Mechanochemically Synthesized Nitrogen-Efficient Mg- and Zn-**Ammonium Carbonate Fertilizers**

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analysis showed properties distinctly different from those of parent ammonium (bi)carbonates. Accordingly, a reduction in NH_3 volatilization in soil was measured with up to 20% more NH_4^+ recovered after the soil experiments at 80% water holding capacity. Further, inhibition of the agriculture-beneficial bacteria Bacillus subtillis in a nutrient medium was dramatically reduced when compared to the ammonium bicarbonate alone, suggesting decreased negative effects on soil biota. Finally, $Mg(NH_4)_2(CO_3)_2$ ·4H₂O and $Zn(NH_3)CO_3$ matched the kinetic nitrogen need of lettuce plants better than the ammonium carbonate control while also keeping it in a form that will be available in the future. The utility of magnesium and zinc double salts in agriculture is paramount if environmentally benign and nutrient-efficient fertilizers from liquid digestate waste are to be enabled.

KEYWORDS: nitrogen, fertilizers, digestate, ammonium, mechanochemistry

INTRODUCTION

The recent global events led to unprecedented market volatility, high energy and fertilizer prices, and food supply chain disruptions.¹ The United States, the European Union, and the global community have since embarked on an ambitious program to develop alternative and innovative fertilizers to lessen the dependence on oil imports, reduce greenhouse gas emissions, improve agricultural sustainability, and provide increased food security. In the US, a new federal Fertilizer Production Expansion Program provided grants to increase or expand the manufacturing or processing of fertilizers and nutrient alternatives and their availability. However, the rules that govern organic² and waste-based fertilizer sources,³⁻⁵ their emerging production or uptake concepts,⁶ and safety⁷ remain to be developed and harmonized.

Establishing a circular nitrogen management system is essential if fertilizer synthesis is to be decoupled from the need to utilize natural gas.8 An opportunity for nutrient recovery arises from the biogas production sector. Liquid digestate is a byproduct of biogas production and contains

significant amounts of nitrogen in the form of ammonium, NH4⁺. Due to the increasing generation of digestate, biogas is viewed unfavorably. Many European countries that produce biogas, e.g., Italy, Denmark, and The Netherlands, struggle with excessive nutrient loads from digestate and its utilization.⁹ Furthermore, the Chinese biogas industry generated 600 million tons of digestate in 2009, which is difficult to dispose of because of the lack of arable land near the facilities.⁹ However, even if applied to soil as a source of nutrients, nitrogen loss in the form of ammonia volatilization takes place concomitantly with soil property degradation.¹⁰ To address these global sustainable energy and nitrogen management challenges and unlock digestate potential, a solid fertilizer that can be stored,

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Figure 1. Mechanochemical Synthesis of the Mg- and Zn-ammonium carbonate double salts and their resulting crystal structures. Two products were synthesized, including $Mg(NH_4)_2(CO_3)_2$ ·4H₂O and Zn(NH₃)CO₃. The crystal structures of the products were visualized using the VESTA software.³⁰

efficiently transported, and release nitrogen in a controlled manner is needed.

No single solution has been available for the nitrogen digestate challenge. The currently marginally utilized method is a synthesis of ammonium sulfate via digestate air stripping and adsorption into H_2SO_4 .^{11–13} It faces many problems, including the need for large external amounts of H₂SO₄ distributed to remote farming places that produce biogas and digestate. The need for pH-adjusted air stripping results in significant utility inputs, which contribute to high global warming potential and eutrophication.¹⁴ Additionally, there is a market saturation of ammonium sulfate since it is available cheaply as a byproduct of caprolactam production¹⁵ with no incentives to address the digestate issue. Atom economy argument,¹⁶ a metric of the process' greenness, suggests that exact stoichiometric quantities of starting materials will result in the highest sustainability.¹⁷ Ammonium bicarbonate (NH₄HCO₃ further referred to as ABC) adheres to these principles and has recently been proposed as a sustainable source of both nitrogen and carbon to soil and plants.¹⁸ ABC was one of the main fertilizers used in China some 20 years ago¹⁹ until its use decreased due to the emergence of urea.²⁰ This is due to its poor environmental stability since it readily decomposes back into NH₃ and CO₂ at room temperature.¹⁸ It is excluded from the organic fertilizer register in the US, not allowed as a standalone fertilizer in the EU and it is currently used as a fumigant.²¹ If the methods can be developed by formulating ABC into solid materials that do not have any negative impacts on the biota, do not volatilize spontaneously, and contribute nitrogen to the plant growth, a tremendous benefit to the agriculture sector would result.¹⁸ The technologies to extract solid ABC from digestate should be available on a large scale for distributed operation and have already been estimated to be cost and environmentally efficient.^{13,14,22} The path in physicochemical stabilization of ABC potentially lies in green mechanochemical stabilization technologies, as recently shown when addressing urea environmental stability problems.²³⁻²⁹ In this work, we performed the mechanochemical synthesis of Mg and Zn containing double salts using widely available minerals such as magnesite, MgCO₃, or smithsonite, ZnCO₃. The resulting multinutrient (N-Mg and N-Zn) materials were characterized physicochemically as well as using soil experiments and

showed increased availability of nitrogen to lettuce combined with better compatibility with agricultural microorganisms.

MATERIALS AND METHODS

Materials for ABC Double Salt Synthesis. Ammonium bicarbonate (NH_4HCO_3 , \geq 99%, Sigma-Aldrich, USA), ammonium carbonate, further referred to as AC, ($(NH_4)_2CO_3$, Merck, Germany), magnesium carbonate (MgCO₃, extra pure, Acros, USA), and zinc carbonate (ZnCO₃, 97%, Zn > 58%, Alfa Aesar, UK) were used as received.

Double Salt Mechanochemical Synthesis. The overall synthesis procedure is shown in Figure 1. ABC double salts with Mg and Zn were produced using a Retsch MM300 mixer mill equipped with a stainless steel 15 mL milling jar from Form-Tech Scientific (Canada) with a milling time of 10 min at 25 Hz using two 8 mm zirconia balls and a total mass of 0.200 g. After the conversion was confirmed using powder XRD, the process was scaled up using a Retsch PM100 planetary mill equipped with a 250 mL stainless steel jar operating at 500 rpm for 5 min containing 20 stain steel balls. The total mass was 20 g, and they were used in soil experiments. In some instances, ammonium carbonate was used as a precursor to ensure that both ABC and AC resulted in the same crystalline structures of double salts. Where compounds containing crystalline water were made during the reactions, a small amount of liquid water (40–150 μ L) was added immediately before milling.

Physicochemical Product Characterization. The crystalline structure of Mg(NH₄)₂(CO₃)₂·4H₂O and Zn(NH₃)CO₃ powders, as well as the corresponding precursors, were characterized using powder X-ray diffraction (XRD) using an Empyrean, PANalytical B.V. diffractometer operating at 45 kV and 40 mA. Scans were performed in the 2θ range between 5 and 60° with a scan step of 0.0131° and Cu K α radiation source ($\lambda = 1.54$ Å).

The thermal stability evaluation was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in SDT 650 equipment (TA Instruments, USA). Approximately 10 mg of the sample was heated from 30 to 500 $^{\circ}$ C at 10 $^{\circ}$ C/min under an air atmosphere with flux of 50 mL/min.

The scanning electron microscopy (SEM) analysis was conducted in a JEOL JSM 6510 to characterize the resulting particle morphology. The samples were dispersed on carbon tape bonded to the surface of a metal disc and coated with gold in an ionization chamber (Baltec Med. 020) before analysis.

The nitrogen (N) content was determined using an elemental analyzer (CHN, PerkinElmer 2400 Series II Elemental Analyzer). The average content of each material was determined in quadruplicate using an average sample size of 10 mg. Moreover, Zn and Mg Table 1. Physical and Chemical Properties of the Soil Collected in the 0-20 cm Layer at Yuma, Arizona

	(α)	·1						. (/1)				. (/1)	
texture	(%)	\$011		water extra	ict	m	acronutrier	its(mg/kg)		micr	onutrien	ts(mg/kg)	
clay	31.0	respiration CO ₂ (kg/ha)	48.8	total nitrogen ^b	26	calcium ^d	5,645.0			iron	13.4	sulfate ^h	156.3
silt	54.0	soil pH^c	8.1	organic nitrogen	13	magnesium ^d	746.0	phosphorus olsen P ^g	17.3	manganese ^e	3.0	sodium ^d	413.0
sand	15.0			nitrate-N ^f	13	potassium ^d	406.0			zinc ^e	1.1		

^{*a*}Procedure for soil particle size (texture) was done according to the hydrometer method.^{39 *b*}Concentrations of total and organic and inorganic N were determined with a Shimadzu TOC-TN analyzer (Shimadzu Corp., Kyoto, Japan). ^{*c*}The pH(H₂O) was determined in a soil:water suspension (1:1, m/v). ^{*d*}K, Ca, Mg, and Na residing on the soil colloid exchange sites were extracted by displacement with ammonium acetate solution buffered to pH 7.0. Cation concentrations are determined using atomic emission (AES), absorption spectrometry (AAS), or ICP-AES instrumentation. ^{*c*}Mn and Zn were extracted using the DTPA (diethylenetriaminepentaacetic acid) micronutrient extraction method, developed by Lindsay and Norvell,⁴⁰ for neutral and calcareous soils. ^{*f*}Inorganic N and exchangeable acidity were extracted using KCl and N levels were expressed as nitrate. ^{*g*}PO₄–P were quantified according to Olsen *et al.*⁴¹ Phosphate from the soil was extracted by 0.5 N sodium bicarbonate solution adjusted to pH 8.5. ^{*h*}Sulfate–S, SO₄–S was determined according to Schulte and Eik⁴² with the following exception: (1) elimination of activated carbon and (2) determination of S by ICP-AES.

determinations were performed by flame atomic absorption spectroscopy (FAAS) using a PerkinElmer model PinAAcle 900T with flame composed of synthetic air (10 mL) and acetylene (2.5 mL) and wavelengths at 213.86 and 285.21 nm, respectively.

Nitrogen-Release Soil Experiments. Nitrogen loss measurements were carried out in an Oxisol collected from the surface layer (30-40 cm) of an agricultural area in São Carlos, São Paulo State, Brazil (21° 95' S, 47° 85' W; 856 m above sea level). The soil (particle size <2 mm) had the following characteristics: 608 g/kg sand, 367 g/kg clay, and 25 g/kg silt, according to textural analysis by the pipet method³¹; water holding capacity (WHC) of 200 g/kg³ pH (H₂O) 5.2, measured with a glass electrode; organic C content of 8 g/kg, measured by the Walkley-Black method³³ ; cation exchange capacity (CEC) of 45 cmolc/kg; and phosphorus content of 4 mg/kg. $Mg(NH_4)_2(CO_3)_2$ ·4H₂O and Zn(NH₃)CO₃ powders were incubated in 10 g of soil using a ratio between 0.9 and 1.1 g-N/kg_{soil} in 125 mL polyethylene bottles. The powders were applied to the soil surface, and the soil moisture content was increased to 80% water holding capacity by adding deionized water (1.6 mL in 10 g of soil). A 5 mL acid trap containing 4% boric acid was attached to the polyethylene bottles to capture the ammonia volatilized during the incubation.^{34,35} The samples were incubated for 3, 7, and 14 days in a temperaturecontrolled room maintained at 25 °C. Volatilized NH₃ was determined by titration of boric acid using HCl (0.01 mol/L). Inorganic N was extracted from the soil by shaking for 1 h with 100 mL of 1 mol/L KCl containing 5 mg/L phenylmercuric acetate as a urease inhibitor. The suspensions were filtered using a slow filter (diameter 12.5 cm, Unifil), and the extracts were stored in 100 mL polyethylene bottles at 5 °C. The NH₄⁺ content in the soil extracts was determined using a colorimetric method.^{36,37} The N content of each fraction was expressed as a percentage of N applied.

Soil Microorganism Compatibility Experiments. The inhibition against an agricultural microbial inoculant was determined by incubating ABC, AC and the synthesized $Mg(NH_4)_2(CO_3)_2\cdot 4H_2O$ and $Zn(NH_3)CO_3$ powders in a Petri dish containing nutrient medium (TSA – Tryptic Soy Agar) and the spores of the bacteria *Bacillus subtilis* (B2084). After the inoculation, the samples in the Petri dish were incubated in an oven at 25 °C for 24 h, and photos were taken to compare the control (microorganism growth in the agar without any other compound) with the microorganism development in the presence of the nitrogenous compounds. The growth inhibition was determined by processing the optical images using the ImageJ software.³⁸

Lettuce Cultivation Pot Experiments. A study was conducted in a greenhouse at the US Arid Land Agricultural Research Center, USDA, Arizona. Samples from the 0–20 cm layer were collected in April of 2023. Typical Silty Clay Loam soil (Table 1) was collected at the University of Arizona (UA) Farm, The Yuma Agriculture Center, in Yuma, Arizona (32.712264, -114.703621). The material was transferred to a greenhouse at the U.S. Arid Land Agricultural Research Center (ALARC), placed in bins, and covered with plastic for solarization. After 2.5 weeks, the bins were uncovered, and the soil was air-dried. Dried soil was ground and sieved (maximum 2 mm).

Levels of phosphorus (P) and N were adjusted based on the results of the soil analysis and following the Guidelines for Head Lettuce Production in Arizona (ACIS).⁴³ P levels were adjusted to 200 lbs P_2O_5 per acre, and N levels were adjusted to 300 lbs N per acre. The application of N fertilizers was split in two. First, 20% before sowing (starter) and 80% at the first true leaves stage (15 days after sowing). For the assays, 1 kg of soil air-dried and processed was placed in pots with a capacity of 1.3 kg. In each pot, four romaine lettuce seeds were sown. Three different nitrogen (N) source materials were used in this study. The materials were the AC control and Mg(NH₄)₂(CO₃)₂· 4H₂O and Zn(NH₃)CO₃ powders. Additionally, a negative control was used with no nitrogen added. The experimental design was completely randomized with four replicates.

Plant Material and Growth Conditions. Pelleted Sparx Romaine Lettuce Seed was purchased from Johnny Seeds, product ID: 3156JP. After 11 days, plants were thin out, and only the largest plantlet was left in each pot. Throughout cultivation, the soil humidity was maintained at around 90% of field capacity with daily irrigations to replace water lost by evapotranspiration (weight difference) using deionized water. The plants were grown in a greenhouse with temperature control set to 25 °C.

Plant Harvest. The lettuce plants were harvested 46 days after sowing with four repetitions at each harvest. Shoot and roots were separated, and the weight was recorded. Roots were manually separated and washed with running distilled water to remove the adhering soil. All materials were freeze-dried; the weight was recorded; and the materials were processed for subsequent tissue analysis.

Soil and Tissue Analysis. After plant harvests, the soil in the pots was homogenized and a sample was withdrawn, freeze-dried, and analyzed. Inorganic N and exchangeable acidity were extracted by using KCl, and N levels were expressed as nitrates in soil samples. Freeze-dried tissue samples were analyzed on a Leco CN-2000 dry combustion analyzer. The analyzer operated on a dry combustion principle with thermal-conductivity detection for N.

Soil Respiration Experiments. Thirty-five grams of air-dried soil was placed in a 50 mL plastic cup, and deionized water was added until 70% field capacity. This small cup was placed inside a 250 mL jar. A colorimetric gel probe for measuring low concentrations of CO_2 was placed in the glass jar when the water was added. The jar was sealed tightly with a silicone gasket lid. The jar was incubated at 20 °C for 24 h. After incubation, the probe's color was read with a digital color reader (DCReader, Woods End Laboratory) to determine the amount of CO_2 respired. Results were reported as SSCB-C in milligrams per kilogram.

Statistical Analysis. A randomized design was used for the experiment. Statistical analysis was done by Statistical Analysis Software, SAS. The data are presented as the average plus standard deviations. The ANOVA significance test was used to identify



Figure 2. Powder XRD patterns of reactants used and products obtained from the small-scale mechanochemical synthesis of (a) $Mg(NH_4)_2(CO_3)_2$ ·4H₂O and (b) Zn(NH₃)CO₃. The peaks from the reported $Mg(NH_4)_2(CO_3)_2$ ·4H₂O^{47,48} and Zn(NH₃)CO₃⁵⁰ patterns are also shown.



Figure 3. Experimental powder XRD patterns of the optimized (a) $Mg(NH_4)_2(CO_3)_2 \cdot 4H_2O$ and (b) $Zn(NH_3)CO_3$ using the planetary mills compared to those of the mixer mill.

significant differences between the variables. When significant differences were detected, the Tukey test was used at P < 0.05 for comparison of the averages.

RESULTS AND DISCUSSION

Magnesium and Zinc Ammonium Carbonate Double Salt Synthesis. The first set of experiments was performed using small-scale (200 mg) reactant amounts to ascertain the role of the reactant stoichiometry and the role of water addition in the conversion of the precursors. As NH₄⁺ precursors, both ABC and AC were utilized. Mechanochemical synthesis was chosen since it is reported as a fast reaction process that can be carried out under mild conditions, without the presence of solvents, and with little waste generation resulting in a high reaction yield.^{23,44} Additionally, mechanochemistry has already been used to produce urea-based cocrystals^{23,25,45} and ammonium magnesium sulfate from mineral serpentine with ammonium bisulfate.⁴⁶ First, magnesium ammonium carbonate tetrahydrate, $Mg(NH_4)_2(CO_3)_2$. 4H₂O, was synthesized mechanochemically by reacting ammonium bicarbonate with magnesium carbonate in a

molar ratio of 2:1 as shown in Figure 2a. The diffractograms were compared with literature data from Erdös et al.47 and Zhang et al.⁴⁸ It can be seen in Figure 2a that the addition of several droplets (40–80 μ L) of water to the reaction mixture resulted in the disappearance of the parent peaks and the appearance of the Mg(NH₄)₂(CO₃)₂·4H₂O. Further increasing water content resulted in several crystalline phases forming, as evidenced by the addition of 150 μ L of liquid water in Figure 2a. This empirical titration was necessary since commercial Mg source used in this study, while marketed as magnesite, is likely a combination of hydrated magnesium carbonate and magnesium hydroxide⁴⁹ according to its XRD pattern shown in Figure 2a. Thus, the necessary water amount to be added cannot be determined from stoichiometric considerations alone. Results shown in Figure 2a suggest that mechanochemical methods can be utilized only using MgCO₃ as a Mg precursor.

Mechanochemical synthesis results of zinc ammonium carbonate is shown in Figure 2b presented similar peaks compared to the diffractograms reported by Khazeni *et al.*⁵⁰ While obtained XRD patterns reproduce very well those of

compound	measured N content (%)	theoretical N content (%)	measured Zn ²⁺ content (%)	theoretical Zn ²⁺ content (%)	measured Mg ²⁺ content (%)	theoretical Mg ²⁺ content (%)
Reactants						
ammonium bicarbonate	18.7 ± 0.7	17.7	0		0	
ammonium carbonate	25.6 ± 0.3	29.2	0		0	
Products						
$\begin{array}{c} Mg(NH_4)_2(CO_3)_2 \\ 4H_2O \end{array}$	9.5 ± 0.3	11.1			9.6 ± 0.1	9.6
$Zn(NH_3)CO_3$	7.3 ± 0.4	9.8	46.9 ± 0.4	45.9		

Table 2. Elemental Analysis of Magnesium and Zinc Ammonium Carbonates Synthesized by Using Mechanochemical Methods

Khazeni *et al.*⁵⁰ and some other works that correspond to $Zn(NH_3)CO_3$ stoichiometry,⁵¹ the overall carbonate ion content from mass balance considerations will always be in excess, e.g., close to $Zn:NH_4^+:CO_3^{2-}$ of 1:1:2 if synthesized from ABC:ZnCO₃ = 1:1. This is also evident from XRD patterns in Figure 2b where a broad peak at 2° theta = 13° was apparent. Attempts to synthesize $Zn:NH_4^+:CO_3^{2-}$ of 1:1:1 using AC:ZnCO₃ = 1:1 led to the absence of the peak due to the $ZnCO_3$. Hence, a dynamic nature at the crystalline phases obtained in $CO_2-NH_3-H_2O$ equilibrium suggests that rarely a pure single AC or ABC phase exists and optimization of the reactant ratio is needed for the mechanochemical synthesis.⁵²

XRD patterns in Figure 2 indicate that magnesium and zinc ammonium carbonate double salts were successfully produced. The importance of the formation of these compounds in an agricultural perspective is that, besides increasing their thermal stability, which will reduce the N losses in soil, it can also be a source of other important nutrients for plants.⁴⁵ While small mill products were used in further physicochemical characterization, optimized 20 g batches were also produced using a planetary mill. The resulting powder XRD patterns are compared with those of the small shaker mill and are identical as shown in Figure 3, suggesting that large-scale mechanochemical production was successful. Optical images of the resulting magnesium and zinc ammonium carbonates are shown in Figure S1 and the Supporting Information.

The measured nitrogen content in synthesized Mg- $(NH_4)_2(CO_3)_2 \cdot 4H_2O$ and $Zn(NH_3)CO_3$ is shown in Table 2. Although the N content for the ABC agrees with its theoretical data, all the other compounds exhibited a lower percentage of nitrogen than expected based on their molecular formula. In particular, ammonium carbonate in a pure form exists as ammonium carbonate monohydrate with N = 25%, e.g., lower than the theoretical value of 29.17% for ammonium carbonate without a crystalline water molecule. Similarly, the ammonium bicarbonate utilized likely contained traces of ammonium carbonate, resulting in slightly higher N content than the expected theoretical level of 17.72%. Both magnesium and zinc ammonium carbonate double salts contained N content lower than their theoretical values, likely due to the excess moisture of carbonate ions present.

Thermal Stability Characterization of Magnesium and Zinc Ammonium Carbonate Double Salts. As shown in the thermal analysis in Figure 4a,b, the thermal behavior of the compounds could be divided into several consecutive stages. Below 150 °C, the precursors AC and ABC exhibited fast decomposition with a total mass loss before 140 °C. This reflects the high thermal instability of AC and ABC, with the latter presenting a thermal degradation at temperatures slightly higher than AC. In the same temperature range,



Figure 4. (a) TGA and (b) DSC curves of magnesium and zinc ammonium carbonate double salts together with their parent compounds.

Mg(NH₄)₂(CO₃)₂·4H₂O lost about 37% of its initial weight. Zhang *et al.* studied the thermal decomposition of Mg-(NH₄)₂(CO₃)₂·4H₂O up to 900 °C.⁴⁸ The results indicated that the Mg(NH₄)₂(CO₃)₂·4H₂O lost its ammonium carbonate fragment around 110 °C to transform into Mg(CO₃)· 3H₂O. The ZnCO₃ lost about 25% of its initial mass at 200– 260 °C. Around this temperature, ZnCO₃ usually transfers to ZnO, which is stable. On the other hand, MgCO₃ does not reach its final stability before 450 °C where it transforms to MgO after losing 55% of its initial weight.

DSC data shown in Figure 4b suggests that $Zn(NH_3)CO_3$ tends to be more stable compared to $Mg(NH_4)_2(CO_3)_2$ ·4H₂O due to the structural differences between both compositions. $Zn(NH_3)CO_3$ has no water molecules in its unit cell, while $Mg(NH_4)_2(CO_3)_2$ ·4H₂O is connected to two carbonate groups compared to one for the former. The endothermal peak centered at 100 °C suggests that the loss of crystalline water is concomitant with the loss of NH₃ and CO₂ from the structure. The Mg(NH₄)₂(CO₃)₂·4H₂O lattice structures tend to lose water or CO₂ to become more stable. On the other hand, in Zn(NH₃), nitrogen forms a coordination bond with Zn, which requires a higher amount of energy to be broken.⁵¹ We associate the complex endothermal peak structure at 250 °C in Zn(NH₃)CO₃ with the complete loss of both NH₃ and CO₂.

phase transformation no.	composition	entropy (J/mol·K)	enthalpy (kJ/mol)	Gibbs free energy (kJ/mol)	T range (°C)
1	$Mg(NH_4)_2(CO_3)_2 \cdot 4H_2O$	256.5	109.9	-2.6	55-110
2		329.2	259.1	-90.2	360-425
1	$Zn(NH_3)CO_3$ from ABC: $ZnCO_3 = 1:1$	179.08	121.01	-10.14	180-280
1	$Zn(NH_3)CO_3$ from AC: $ZnCO_3 = 1:2$	163.83	110.50	-5.81	170-270
(a) ⁸⁰ 60 (%) 40 40 20	a b c c d d d d d d d d d d d d d d d d d	(b) 60 (b) 60 (c) 60 (c	b a a	a a a a a a a a a a a a a a a a a a a	- - - b, -
			· · · · ·	Ln(NH ₃)CO ₃	-
0	2 4 6 8 10 12		2 4 6	8 10 12 14	
	Time (days)		Ti	me (days)	

Table 3. Thermodynamic Parameters, Including Entropy, Enthalpy, and Gibbs Free Energy Calculated from the Thermal Decomposition Data Using the Coats-Redfern (CR) Model⁵³

Figure 5. (a) Cumulative profiles of NH₃ volatilization during aerobic incubation in soil of ABC, $Mg(NH_4)_2(CO_3)_2 \cdot 4H_2O$ and $Zn(NH_3)CO_3$. The vertical bars are standard deviations. (b) Recovery of N as NH₄⁺ during aerobic incubation in soil of ABC and the respective double salts. The vertical bars are standard deviations. Differences between mean values were determined by analysis of variance (ANOVA), and differences between treatments were compared using the Tukey's test (p < 0.05), while the data is shown in Table S1 in the Supporting Information.

The thermodynamic parameters (entropy, enthalpy, and Gibbs free energy) were computed for the main thermal transformations using the Coats–Redfern (CR) model⁵³ as shown in Table 3. The $\ln(-\ln(1 - x)/T^2)$ versus 1000/T plot was used to calculate the parameters. It can be noticed that the entropy value is highly positive for Mg(NH₄)₂(CO₃)₂·4H₂O with 256.5 J/mol·K, indicating the disorder of the structure. At the same time, the low negative value of the Gibbs free energy, about -2.6 kJ/mol, implies that the produced Mg(CO₃)·3H₂O is still thermodynamically unfavored and will thermally degrade to transform to a more stable structure.

 $Zn(NH_3)CO_3$ comes from two different reactions, ABC:Zn- $CO_3 = 1:1$ and AC:Zn $CO_3 = 1:2$. Both $Zn(NH_3)CO_3$ compositions exhibit quite similar thermal behavior. Both reach a stability plateau around 270–280 °C after losing approximately 38% of the initial weight. The negative values of Gibbs free energy, -10.14 and -5.81 kJ/mol, for the double salt derived from ABC and AC, respectively, reveal the spontaneous reaction under these conditions, while the product is thermally stable.

Morphological Characterization (SEM and EDS). SEM images of (a) ABC, (b) AC, (c) $Mg(NH_4)_2(CO_3)_2 \cdot 4H_2O$, and (d) $Zn(NH_3)CO_3$ are shown in Figure S2 in the Supporting Information. The porous particles of ABC and AC completely transformed into well-defined particles of Mg and Zn containing double salts of ammonium carbonate.

 NH_3 Volatilization and NH_4^+ Recovered From Soil. One of the main losses of nitrogen-based fertilizers is due to NH_3 volatilization. The ammonia volatilization curves of the different treatments are shown in Figure 5a. The NH_3 volatilization curves can be divided into two groups. The first group corresponds to ABC, which showed high ammonia emission, reaching 71% in 7 days of incubation in the soil. $Mg(NH_4)_2(CO_3)_2 \cdot 4H_2O$ and $Zn(NH_3)CO_3$ exhibited intermediate NH₃ volatilization. They showed similar profiles, as well as reductions in NH₃ volatilization compared to ABC. Reductions reached 20.0 and 26.5% compared to ABC on the third day of incubation. In addition, there were reductions in emissions at 7 and 14 days of incubation, being pronounced for Zn(NH₃)CO₃, reaching 12.2 and 7.4%, respectively. The results suggest that in this condition, the buffering capacity of the soil was more effective (not affected by the local pH changes promoted by carbonate ions), leading to lower NH₃ volatilization. Hence, the interaction of ammonium (NH_4^+) ions with Zn^{2+} in a double salt structure was effective in reducing losses of N by volatilization, shown also in Figure 5a.

The NH₄⁺ recovered curves in the soil are shown in Figure 5b. ABC control presented lower NH₄⁺ values compared to those of the other treatments, agreeing with its higher volatilization. Low NH₄⁺ values are associated with increased N loss through NH₃ volatilization. Zn(NH₃)CO₃ showed the highest NH₄⁺ content in 3 days of incubation, reaching 52.2%. The double salt interaction allowed N stabilization in the NH₄⁺ form in the soil, reducing its conversion/transformation to NH₃. Mg(NH₄)₂(CO₃)₂·4H₂O showed higher NH₄⁺ values than ABC, reaching 48% in 3 days of incubation. It is worth noting that NH₄⁺ concentrations in soil reduced after the third day, which is associated with its transformations in the soil and consequent NH₃ volatilization.

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Figure 6. Growth inhibition of ammonium bicarbonate, $Mg(NH_4)_2(CO_3)_2$ ·4H₂O, and $Zn(NH_3)CO_3$ on agriculture-beneficial bacteria *Bacillus subtilis* in a nutrient medium.



Figure 7. Plant biomass production (dry weight, DW) under different fertilizers. Data represent the mean \pm SD of four different replicates 46 days after planting. Different capital letters indicate significant differences among different treatments (p < 0.05).

Compatibility with Microbial Inoculants. Several studies reported that low-stability ammonia-releasing materials, such as ABC alone, can act as fumigation agents against some plant pathogens.^{54–56} However, while decreasing the phytopathogen incidence, these compounds can also negatively affect the rhizosphere microbial community, reducing the viability of some beneficial microorganisms for plant growth

and development. In this context, an *in vitro* experiment was carried out to compare the compatibility between Mg- $(NH_4)_2(CO_3)_2$ ·4H₂O and Zn $(NH_3)CO_3$ as well as ABC with the microbial inoculant *Bacillus subtilis* (B2084), a plant growth-promoting microorganism.

As can be noticed in Figure 6, the addition of ABC in the center of the dish inhibited microorganism growth by



Figure 8. Total nitrogen in lettuce shoot tissue (g/g) growing under different nitrogen fertilizers. Data represent the mean \pm SD of four different replicates. Different capital letters indicate significant differences among different treatments at the same evaluation time (p < 0.05).



Figure 9. Soil NO₃-N (mg/kg) at the harvest point, 46 days after sowing. Data represent the mean \pm SD of four different replicates. Different capital letters indicate significant differences among different treatments (p < 0.05).

approximately 90%. When $Mg(NH_4)_2(CO_3)_2 \cdot 4H_2O$ and Zn(NH₃)CO₃ with the same N-content as ABC were added to the growth medium, a much lower percentage of inhibition was observed. Mg(NH₄)₂(CO₃)₂·4H₂O presented lower values (only 1.4%), while the addition of $Zn(NH_3)CO_3$ reduced the bacterial growth by approximately 10%. This higher inhibition rate can be explained by the fact that high Zn concentrations can be toxic to soil bacteria.⁵⁷ In the Petri dish, the bacteria closest to the cocrystal sample were more exposed to this Zn toxic effect, which can decrease their survivability. Additionally, it is important to highlight that the presence of the plant nutrients Mg and Zn can also positively influence microorganism development since these elements are enzymatic cofactors, which are essential for microbial metabolic activity.⁴⁹ It means that besides providing better compatibility with chemical and biological products to increase agricultural productivity, $Mg(NH_4)_2(CO_3)_2 \cdot 4H_2O$ and $Zn(NH_3)CO_3$ can also promote the soil microbial community by providing essential elements for microorganism development.

Lettuce Growth and Mineral Nutrition. Sparx Romaine lettuce plant appearance under three N treatments is shown in Figure 7. There were clear effects of N deficiency on morphological components of growth after 46 days of cultivation in the no added N control and significantly increased biomass in all N treatments. Shoot-root biomass allocation did not differ among the treatments and was significantly lower in N-limited plants.

Lettuce cultivation is both nutritionally intensive and timedependent, relying on elevated amounts of N matched to plant growth to maximize productivity. When nutrients are abundant, plant intake will match the carbon growth potential. When essential nutrients are limiting, the growth rate is reduced accordingly.⁵⁸ Additionally, N starvation can affect several genes directly or indirectly in the photosynthesis process/machinery such as the light-harvesting complex (LHC), the photosystem-I (PS-I) reaction center, and RuBisCO.⁵⁹ In the pot experiment, the N concentration in the shoots was inversely related to biomass production. When N was limiting, overall plant biomass was reduced but N concentration was slightly elevated resulting in lower overall N uptake (Figure 8). Others have found similar results that under continuous nonlimiting N supply (for 40 days), there were no net changes in N concentration in lettuce leaves.⁶⁰ Results obtained here are congruous with the $Mg(NH_4)_2(CO_3)_2$ · $4H_2O$ and $Zn(NH_3)CO_3$ treatments providing N to the lettuce when needed for plant growth similar to previous N fertility studies.⁵⁹

Soil Respiration and Residual Nitrogen. The remaining N-NO₃⁻ in the soil after harvest was dependent on the N source used as shown in Figure 9. The lowest concentration of N-NO₃⁻ occurred under the control with no N added, followed by ammonium carbonate and Mg(NH₄)₂(CO₃)₂. 4H₂O and Zn(NH₃)CO₃ treatments having the highest N concentration. These data suggest a controlled N release rate, which is beneficial for plant production as well as reduction of N loss by leaching, which is a common issue linked to lettuce production in the southwest US.⁶¹

A similar trend was observed in soil respiration, where $Mg(NH_4)_2(CO_3)_2 \cdot 4H_2O$ and $Zn(NH_3)CO_3$ treatments had the highest soil respiration rate $(CO_2 kg/ha)$, while AC did not differ from the control as shown in Figure 10. Studies have shown the stimulation of soil respiration by N fertilization.⁶² Even when C pools below-ground vary, the same response is observed.⁶³



Figure 10. Soil respiration (CO₂ kg/ha) response to different nitrogen fertilizers. Basal corresponds to Δ , control treatment (no nitrogen added), and mass, which is subtracted from the other treatments. Control average value for Soil respiration was 52.49 and 59.21 CO₂ kg/ha during mid growth and harvest, respectively. Data represent the mean \pm SD of four different replicates. Different lowercase letters indicate significant differences between evaluation time (midgrowth and harvest) in the same treatment (p < 0.05). Different capital letters indicate significant differences among different treatments at the same evaluation time (p < 0.05).

A meta-analysis showed positive correlations between soil respiration, microbial biomass, root, and fine root biomass to N addition.⁶² The soil respiration is a result of microbial/heterotrophic respiration during organic matter decomposition as well as root/autotrophic respiration, during root growth and maintenance.^{64,65}

Note that changes in soil respiration occurred more rapidly than changes in total nitrogen, shoot tissue, or growth responses. A short growth cycle under N-depleted conditions could lower the level of tissue N without affecting growth and biomass. On the other hand, soil respiration and soil remaining N-NO₃⁻ showed a linear response (R^2 = 0.9356) (Figures 9 and 10). Potential nitrogen mineralization has been described as the highest positive correlation with potential soil respiration among multiple soil factors. 66

Furthermore, as it was previously reported, increasing nutrient levels results in increased microbial activity in soils, showing a positive response to N fertilization,⁶⁷ which may be happening in our treatments. It is important to highlight that this study does not aim to indicate the use of fertilizers containing micronutrients indiscriminately. On the contrary, we encourage any potential users to investigate and have comprehensive knowledge of the area history as well as the soil properties. In this view, Zn is a micronutrient fundamental for plant and other organisms' proper development. However, just like most micronutrients, Zn in high doses can present toxicity.⁶⁸ Additionally, it is important to highlight that the fertilizer we have been developing here is not intended to be applied, under an agronomical context, as the only N source for plants since the Zn content will limit the total application. In other words, its application supposes that most of the N will be supplied by a conventional fertilizer (e.g., urea, ammonium nitrate, etc.) and supplemented by the N carried on with the Zn double salt here synthesized. Since the amount of N in wastewater is an environmental problem, its utilization as fertilizer in this strategy is an interesting strategy to dispose of the residue while supplementing the N demand from plants. Moreover, the main goal with the association of N and Zn in the same product is that, besides being a micronutrient for plants growth, Zn is also an important cofactor for N uptake by plants, which makes this association very interesting.

In calcareous soils, Zn deficiency is the main micronutrient disorder in rice (*Oryza sativa* L.).⁷⁰ Numerous studies have been performed with Zn fertilizers in different countries⁷¹ and Zn is the most common micronutrient fertilizer applied to rice (*Oryza sativa* L.) in the USA.⁷² The Zn(NH₃)CO₃ fertilizer is an environmentally friendly option for these cases, offering N and Zn from nutrient recovery. In our study, the addition of Zn in the soils did not impact Zn concentration in plant tissues (Table 4). This result suggests that the tested plants were able

Table 4. Effect of Different Nitrogen Fertilizers on the Zn Concentration of Leaves in Lettuce $Plants^a$

treatment	zinc in shoot tissue	mg/kg
no nitrogen added	12.00 ± 2.83	А
ammonium carbonate	10.18 ± 1.36	А
$Mg(NH_4)_2(CO_3)_2 0.4H_2O$	11.25 ± 0.96	А
Zn(NH ₃)CO ₃ from AC	11.60 ± 1.74	Α

^{*a*}Data represent the mean \pm SD of four different replicates. Different capital letters indicate significant differences among nitrogen fertilizer at the same Cu level and collect (p < 0.05) ND* (data not available).

to maintain Zn homeostasis, as they adjusted their growth and development. Besides the plant material, other important factors will determine how the concentration of micronutrients play in this complex scheme, bioavailability being the most pronounced.⁷³ Overall, it was shown that all N fertilizers increased lettuce yield from the control.

CONCLUSIONS

The emerging agriculture and energy problems provide opportunities for a completely new fertilizer material design and sustainable synthesis. Liquid biomass anaerobic digestion byproduct contains NH_4^+ , which can be recycled in a solid fertilizer form, such as ABC, but its usability has been starkly limited due to poor environmental stability. We hypothesized that combining ABC or AC, which often crystallize in mixtures due to the complex phase equilibria, in a form of nutrient metal containing double salts, Mg(NH₄)₂(CO₃)₂·4H₂O and Zn- $(NH_3)CO_3$, would provide for more nutrient efficient materials with a potential of increased environmental stability. We utilized naturally abundant metal carbonate sources and mechanochemistry to obtain the double salts. This constituted a conceptually new synthetic approach to these double salts, which was more sustainable and directly scalable, as evidenced by successful synthesis using both a shaker and planetary mill. The crystalline structure of the resulting materials was confirmed using powder XRD and thermal analysis showed distinctly different properties from those of parent ABC or AC. The soil testing results confirm that the association of ammonium carbonate in Zn and Mg cocrystals can benefit the N uptake (by reducing its volatilization). Additionally, these double salts reduced beneficial agricultural microorganisms inhibition, which is an interesting characteristic since it can allow the positive action of biological and chemical fertilizers on plants growth.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c07785.

Optical images of the mechanochemically synthesized materials; SEM micrographs of ABC, AC and the synthesized double salts; and analysis of variance of soil N-release experiment (PDF)

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Notes

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