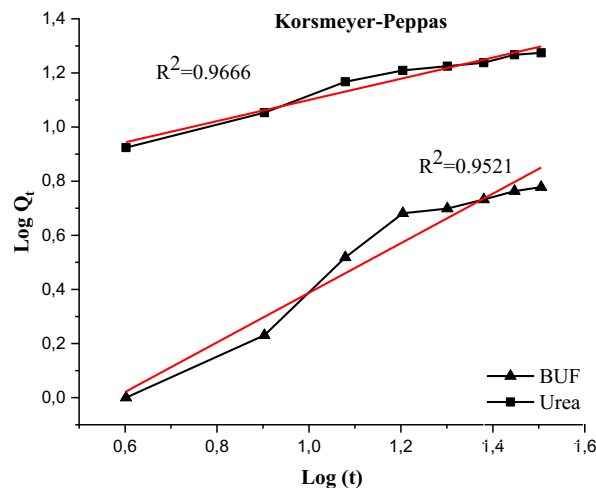


In the equations of first-order kinetics model describing the ammonia volatilization process of pure urea and BUF, it was found that the lowest ammonia volatilization values (indicates the stabilization value of the volatilization process) belong to BUF (0.6%), 68% lower than urea (1.9%). The first-order model shows that the ammonia volatilization is

concentration-dependent, in other words, the higher the concentration, the faster is the volatilization. The first order rate of ammonia volatilization increased from 0.01 (day^{-1}) to 0.03 (day^{-1}) for urea, while for BUF the first order rate remained at 0.0025 (day^{-1}). These results shows that BUF is a potential fertilizer to be used in place of pure urea, as it grants a lower and constant loss of nitrogen, while urea presents rapid, increasing and higher losses.

Figure 41 shows the experimental data fitted by Korsmeyer-Peppas model. This model is generally used to analyze the release of an active compound from a matrix when the diffusion mode is not well known.

Figure 41. Comparison of urea release kinetics from BUF and urea in Neosol, using Korsmeyer-Peppas model.



BUF has a Non-Fickian diffusion in soil according to the KP model, which presented a n value of 0.83 indicating that the release mechanism is controlled by both diffusion from the bentonite matrix as well as the erosion of this nanoclay. The diffusion-controlled mechanism, as in the case of a water-soluble active compound as urea, comes from an homogeneous matrix with a slow-release behavior (MADUSANKA et al., 2017). Thus, it can be concluded that when BUF contacts soil, urea was released from the bentonite matrix in a slow and controlled diffusion but also by a gradual erosion of the fertilizer pellet. For urea, the diffusion behavior was a Hindered Fickian with a n value of 0.40. This diffusion mechanism indicates that there is a release of a non-swelling matrix. The value of the release constant of the KP model (K_{KP}) was 0.03 h^{-1} for BUF and 1.31 h^{-1} for urea, showing a urea release from BUF around 44 times slower than pure urea.

4.4 CONCLUSIONS

This study showed the critical role of soil pH in regulating ammonia volatilization, emphasizing its importance in agricultural and environmental contexts. The findings presented herein demonstrate that soil pH significantly influences the transformation and fate of ammonia in the soil, with acidic conditions favoring increased ammonia volatilization. The mechanisms underlying this relationship involve the pH-dependent equilibrium between ammonium (NH_4^+) and ammonia gas (NH_3), with higher pH levels promoting the formation of NH_3 , which is more susceptible to volatilization.

This research also demonstrates that bentonite-urea fertilizer (BUF) stands out as a significantly more efficient and sustainable choice compared to urea in terms of reduced and slower ammonia volatilization. Ammonia volatilization is a key concern in modern agriculture due to its adverse environmental and economic consequences. The slower release of nitrogen from BUF when compared to urea, significantly reduces the immediate formation of ammonia gas when the fertilizer is in contact with the soil. The slower release, due to the inherent physicochemical properties of bentonite clay, as the octahedral sheets, results in a substantial decrease in ammonia volatilization compared to traditional urea fertilization. This reduced ammonia loss not only preserves valuable nutrients for plant uptake but also has profound implications for environmental conservation by mitigating the release of ammonia into the atmosphere, where it can contribute to air pollution and ecosystem damage. In addition, the formation of urea requires the use of fossil fuels, i.e. non-renewable energy. Therefore, in addition to minimizing the environmental impact of excessive fertilization, BUF is a fertilizer of interest because it reduces the carbon footprint due to a lower need for urea and, consequently, a lower production of this nitrogenous compound.

Furthermore, BUF efficiency is not limited to reducing ammonia volatilization; it also extends to enhancing nitrogen use efficiency, reducing the need for frequent applications, and minimizing the risk of over-fertilization. This translates into tangible economic benefits for farmers and a more sustainable approach to nitrogen management in agriculture.

The kinetic studies allowed us to observe that when BUF contacts soil, depending on pH value, urea releases from the bentonite matrix in a controlled diffusion but also dependent of the bentonite exfoliation. Furthermore, it was possible to conclude that ammonia volatilization is 68% higher than BUF in the same period. In addition, ammonia volatilization is faster and higher when urea is used as fertilizer than BUF is used. This slower and sustained

urea release gives BUF the important characteristic of an efficient slow-release nitrogen fertilizer.

5 FINAL CONSIDERATIONS

In conclusion, this thesis has examined the comparative efficacy of a new slow-release fertilizers (BUF) versus pure urea, focusing on their impact on ammonia volatilization and nitrogen release. The findings presented here underscore the superiority of BUF over pure urea in agricultural applications. The final considerations can be summarized as follows:

- **Reduced Ammonia Volatilization:** One of the key advantages of BUF over pure urea is its ability to significantly reduce ammonia volatilization. Ammonia volatilization is a major concern in agriculture, as it leads to nitrogen loss, environmental pollution, and decreased fertilizer efficiency. BUF, with its controlled-release mechanism because of the urea intercalation into bentonite lamellas, effectively moderates this issue, ensuring that a higher proportion of applied nitrogen is utilized by crops.
- **Enhanced Nutrient Efficiency:** BUF nature allows for a more gradual and sustained release of nitrogen, matching the nutrient demand of crops over time. This results in improved nutrient efficiency, as plants can access nitrogen when needed, reducing the risk of nutrient loss by volatilization. Pure urea, on the other hand, can lead to nutrient imbalances and waste due to its rapid release.
- **Lower Environmental Impact:** The reduced ammonia volatilization associated with BUF not only benefits crop yield but also has a positive impact on the environment. Lower ammonia emissions contribute to improved air quality and a decrease in environmental pollution, which is a significant concern in agriculture nowadays.
- **Longer Lasting Effects:** BUF formulation has the advantage of providing nutrient availability for an extended period. This not only benefits the current crop but also has carryover effects for subsequent crops. In contrast, pure urea

typically requires more frequent applications to maintain adequate nutrient levels, resulting in increased labor and fertilizer costs.

- **Economic Viability:** While BUF may have a slightly higher upfront cost compared to pure urea, its long-term benefits in terms of improved crop yields, reduced fertilizer application frequency, and lower ammonia volatilization losses make it a cost-effective choice for farmers in the long run.

In conclusion, the results strongly support the claim that BUF, by decreasing ammonia volatilization and providing a sustained nutrient supply, outperform pure urea as a fertilizer option. Considering the pressing global challenges related to food security, environmental sustainability, and climate change, the adoption of controlled-release fertilizers like BUF emerges as a promising solution. Our research reinforces the notion that slow-release fertilizers can play a pivotal role in optimizing nutrient management strategies, minimizing ammonia volatilization, and promoting a more environmentally friendly and economically viable approach to modern agriculture. It is imperative that farmers, politicians, and investors recognize the advantages of slow-release fertilizers as BUF and consider its widespread adoption as a crucial step towards a sustainable and responsible future for agriculture.

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