

# Investigation of Carbon Distribution with $^{14}\text{C}$ as Tracer for Carbon Dioxide ( $\text{CO}_2$ ) Sequestration through $\text{NH}_4\text{HCO}_3$ Production

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## Abstract

This work studies carbon fate using  $^{14}\text{C}$  tracer technique in ecosystems when synthesized fertilizer is applied. The concept of aqueous ammonia solution scrubbing  $\text{CO}_2$  from flue gas is used in the fertilizer synthesis. Products after the capture are ammonium bicarbonate (ABC,  $\text{NH}_4\text{HCO}_3$ ) or long-term effect ammonium bicarbonate (LEABC,  $\text{NH}_4\text{HCO}_3$ ), an economic source of nitrogen fertilizer. The fertilizer (ABC or LEABC) is used as a “carrier” to transport  $\text{CO}_2$  from the atmosphere to the crops and soil. An indoor greenhouse was built and wheat was chosen as the plant to study in this ecosystem. The investigated ecosystem consists of plant (wheat), soils with three different pH values (alkaline, neutral and acidic), and three types of groundwater (different  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations). After biological assimilation and metabolism in wheat receiving ABC or LEABC, it was found that a considerable amount (up to 10%) of the carbon source is absorbed by the wheat with increased biomass production. The majority of the unused carbon source (up to 76%) percolated into the soil as carbonates, such as environmentally benign calcium carbonate ( $\text{CaCO}_3$ ). Generally speaking, alkaline soil has a higher capability to capture and store carbon. For the same soil, there is no apparent difference in carbon capturing capability between ABC fertilizer and LEABC fertilizer. These findings answer the question how carbon is distributed after synthesized fertilizer is applied into the ecosystem. In addition, a separate post-experiment on fertilizer carbon forms that exist in the soil was made. It was found that up to 88% of the trapped carbon exists in the form of insoluble salts (i.e.,  $\text{CaCO}_3$ ) in alkaline soils. This indicates that alkaline soil has a greater potential for storing carbon after the use of the synthesized fertilizer from exhausted  $\text{CO}_2$ .

*Keywords:*  $\text{CO}_2$  sequestration, fertilizer, ammonium bicarbonate, ecosystem,  $^{14}\text{C}$  isotope

## 1. Introduction

It has been well known that greenhouse effects lead to “global warming,” which severely threatens our living environment. It was predicted that greenhouse gases such as carbon dioxide ( $\text{CO}_2$ ) could increase the average global temperature 1.5 to 4.5°C and the sea level 0.25 to 0.5 m [1]. It is estimated that  $\text{CO}_2$  makes the largest contribution (63%) to this climate change and is regarded as the primary greenhouse gas [2]. Each year, over 20 tera ( $20 \times 10^{12}$ ) tons of  $\text{CO}_2$  has been released into the atmosphere as combustion exhaust [3]. Since the beginning of the industrial era,  $\text{CO}_2$  concentration in the atmosphere has risen from 280 ppm to 360 ppm [4]. The famous “*Kyoto Protocol*” commits the developed countries to reduce greenhouse gas emissions by 5.2% of their 1990 level by 2012 [1].

Stationary power generation contributes over one-third of the anthropogenic  $\text{CO}_2$  released from fossil fuel combustion [5], which raises an uncertainty about future generation of  $\text{CO}_2$  through combustion. The goal of reducing  $\text{CO}_2$  concentrations in the atmosphere can be met either by decreasing the rate at which  $\text{CO}_2$  is emitted into the atmosphere or by increasing the rate at which it is removed from it [1]. Extensive researches have been conducted on determining a fast and inexpensive method to sequester carbon. These methods are roughly classified into two categories [6],  $\text{CO}_2$  fixation by natural sinking process for  $\text{CO}_2$ , or direct  $\text{CO}_2$  sequestration by artificial processes. The natural sinking processes are the formation of fossil fuels via photosynthesis and rock weathering. The relevant options are ocean fertilization and mineral carbonate. The atmospheric  $\text{CO}_2$  would be fixed after conversion to more stable forms such as organic matter or carbonates, to be sequestered. Weather or natural carbonation is a very

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slow process and may take hundreds of years. In direct sequestration, CO<sub>2</sub> produced from sources such as coal-fired power plants, would be captured from the exhausted gases. A number of capturing techniques including absorption/stripping, adsorption/desorption, membrane separation [6] have been proposed and developed, including the use of chemical solvents, physical adsorption, and cryogenic methods [7,8]. Physical solvents are favored by high pressures and low concentrations of inert gases. CO<sub>2</sub> can be physically absorbed in a non-reactive solvent according to Henry's law and then regenerated using pressure reduction or heating. Chemical solvents are preferred for cases with low concentrations or amounts of CO<sub>2</sub> in the combustion gases and do not gain significant advantage by operating at elevated pressure. The chemical solvent methods are generally recognized as the most effective technologies at present. However the cost for separation of CO<sub>2</sub> is high, typically in the range \$40-200/ton of carbon [9]. The chemical solvent method also has some major problems, such as a slow absorption rate, small solvent capacity, and special equipment requirement. Currently, the monoethanolamine (MEA) process is widely used for CO<sub>2</sub> capture and regeneration. But this is an expensive option. Low cost and high capacity solvent is becoming the goal for chemical separation of CO<sub>2</sub>.

Current commercial approaches in the fertilizer industry which involves the reaction between CO<sub>2</sub> and NH<sub>3</sub> may provide an inexpensive and effective route of reducing CO<sub>2</sub> emissions from power plants [10]. NH<sub>3</sub> scrubbing capacity based on breakthrough curves is around 0.35 mol CO<sub>2</sub>/mol NH<sub>3</sub> on a molar basis or 0.9-1.2 kg CO<sub>2</sub>/kg NH<sub>3</sub> on a mass basis. The removal efficiency is approximately 99% and the CO<sub>2</sub> loading capacity can approach 1.2 kg CO<sub>2</sub>/kg NH<sub>3</sub> [11-12]. The maximum CO<sub>2</sub> removal efficiency and loading capacity by MEA absorbent is 94% and 0.40 kg CO<sub>2</sub>/kg MEA. A multi-pollution control concept with spraying aqueous ammonia into actual flue gas to capture CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub> emissions was proposed and developed [13] and the capture efficiency of CO<sub>2</sub> in the absorber was in the range of 76% - 91% at 35°C.

The products in the aqueous scrubber could include ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>, also called ABC), ammonium carbonate (all in crystalline or aqueous solution), plus reagent CO<sub>2</sub>, NH<sub>3</sub>, and NH<sub>4</sub>OH. Of these by-products, ammonium bicarbonate has been utilized by certain developing countries as a crop fertilizer [14] for over 30 years. Also the ammonia (NH<sub>3</sub>) in ammonium bicarbonate can be regenerated easily [11]. Therefore aqueous ammonia scrubbing techniques present many advantages such as lower cost, higher loading capacity, and higher CO<sub>2</sub> absorption efficiency, lower decomposition temperature and less corrosive environment for CO<sub>2</sub> capture over MEA.

The aqueous ammonia scrubbing process is assumed to be a very promising technique for CO<sub>2</sub> sequestration from flue gas. However, this type of CO<sub>2</sub> removal is best for systems that have the characteristics of low CO<sub>2</sub> concentration and operate at atmospheric pressure, high temperature and have a high volume flow rate. Continuous operation and a large capacity of CO<sub>2</sub> sequestration are highly desirable for practical application of this technique in power plants.

In this work, the scrubbing technique concept was applied and further extended to study carbon distribution in a closed ecosystem (air, plants, soil, undergroundwater) after NH<sub>4</sub>HCO<sub>3</sub> is applied. The process of CO<sub>2</sub> capture and storage in this work is shown in Fig. 1. It consists of three stages: CO<sub>2</sub> capture to form fertilizer; CO<sub>2</sub> storage by photosynthesis to form biomass; and insoluble salt formation in soil/under groundwater. Quantitative examination of carbon distribution in an ecosystem is a challenging task since carbon contents from the original ecosystem and from the added fertilizer need to be accurately and separately measured and quantified. Instead of using regular carbon, isotope <sup>14</sup>C tagged NH<sub>4</sub>H<sup>14</sup>CO<sub>3</sub> was synthesized in the laboratory. CO<sub>2</sub> in combustion exhaust gas was absorbed with aqueous ammonia solution through scrubbing. The captured CO<sub>2</sub> was then used to synthesize ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>). This fertilizer was used as a "carrier" to "transport" [15] CO<sub>2</sub> from the atmosphere to crops. After biological assimilation and metabolism of crops applied with NH<sub>4</sub>HCO<sub>3</sub>, a considerable amount of the carbon source is absorbed by plants with an increase in the amount of biomass production. The majority of the unused carbon source percolates into the soil as carbonates, such as calcium carbonate (CaCO<sub>3</sub>) and magnesium carbonate (MgCO<sub>3</sub>). These carbonates are environmentally benign. As insoluble salts, they are found in normal rocks and can be stored safely and permanently in soil. An important point of this work is to transform CO<sub>2</sub>, a greenhouse gas, into a profitable fertilizer.

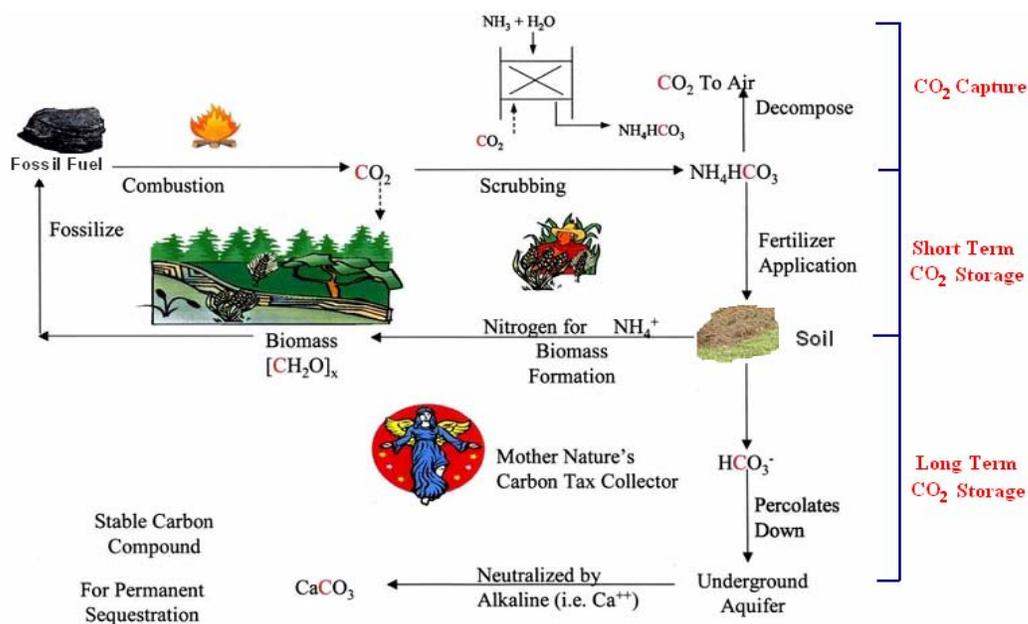


Figure 1 A schematic of three stages of sequestering CO<sub>2</sub> by the ecosystem [19].

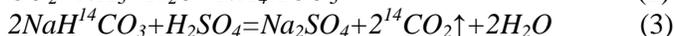
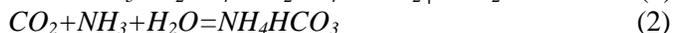
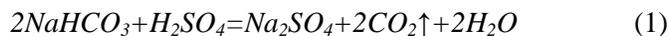
Fertilizer NH<sub>4</sub>HCO<sub>3</sub> is a white solid at room temperatures and ambient pressures. This unique feature makes the transportation and application of NH<sub>4</sub>HCO<sub>3</sub> as a CO<sub>2</sub> carrier much easier and more cost-effective. In order to further improve the stability of NH<sub>4</sub>HCO<sub>3</sub>, dicyandiamide was added during the synthesis process and forms long-term-effect ammonium bicarbonate (LEABC) [14]. LEABC considerably prolongs the effective time of ABC and increases its nitrogen utilization efficiency by inhibiting the natural decomposition reaction. Moreover, LEABC can enhance the chemical reactions to form insoluble carbonate salts. Thus, the total CO<sub>2</sub> sequestration is significantly improved.

Key questions to be answered are, after NH<sub>4</sub>HCO<sub>3</sub> (ABC) or LEABC is applied to plants, how much of the carbon source can be stored in plants as uptake, how much is stored as insoluble carbonate salts in soil and in undergroundwater, and how much is released back to the atmosphere as CO<sub>2</sub> gas. The radioactive isotope tracing method for monitoring the fate of carbon after the fertilizer is applied is the best choice. Fertilizer NH<sub>4</sub>HCO<sub>3</sub> (ABC) and LEABC used here were <sup>14</sup>C-tagged and carbon distribution in samples can be detected using a Liquid Scintillation Counter (LSC). Thus, the carbon distribution of the fertilizer applied to plants can be determined. A detailed protocol to study carbon distribution using radioactive isotope was developed in this work.

## 2. Experimental System, Methods and Materials

### 2.1 Fertilizer synthesized from <sup>14</sup>CO<sub>2</sub>

The synthesis process is performed under initial conditions of ambient pressure and room temperature and the procedure shown in Fig. 2 is followed. The authors were licensed to synthesize <sup>14</sup>C labeled fertilizer in the laboratory. The technical route is to first generate <sup>14</sup>CO<sub>2</sub> from commercial NaH<sup>14</sup>CO<sub>3</sub> (Moravek Biochemical and Radiochemical, MC 208), then synthesize <sup>14</sup>C tagged NH<sub>4</sub>H<sup>14</sup>CO<sub>3</sub> from labeled <sup>14</sup>CO<sub>2</sub>. The relevant reactions are listed as follows:



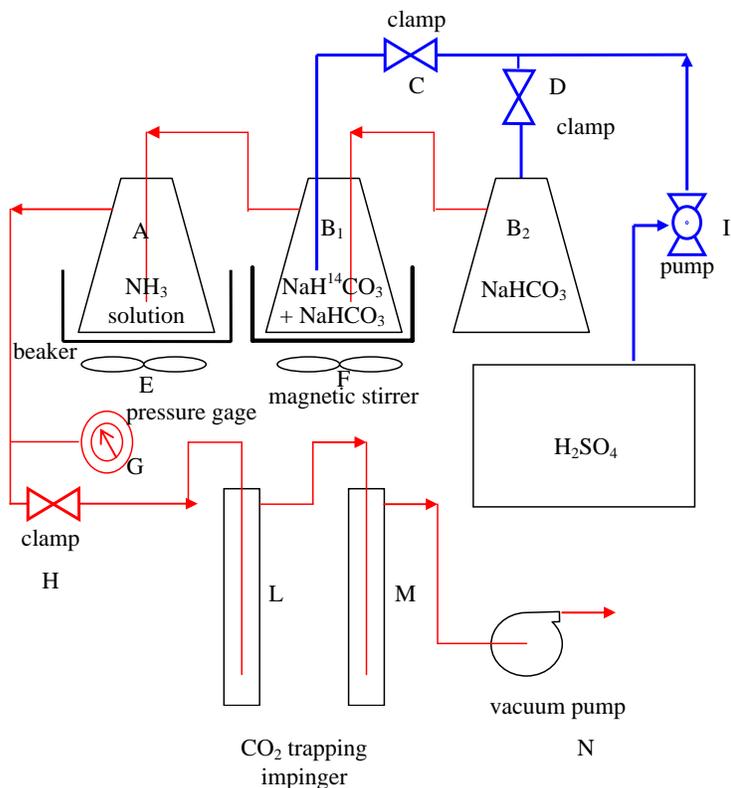


Figure 2 A schematic of  $\text{NH}_4\text{H}^{14}\text{CO}_3$  synthesis process.

The process is described as: pump I is used to control  $\text{H}_2\text{SO}_4$  flow rate. Clamps C and D are used to control the  $\text{H}_2\text{SO}_4$  pass to generate  $\text{CO}_2$  or  $^{14}\text{CO}_2$  during different phases. Flask B<sub>2</sub> contains 70 g  $\text{NaHCO}_3$  powder to generate regular  $\text{CO}_2$  to “flush” the system reduce (i.e., air) at the beginning. Flask B<sub>1</sub> contains 8.0 g  $\text{NaHCO}_3$  powder, two pieces of litmus papers, 100 ml  $\text{NaH}^{14}\text{CO}_3$  (50 mCi activity) and 3-5 drop 5%  $\text{NaOH}$  solution which is used to avoid  $\text{CO}_2$  emission. Flask A contains 50 ml ammonium hydroxide with 2 drops phenolphthalein solution. Flask A sit in an ice-bath. Pressure gauge G is used to monitor pressure change during the whole process. The pressure change ranges from  $-0.7 \text{ lbs/in}^2$  (vacuum, pressure gauge) to  $0.7 \text{ lbs/in}^2$  (gauge pressure). Impingers L and M contains 1000 ml saturated lime solution to trap escaped  $^{14}\text{CO}_2$  if necessary. Reaction (1) occurs in flask B<sub>2</sub> to flush the system at the beginning (clamp C was closed) until all the system is filled with  $\text{CO}_2$ . Then clamp D is closed and clamp C opened to generate  $^{14}\text{CO}_2$ . Reaction (3) occurs in flask B<sub>1</sub>. Reaction (4) occurs in flask A.

## 2.2 Greenhouse

In order to assure the reliability of the proposed method to securely sequester  $\text{CO}_2$  in soil and groundwater, it was essential to verify and monitor such sequestration. A lab-scale in-door greenhouse was set up. An indoor greenhouse consists of high intensity light system, six triple-growth chambers, air supply system,  $\text{CO}_2$  trapping system and an irrigation system. One corner of the greenhouse is shown in Fig. 3.



Figure 3 A corner of the indoor greenhouse.

### 2.2.1 Growth chambers

Each growth chamber (see Fig. 4) includes three individual growth cells. The chamber size is 91 cm (length)  $\times$  31 cm (width)  $\times$  76 cm (height). Each individual cell of the triple-cell has soil and groundwater separated from each other, but three cells share the same air layer to reduce sampling load. The groundwater layer of each cell holds a different type of water. The layout of this combined system can represent the case for crop planting in the same air system, but in different soil and groundwater ecosystems. All the ports for air and water injection were designed with one way, quick-disconnect couplings to prevent radioactive  $^{14}\text{CO}_2$  leakage during operation. Plants grew in each unit cell with sufficient sunshine, nutrition and moisture.

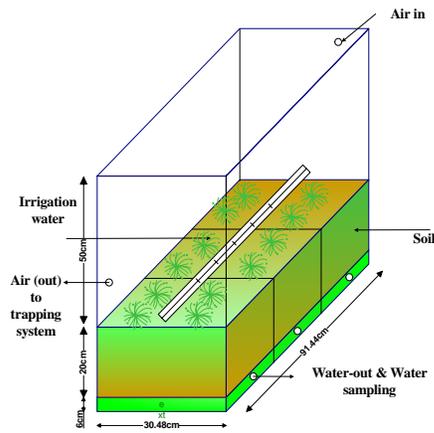


Figure 4 A schematic of the triple-growth chamber.

### 2.2.2 *Indoor HID growth light*

HID (High Intensity Discharge) growth lights were used to insure indoor crops' healthy growth. There are two types of HID growth lights used currently for horticultural lighting: metal halide and high pressure sodium. Metal halide bulbs produce an abundance of light in the blue spectrum. This wavelength of light promotes plant growth and is excellent for green leafy plant growth and keeping plants compact. It is the best type of light to be used as a primary light source (if little or no natural sunlight is available). High-pressure sodium bulbs emit an orange-red glow. This band of light triggers hormones in plants to increase flowering/budding in plants. They are the best lights for secondary or supplemental lighting (used in conjunction with natural sunlight). This is ideal for greenhouse growing applications.

### 2.2.3 *Irrigation system*

It is very important to design the irrigation system properly before planting in a closed cell. Water stress occurs not only due to an insufficient supply of water, but also can result from excess water (flooding). Flooding causes plant roots to suffer from lack of oxygen that is required for proper root function. Generally speaking, a soil's moisture in the greenhouse should be kept at a level of 60-70% of the soil's water capacity in order to meet the needs of the plants for optimum growth. In order to simulate real ecosystem conditions, the average annual precipitation in the Bowling Green locality (1265 mm or 49.8 inches) was used as the criteria for the irrigation system in the growth cell.

Pipe sprinklers with parallel fine holes were made. These pipe sprinklers were placed on the soil surface. Water was injected into the pipe sprinklers with a syringe that could avoid radioactive  $^{14}\text{CO}_2$  leakage and also precisely count the amount of water added.

### 2.2.4 *Air supply system*

Plants need  $\text{CO}_2$  for photosynthesis during growth as well as oxygen for the development of their roots. An air supply of 8-12 liters/day, which was measured by mass flow controllers, was added to each growth cell.  $\text{CO}_2$  concentration was maintained at an appropriate level. Previous research indicates that the net photosynthesis rate of leaves is positive if the  $\text{CO}_2$  concentration is below  $1000 \text{ mL/m}^3$ . The saturation point of  $\text{CO}_2$  concentration for plant growth is  $1600 \text{ mL/m}^3$ . Beyond this saturation point, plant growth may be inhibited. Therefore, the  $\text{CO}_2$  concentration in the closed growth cell during the entire growth period was monitored closely by a portable  $\text{CO}_2$  analyzer to maintain the concentration at the appropriate level. In order to prevent the outlet gas of this analyzer from diffusing into ambient air, the  $\text{CO}_2$  analyzer was placed in a clear sealed plastic bag. The air in this sealed bag was sucked back to a closed growth cell by a special syringe.

### 2.2.5 *$\text{CO}_2$ trapping system*

With a continuous supplement of fresh air for the closed system, the pressure could build up. In order to avoid this build up, a special  $\text{CO}_2$  trapping system was designed to release pressure. It consists of three-stage impingers. Overflow gases that contain  $^{14}\text{CO}_2$  are trapped completely in 1 M NaOH solutions after three stages. Other escaped gases from the NaOH solution are directed into fume hoods directly. Impingers also have valve-controlled openings in the bottom. Another main function of these impingers is to collect the solution with  $^{14}\text{C}$  during the experiment or at the end of the experiment for LSC analysis.

### 2.2.6 *Groundwater*

All of these groundwater sources are located in the Mammoth Cave National Park. Groundwater is placed under the bottom of the growth chamber. A screen with filter is placed at the bottom of the chamber to separate the soil and groundwater, which will hold soil, but allow water to seep into the soil. The groundwater used contains more  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  than that in rainwater in Bowling Green, KY. The concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the groundwater ranges from 46-60 ppm to 6-11 ppm.

The plants were seeded in pots according to the seeding population, which is 10 ~12 seeds/ft<sup>2</sup> for wheat. The unit cells were closed during the experimental period.

### 2.3 Instruments

One sample preparation system (Model 307 PerkinElmer Sample Oxidizer) was applied for  $^{14}\text{C}$  samples. Automatic operation produces consistently reproducible, high quality samples for analysis. This technique, particularly in the case of “difficult” samples (e.g.  $^3\text{H}/^{14}\text{C}$  dual label), give better results than those associated with traditional methods. Solid samples such soil, plants were burned conveniently and therefore  $^{14}\text{CO}_2$  could be trapped in solution for Liquid Scintillation Counter (LSC) analysis.

Liquid Scintillation Counter (LSC, PerkinElmer Tri-Carb 3100TR) was used to measure radioactivity of samples from collected soils, plants, groundwater, and  $^{14}\text{CO}_2$ -trapped alkaline solution. This liquid scintillation counter relies on the interaction between a beta-emitting radionuclide and a scintillator, a component of the scintillation cocktail. The scintillator converts ionizing radiation from the radionuclide into photons of light (scintillation). The intensity of the light produced during scintillation was proportional to the initial energy of the beta particle. Carbon distribution after fertilizer is applied is determined based on LSC analysis results.

### 2.4 Materials and Analysis Methods

Agricultural purpose chemical CaO and S were used to adjust soil pH value. The amount used was: CaO (4.5 g/kg soil) and S (8.5 g/kg soil). Except  $^{14}\text{C}$  labeled fertilizer ( $\text{NH}_4\text{H}^{14}\text{CO}_3$ ), other nutrients (P, K) were needed for plant healthy growth. The amounts of fertilizer were added as  $\text{NH}_4\text{HCO}_3$  (0.765g/kg soil),  $\text{KH}_2\text{PO}_4$  (0.16g/kg soil) and  $\text{K}_2\text{SO}_4$  (0.064g/kg soil). All analytical methods were based on ASTM standard methods.

## 3. Results and Discussion

### 3.1 $\text{NH}_4\text{H}^{14}\text{CO}_3$ and Long-term Effect $\text{NH}_4\text{H}^{14}\text{CO}_3$

Although the aqueous ammonia scrubbing process is an attractive way to capture low concentrations of  $\text{CO}_2$  from flue gas, chemical reactions among  $\text{CO}_2$ , ammonia and  $\text{H}_2\text{O}$  are very complex and poorly understood - many species co-exist in the solution in an unstable transition. These species could include, but are not limited to, ammonium bicarbonate, ammonium carbonate, and ammonium carbamate (all in crystalline and aqueous solution forms), plus  $\text{CO}_2$ ,  $\text{NH}_3$ , and  $\text{NH}_4\text{OH}$ . Previous work [16] in the research group used various analytical techniques to determine ABC in the products of a bench-scale aqueous ammonia  $\text{CO}_2$  scrubbing system. Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) were used to qualitatively distinguish ABC from ammonium carbonate (ACN) and ammonium carbamate (ACM). CHN elemental analysis and Near-IR spectroscopy were used to quantify the ABC and show that an acoustooptical tunable filter (AOTF)-based Near-IR spectrometer is an ideal tool for on-line measurement of ABC. The principal reason for the success of the Near-IR spectrometer is that this technology allows for fast scanning with no moving parts and there is no need to recalibrate the system. Current work has its unique characteristics and it is unsafe and non-economical to do all analysis for  $^{14}\text{C}$  tagged products. Instead, an exact replica of the same system as shown in Fig. 7 was built in parallel to do synthesis work with regular  $\text{NaHCO}_3$  (not  $\text{NaH}^{14}\text{CO}_3$ ). In this way the products can be analyzed as described in reference [16].

The synthesis process was mentioned earlier (Fig. 2). It was found that the  $\text{CO}_2$  concentration changed from 0% to be saturated. The solubility of  $\text{CO}_2$  in water is 1:0.4 (1.45%) and the solubility of  $\text{NH}_3$  is 1:702 (34%). The possible carbonates in solution are  $\text{NH}_4\text{HCO}_3$ ,  $\text{NH}_4\text{HCO}_3 + (\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$  or  $\text{NH}_2\text{COONH}_4 + \text{NH}_3$  (see Fig. 5, the  $\text{NH}_3$ - $\text{CO}_2$ - $\text{H}_2\text{O}$  phase diagram). Table 1 summarizes the analytical results of five synthesized samples (ABC or LEABC) and three standard samples. Four samples were synthesized at ambient pressure and one was synthesized at 5 lbs/in<sup>2</sup>. Elemental analysis (C, H, and N) of all five samples was done. The amounts of nitrogen in all synthesized samples (ID's 4-8) are under 20%, which indicates the main component is  $\text{NH}_4\text{HCO}_3$ . The carbon concentrations for all samples are under 15% and the hydrogen concentrations for four samples are over 6.42%, which indicates more water is contained in these samples. As was shown in Reference 16, the majority of the components were ABC.

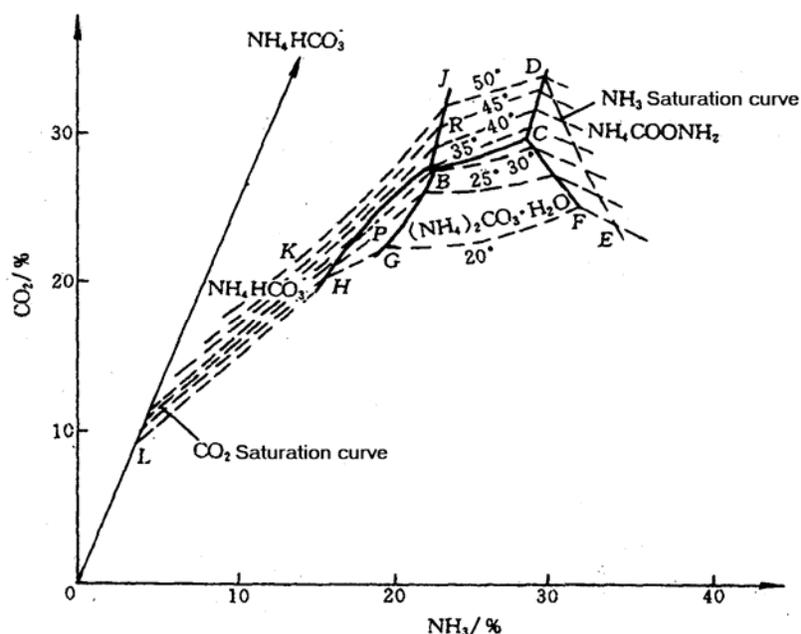


Figure 5 Gu-Pis phase diagram of  $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$  system.

Table 1. Summary of CHN elemental analysis for the synthesized samples and standard samples.

ID	Sample	Pressure (gauge pressure)	Measured results			Calculated results		
			C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
1	Standard sample $(\text{NH}_4)_2\text{CO}_3$	-	15.46	7.51	30.41	12.50	8.39	29.16
2	Standard sample $\text{NH}_4\text{HCO}_3$	-	15.13	6.42	17.46	15.19	6.37	17.72
3	Standard sample $\text{NH}_2\text{CO}_2\text{NH}_4$	-	15.42	7.91	35.82	15.38	7.75	35.89
4	Synthesized ABC	0	11.28	6.77	17.25	-	-	-
5	Synthesized ABC	0	10.46	8.18	18.09	-	-	-
6	Synthesized ABC	5 lbs/in <sup>2</sup>	12.11	7.29	18.99	-	-	-
7	Synthesized LEABC	0	12.28	6.98	16.40	-	-	-
8	Synthesized LEABC	0	14.02	6.35	16.69	-	-	-

It is found that the recovery rate of  $^{14}\text{C}$  depends on the amount of  $\text{NaHCO}_3$  added and flowrate of  $\text{H}_2\text{SO}_4$  added. The more regular  $\text{NaHCO}_3$  is added in flask B<sub>1</sub> and the slower the  $\text{H}_2\text{SO}_4$  is added, the higher the recovery rate will be. The recovery rates are shown in Table 2.

Table 2. Summary of  $^{14}\text{C}$  recovery rates during synthesis processes

Synthesized products	Input $^{14}\text{C}$ activity mCi	Recovered $^{14}\text{C}$ activity mCi	Recovery rate (%)
ABC	25.00	23.08	92.3
LEABC	25.00	17.55	70.2
ABC	25.00	24.09	96.3
LEABC	25.00	24.10	96.4

### 3.2 Carbon Distribution

Wheat was seeded in 18 unit growth cells. Each cell represents a unique growth condition which is combined by soils or undergroundwater or fertilizer. Table 3 summarizes various experimental conditions for this work. There are one type of plant (wheat), two types of fertilizer (ABC, LEABC), three types of soil (pH value less than 7, equal to 7 and greater than 7) and three kinds of groundwater (from Echo Spring, Green River Water and Hawkins River). The cross sections of six triple-growth cells were given in Fig. 6 to see the detail of the combination for experimental conditions. After a 50 day growth period, the plants were harvested. Then soil, groundwater, plant and air samples were handled for radioactive analysis by LSC. The measured  $^{14}\text{C}$  distribution should directly represent the carbon fate from fertilizer, as reported in references [17-18]. The comprehensive experimental results for  $^{14}\text{C}$  distribution are listed in Table 4.

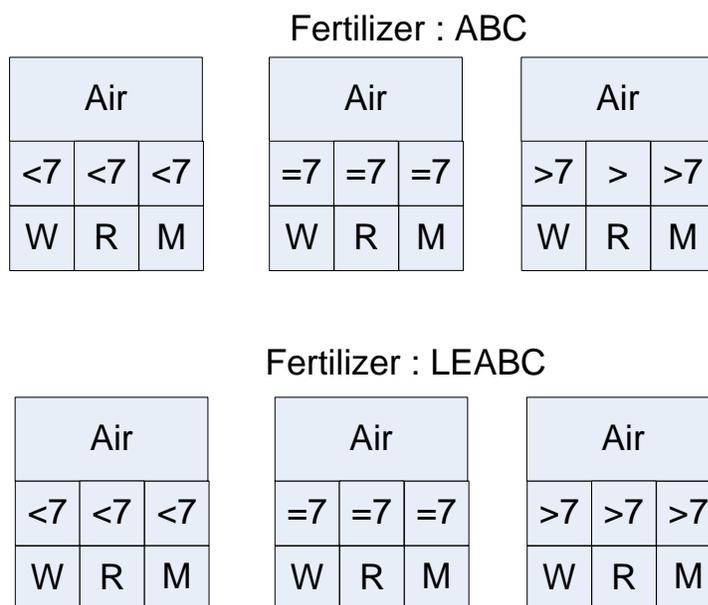


Figure 6 Cross sections of six triple-growth chamber (W: echo spring water; R: Green river water; M: Hawkins river).

#### 3.2.1 Carbon stored in soil

Trapped carbon in soil portion varied from 38.21% to 77.29% among the 18 growth cells. For alkaline soil, there are high percentages of carbon trapped in the soil, for example, 75% (ABC) and 76.06% (LEABC). It was found that there was only a slight difference (about 1%) in trapped carbon percentage between the test using the two types of fertilizer (ABC and LEABC). For the same type soil,

percentages of trapped carbon are close to each other even though there is a different fertilizer or a different groundwater. However, there are exceptions, for example the cell ID A-3 (alkaline soil, ABC, Hawkins River water) and D-2 (alkaline soil, LEABC, Green River water). It is concluded that soil pH value affects carbon capture significantly. Alkaline soil has higher capture percentage (up to 75%), neutral soil has the second highest capture percentage, and the acidic soil has the lowest capture percentage.  $\text{HCO}_3^-$  ion is captured more easily in weakly alkaline conditions.

Table 3 Summary of experiment conditions

Growth chamber ID	plant	fertilizer	Soil pH value	Water source
A-1	wheat	ABC	>7	Echo spring
A-2			>7	Green river
A-3			>7	Hawkins river
B-1			<7	Echo spring
B-2			<7	Green river
B-3			<7	Hawkins river
C-1			=7	Echo spring
C-2			=7	Green river
C-3			=7	Hawkins river
D-1		LEABC	>7	Echo spring
D-2			>7	Green river
D-3			>7	Hawkins river
E-1			<7	Echo spring
E-2			<7	Green river
E-3			<7	Hawkins river
F-1			=7	Echo spring
F-2			=7	Green river
F-3			=7	Hawkins river

### 3.2.2 Carbon stored in plant

The carbon from fertilizer is assimilated into plants through the photosynthesis process or root breathing process. About 10% of the carbon from fertilizer was eventually stored in wheat. The stored carbon percentage varies from 3.07% to 11.38%. Wheat grown in neutral soil has a trend to store more carbon.

### 3.2.3 Carbon stored in undergroundwater

Very little carbon from fertilizer percolated down to be stored in groundwater. The percentage varied from 0.64% (ID F-2, LEABC, pH = 7, Green River water) to 4.74% (ID A-1, ABC, pH>7, Echo Spring water). No difference in carbon capture was seen as a function of groundwater under different experimental conditions.

### 3.2.4 Carbon released in air or loss

There were substantial losses of fertilizer carbon released into the air or lost during the whole growth period. The percentages are in the range of 20% - 50%. Carbon loss is worse for acidic soils with a loss percentage up to 52.01% (ABC, pH>7, Echo Spring water).

### 3.3 Different effects of carbon storage between ABC and LEABC

Different fertilizer (ABC or LEABC) effects on carbon storage can be observed based on the comparison for grouped samples. As shown in Table 3, sample groups A-1 and D-1 only have different fertilizers, but have the same plant, groundwater and soil. For group A-1, 71.03% ABC fertilizer carbon is stored in the soil. For group D-1, 76.06% LEABC fertilizer carbon is stored in the soil. There is only a 5% difference for the fertilizer carbon storage in soil. Similarly, when considering plants, there is less than a 1% difference for fertilizer carbon storage, and less than a 3% difference for fertilizer carbon storage when considering groundwater sources. The comparison for the rest of the groups leads to very similar conclusions, that is, ABC and LEABC themselves do not show an obvious difference in effects of fertilizer for carbon storage, even though there is an advantage for LEABC since it is more stable.

Table 4 Carbon distribution in soil, plant, groundwater and air

Growth chamber ID	<sup>14</sup> C trapped in soil (%)	<sup>14</sup> C stored in plant (%)	<sup>14</sup> C stored in groundwater (%)	<sup>14</sup> C released to air and loss (%)
A-1	71.03	3.90	4.74	20.34
A-2	75.00	3.59	1.62	19.78
A-3	55.68	8.12	2.31	33.89
B-1	40.65	4.56	2.78	52.01
B-2	39.76	6.24	1.23	52.77
B-3	46.61	5.72	1.12	46.55
C-1	43.15	6.49	5.77	44.59
C-2	47.48	7.22	0.87	44.42
C-3	51.13	6.51	1.39	40.97
D-1	76.06	3.07	1.57	19.3
D-2	54.46	4.97	1.48	39.1
D-3	77.29	4.63	2.06	16.02
E-1	38.21	5.89	2.78	53.11
E-2	43.43	6.79	1.36	48.41
E-3	39.77	5.41	1.99	52.83
F-1	39.43	11.38	1.19	48
F-2	55.92	8.31	0.64	35.13
F-3	45.84	7.82	1.42	44.92

### 3.4 Carbon storage effects among different soils

Different soil pH values have completely different capabilities for storing fertilizer carbon. As shown in Table 4, comparisons of carbon distribution among groups A, B and C or D, E, and F indicate that alkaline soils have the highest capability for storing carbon in soils, while neutral soils and acidic soils have similar capabilities for carbon storage when considering experimental uncertainties. This can be explained by the fact that HCO<sup>3-</sup> ions tend to combine with Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in weak alkaline conditions.

### 3.5 Carbon forms in soil and calcium availability

As mentioned earlier, a higher percentage of carbon from fertilizer is captured in the soil. What kind of carbon forms exist in the soil? After the fertilizer ABC or LEABC is applied to soil, carbon in soil can go in four directions: air, plant, soil and water or groundwater, as shown in Fig. 7. Fertilizer carbon enters the soil by two different ways, residues directly from the fertilizer or through photosynthesis and growth of roots from decomposed CO<sub>2</sub> from fertilizer. As shown in Fig. 7, soil is a very important pool and fertilizer carbon exists in two forms, organic carbon and inorganic carbon. Organic matter in soil can be classified into macromolecule organic matter, carbohydrate, fat and protein etc, and low molecular weight organic matter. Inorganic carbon includes soluble carbonate, hydrocarbonate and insoluble carbonate. After <sup>14</sup>C tagged ABC or LEABC is applied to soil over 50 days, it could be classified into three groups by washout with DI water and acid, as shown in Fig. 8. The important operation parameters for this washout process are time and acid concentration. Long washing times and high acid concentrations can cause macromolecules to hydrolyze to small molecule organic matter. In this work, washing time is over one hour and HCl concentration is 0.5 N (soil used for the experiment has relative high carbonate content).

Six representative post-experiment soil samples were selected to perform carbon form experiments. The results are listed in Table 5. It is very encouraging that up to 88% of the carbon from fertilizer exists in insoluble salts (i.e. CaCO<sub>3</sub>) in the alkaline soil, regardless of fertilizer type ABC or LEABC. However, for acid soil, the percentage of CaCO<sub>3</sub> in soil is low so the level is reduced to 10% to 25%. There is an abundance of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in the selected soil. The Ca<sup>2+</sup> ions concentration is 857 ppm and the Mg<sup>2+</sup> ions concentration is 1238 ppm. The availability of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in soil is a key source for storing carbon in soil.

Table 5 <sup>14</sup>C existing forms in soil

Fertilizer applied	Soil type (pH value)	Growth chamber ID	Dissociated carbonate or small organic molecule (%)	CaCO <sub>3</sub> (%)	Macromolecule organic carbon (%)
ABC	<7	B-3	17.75	10.98	71.27
	=7	C-3	2.33	81.85	16.62
	>7	A-2	1.22	88.91	9.87
LEABC	<7	F-3	17.82	24.27	57.91
	=7	E-2	0.06	84.85	15.09
	>7	D-3	7.62	83.41	8.97

### 3.6 Carbon 14 Tracer Technique in this work

Methodology to trace carbon changes at each part of the greenhouse for evaluating a carbon balance requires carbon isotope dilution studies. Three principal isotopes of carbon occur naturally - carbon 12 (<sup>12</sup>C), carbon 13 (<sup>13</sup>C) and carbon 14 (<sup>14</sup>C). The mass percentage of carbon-12 is 98.89%, of carbon-13 is 1.11% and of carbon-14 is 0.000000001%. Of these, carbon-14 is radioactive and can be used as a tracer. The limitation in determining ecosystem carbon sequestration in this study is the accuracy of the methods used to assess changes in total carbon of each portion, especially the soil and groundwater portions, because carbon entering the soil through the fertilizing process is much smaller compared to the background soil carbon. Among the three carbon isotopes, <sup>14</sup>C isotope dilution approach can overcome this problem due to its extremely low content in nature and high radioactive property. It follows the same pathway as the more abundant isotope <sup>12</sup>C.

$^{14}\text{C}$  is not an external exposure hazard because its low-energy beta radiation will not penetrate the gloves and skin.  $^{13}\text{C}$  is a good tracer for tracking the carbon cycle also, since it always has a consistent ratio to  $^{12}\text{C}$ . However, its high background value required a large quantity for this research, which limited its use in the project because of its high cost.

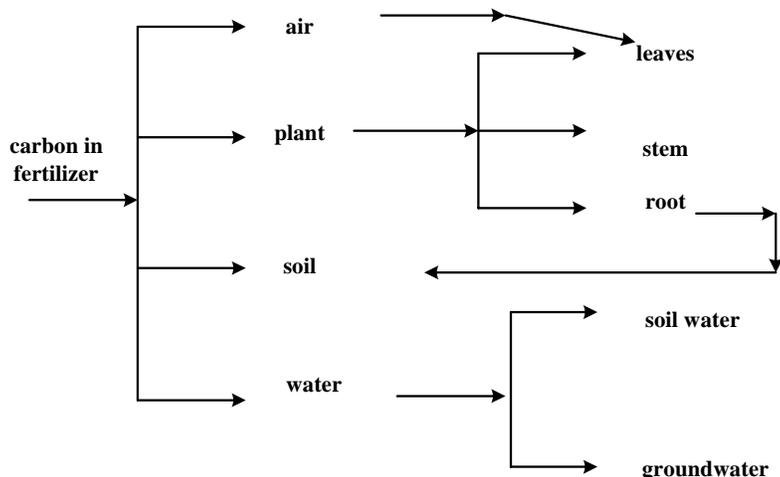


Figure 7 Flow chart of fertilizer carbon.

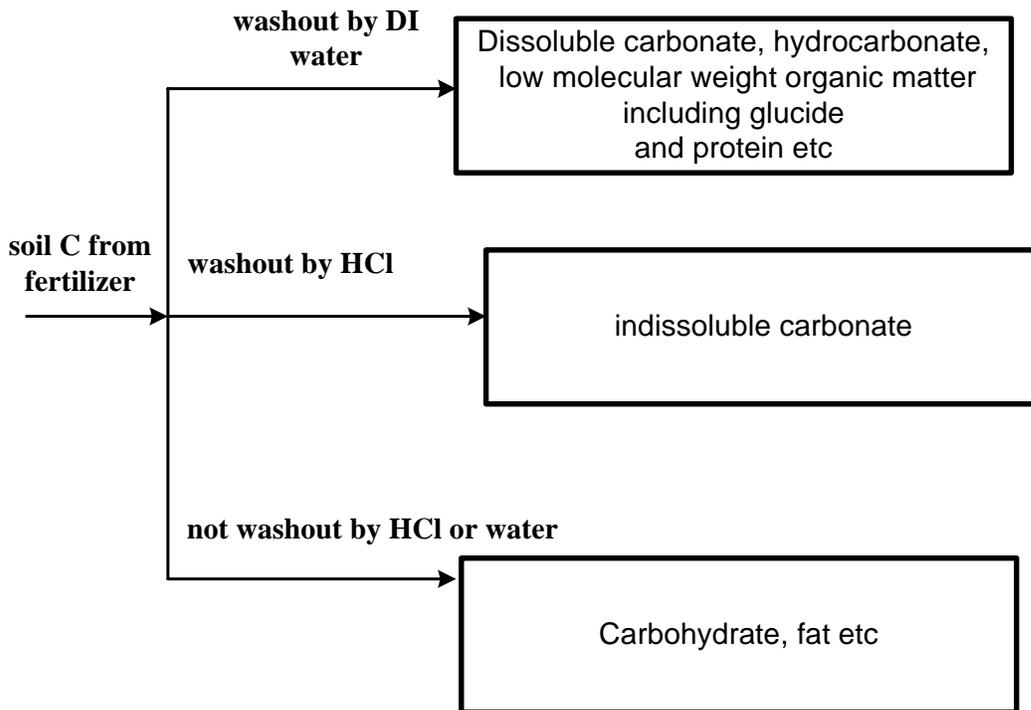


Figure 8  $^{14}\text{C}$  existing form in soil after 50 days growth period.

Generally, the  $^{14}\text{C}$  radioactive isotope technique is used in chemistry and biochemistry research to study detailed molecular structures and reaction mechanisms. In this work, this technique was

successfully extended to CO<sub>2</sub> sequestration research involving a complex engineered ecosystem. This also can greatly contribute to other engineering technology developments and to other CO<sub>2</sub> sequestration research underway.

#### 4. Conclusions

This work only focused on the carbon distribution after a synthesized fertilizer was applied to soils. The fertilizer studied is ammonium bicarbonate, which can be produced through the capture of CO<sub>2</sub> by aqueous ammonia scrubbing process. <sup>14</sup>C tagged ammonium bicarbonate (ABC, NH<sub>4</sub>HCO<sub>3</sub>) and long-term effect ammonium bicarbonate (LEABC, NH<sub>4</sub>HCO<sub>3</sub>) were synthesized from <sup>14</sup>CO<sub>2</sub> in the laboratory. The fertilizer (ABC or LEABC) is used as a “carrier” to transport CO<sub>2</sub> from the atmosphere to the crops and soil. Carbon (from fertilizer) distribution was determined by measuring <sup>14</sup>C activity in soils, plants, groundwater and air. After biological assimilation and metabolism in crops receiving ABC or LEABC, a considerable amount (up to 10%) of the carbon source is absorbed by the plants with increased biomass product. The majority of the unused carbon source (up to 76%) percolates into the soil as carbonates, such as an environmentally benign calcium carbonate (CaCO<sub>3</sub>). The soil carbon which originally comes from fertilizer is analyzed in detail. Up to 88% of the soil carbon from fertilizer exists as insoluble carbonate, such as CaCO<sub>3</sub>. These findings answer the questions how carbon is distributed after synthesized fertilizer is applied into the ecosystems. In addition, a separate post-experiment on fertilizer carbon forms existing in soil was made. It was found that up to 88% of the trapped carbon exists in the form of insoluble salts (i.e., CaCO<sub>3</sub>) for alkaline soil. This indicates that alkaline soil has a greater potential to store carbon after the use of the synthesized fertilizer

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