Quantification of Nitrogen and Phosphorus Transformation in Fertilizer Products

July 2020

IFDC
INTERNATIONAL FERTILIZER DEVELOPMENT CENTER
PO BOX 2040 | MUSCLE SHOALS, AL 35662 | USA

Table of Contents

1 Introduction

The laboratory and agronomic studies conducted by IFDC covers from routine soil and plant tissue analyses to a wide range of laboratory and greenhouse experiments and field trials. The latter includes field trials conducted by IFDC in collaboration with universities and national agricultural research services (NARS) in the United States and overseas. IFDC scientists also coordinate field trials conducted by other institutions, agricultural consultants, or farmer groups. The coordination includes design of experiment (layout, treatments, replications, frequency of sampling, variables sampled), monitoring of trial through actual field visits, remote observations or status reports, and quality control where selected samples may be analyzed at IFDC laboratory.

With expertise in fertilizer production, chemistry, soil science, plant nutrition, statistics, and economics, the recommendations and feedback from the research are targeted to improve the performance of product or technology being tested. This document provides information on the evaluation of N and P fertilizers. All proposed studies have a control treatment(s), without N and/or P. All fertilizer products will be analyzed at IFDC for nutrient content total P, citrate-soluble P, total N, urea-N, ammonium-N, and nitrate-N.

Laboratory and greenhouse studies have some limitations, such as anhydrous ammonia is not suitable for soil incubation. Growing corn to maturity in pots or leaching columns is not ideal, so either corn is grown to tasseling stage or an alternative crop such as sorghum is grown to maturity.

2 Quantification of Ammonia Volatilization

2.1 Background and Rationale

The major N loss from N fertilizers is due to ammonia (NH_3-N) volatilization, resulting in monetary loss and negative impact on the environment when deposited on land, causing soil acidification and eutrophication. NH_3 in the air is a public health concern, with NH_3 reacting with other air pollutants and lodging in lungs (Stokstad, 2014; Wu et al., 2016). The laboratory procedure to quantify ammonia (NH_3-N) volatilization loss has been standardized and calibrated to field conditions. The proposed evaluation would quantify the effectiveness of N fertilizers (enhanced efficiency fertilizers (EEFs), biofertilizers, etc.) in reducing urea hydrolysis/reducing NH_3-N volatilization. The efficiency of test products in reducing volatilization loss is compared with standard N fertilizers: urea, ammonium sulfate, urea ammonium nitrate (UAN), and control (no N applied). The experiment is designed for worst case scenario with surface application of N

fertilizers on a moist soil. *The effect of irrigation or rainfall in reducing volatilization loss by percolating N below the soil surface will not be captured*.

2.2 Materials and Method

A single NH_3-N volatilization run consists of 30 pots, so each run can have as many as 10 treatments with 3 replications or 30 treatments (N Products or N Products x soils) per run. For the latter, depending on the number of replications, three to four runs will be required to complete the study.

The N sources are applied at a rate of 0.90 g N (the equivalent of 200 kg N ha^{-1}) to eight kg soil in volatilization pots with inner diameter of 24 cm. The fertilizer granules are evenly distributed on the soil surface. Soil moisture content throughout the volatilization period is maintained at 75% field moisture capacity.

The pots are sealed tight with air inflow from a compressed air system and outflow to the acid traps (Figure 1). Air is passed through an acid scrubber to remove any NH_3 (in the air) and humidified before entering the pots. The airflow rate is adjusted to 5.0 L min^{-1} for each pot to allow for complete mixing and maximum removal of any ammonia formed. All ammonia (outflow from the pots) is captured in phosphoric acid traps (Figure 1). During the first three days, these traps are sampled and changed on a daily basis. The samplings are done on alternate days during the latter stages of the experiment when the volatilization rate drops.

The time intervals for NH_3-N collection are as follows: 1, 2, 3, 5, 7, 9, 12, 15, 18, 21, and 24 days. *The duration will be extended by 7-10 days for slow-release products*. Solutions from acid traps are analyzed for ammoniacal-N with a Skalar SAN^{plus} segmented flow at least two to three times a week. The automated procedure for ammoniacal-N determination is based on the modified Berthelot reaction (Krom, 1980; Searle, 1984). The spectrophotometric determination of ammonia complex is done at 680 nm. Air temperature in the laboratory and soil temperature in the pots are taken from selected treatments.

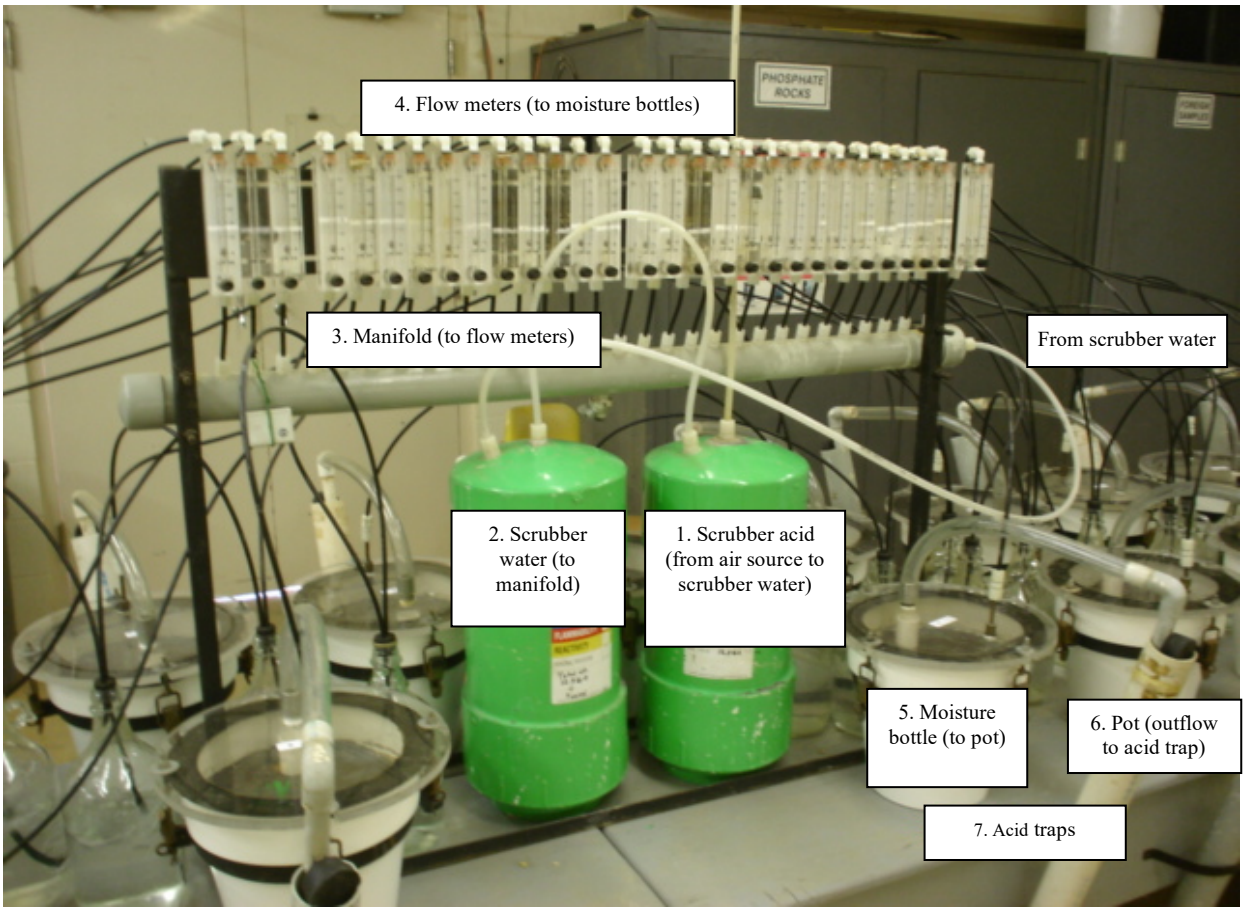

Figure 1. Layout of Experiment with Air From Compressor Flowing into (1) Scrubber Acid; (2) to Scrubber Water; (3) to Manifold; (4) to Separate Flow Meters for Each Pot; (5) to Moisture Bottles; (6) to Pots; and finally (7) to Acid Traps. Each Pot Contains Approximately 8 kg of Soil.

3 Quantification of Nitrogen Transformation with EEFs Relative to Urea Using Soil Incubation Technique

3.1 Background and Rationale

The N transformation of EEFs and reference fertilizers (urea, ammonium sulfate, UAN, etc.) is conducted to quantify and compare the rates of transformations of nitrogen on wide range of soils (up to 5) at 2-3 temperature regimes. The soil selection is based on soil pH, soil texture, and organic matter content. The study can also test the hypothesis that application of EEFs may result in lesser decrease in soil pH compared with the decrease in soil pH resulting from application of the same amount of N as urea or ammonium sulfate. Nitrification of NH_4^+ in ammoniacal nitrogen fertilizers usually results in soil acidification (Evans et al., 1998; Xu et al., 2006).

3.2 Materials and Method

Laboratory incubation experiments are carried out to measure and compare rates of N transformation and the changes in soil acidity levels of selected soils when applied with EEFs compared with reference fertilizers. *Each soil is pre-incubated for 12 days* at 75% field moisture content before fertilizer application.

To fifty grams (50 g; air-dry equivalent) of soil, 10 mg N of respective N-sources are added into a soil sample cup and incubated for a period of 12 weeks. Fertilizer granules (or solution) are lightly incorporated into the soil for all treatments on the same day. The incubation cups are kept at 75% field moisture capacity throughout the duration of the experiment. The incubation study can also quantify the effect of temperature on N transformation: e.g., fixed temperature of 15°C, 20°C, and 30°C, and/or a treatment with variable temperature increasing from 5°C to 30°C over the 12-week incubation period.

A factorial experiment of x N-source treatments (EEFs, urea, AS, UAN, check) * y temperature levels * z soils are combined to provide a total of xyz treatments. Each treatment is replicated four times:

4xyz experimental units = x sources * y soils x z temperature x 4 reps

Twelve batches (for each incubation sampling) of the 4xyz experimental units are incubated, and periodically one batch is removed to analyze changes in N forms and to quantify the rates of N transformation of the fertilizer N products. All incubation samples are periodically weighed to ensure moisture content was maintained at 75% field capacity. The incubated samples are removed at the following times: (a) time = 0, (b) 2 days, (c) 4 days, (d) 1 week, (e) 2 weeks,

(f) 3 weeks, (g) 4 weeks, (h) 5 weeks, (i) 6 weeks, (j) 8 weeks, (k) 10 weeks and (l) 12 weeks. The acidification effect from the EEF (test) products could be different from that of conventional fertilizers. Changes in soil pH are monitored at 0-, 6- and 12-week incubation for all soils and temperatures.

3.3 Analysis of Urea-N, NH_4-N, NO_3-N and pH

After each incubation period, measurements are made for NH_4^+-N and NO_3^--N. During the 0-, 2-, 4- and 7-day incubation period, urea-N is also analyzed. Soil from each cup is analyzed for urea-N, NH_4^+-N and NO_3^--N by 2 *M* KCl extraction to quantify the rates of N transformation of the fertilizer N products. Urea-N, ammoniacal-N and NO_3^--N are analyzed with a Skalar SAN^{plus} segmented flow system (Skalar Analytical B.V., Inc., Breda, the Netherlands). For the 0-, 6- and 12-week incubation samples, soil pH (1:1 soil:water) is determined first by adding 50 mL of deionized (DI) water and then extracting with additional 50 mL of 4 *M* KCl following the procedure described above. The automated procedure for ammoniacal-N determination is based on the modified Berthelot reaction (Krom, 1980; Searle, 1984). The spectrophotometric determination of ammonia complex is done at 680 nm. Nitrate-N is determined by reduction to nitrite, diazotizing with sulfanilamide and coupling with α-naphthylethylenediamine dihydrochloride to form an azo dye that is measured at 540 nm.

The above incubation procedure can be modified for sulfur (enhanced release elemental S), phosphorus, phosphate rock, etc. Pi (Fe strip method) will be used to determine available P during the incubation period.

4 Nitrogen Leaching from EEF Products

4.1 Background and Rationale

The evaluation of EEFs (test products) for urea-N, ammonium-N and nitrate-N leaching and phosphate leaching for P fertilizers is generally conducted on sandy soils. We test the hypothesis that leaching losses on application of EEFs would be lower than on application of urea or UAN. Leaching loss quantification is done for all EEFs including those that may contain only urease inhibitor.

4.2 Materials and Method

Leaching columns are used to quantify N leaching emanating from EEFs and reference N fertilizers (urea, AS, UAN, etc), relative to an unamended check (Figure 2). Experimental soils are air-dried and passed through a 2-mm sieve. Each column (5 cm id and 50 cm length) contains 1.3 to 1.8 kg of soil. Field capacity moisture content of each soil is pre-determined. Each column is attached to a Buchner funnel (lined with polypropylene mesh) and covered to reduced moisture loss, with the option for maximum vacuum suction of 10 kPa (0.1 bar) that drains leachate into glass jars.

Each of the columns is brought to saturated moisture content by adding 50 mL of water daily (equivalent to 25.4 mm/day reflecting high rainfall regime) until the columns begin to leach. The weight of each column is recorded immediately after leaching stopped; this would be considered the saturated moisture content. Additional suction (0.1 bar) is applied for 10 minutes to bring columns below saturated but above the field moisture capacity. The above steps are repeated for 3-4 days to stabilize the columns before fertilizer application. The weight of each column (after 10 min. suction) is recorded as the target for the leaching columns. N fertilizers (EEFs, urea, AS, UAN, and no N check) is surface applied and lightly incorporated at 60-90 mg N per column.

Immediately after fertilizer application, water is added onto the soil surface equivalent to 20 mL day^{-1} (other rates such as 50 mL day^{-1} as additional treatments) for three days, followed by 0.1 bar suction after each leaching event. The leachate from each column is quantified and analyzed for urea-N, NH_4-N, and NO_3-N. No additional water is added to these columns for the next 6 days. On day 10, columns are re-watered with a known/measured amount of water that is added until leaching began. The leaching process continued for the next 16 days. The cycle – 7-9 days of drying followed by 24 days of leaching – is followed until day 60 (Table 1).

Analysis: Measurements for urea-N, NH_4-N, and NO_3-N of the leachates from all of the treatments are done at specified intervals. At the end of the study, soils are analyzed at 0-10 cm, 10-30 cm, and 30-50 cm depth for NH_4-N, and NO_3-N.

The above leaching study can be done for S and P leaching as well.

Table 1. Example Sampling Schedule for Leaching

Date	Day		Add Water (mL)	Apply Fertilizers	Add Water (to bring to weight)	Weigh Columns	Collect Leachate (vacuum suction)
10/10/2017			50				
10/11/2017			50			X	X - No Vacuum
10/12/2017			50			X	X - No Vacuum
10/13/2017			50			X	X - No Vacuum
10/14/2017							
10/15/2017							
10/16/2017			50			X	X
10/17/2017			50			X	X
10/18/2017			50			X	X
10/19/2017			50			X	X
10/20/2017			50			X	X
10/21/2017							
10/22/2017							
10/23/2017	1	X	20	X		X	X
10/24/2017	2	X	20			X	X
10/25/2017	3	X	20			X	X
10/26/2017	4						
10/27/2017	5						
10/28/2017	6						
10/29/2017	7						
10/30/2017	8						
10/31/2017	9					X	X
11/01/2017	10	X	20			X	X
11/02/2017	11	X	20			X	X
11/03/2017	12	X	20			X	X
11/04/2017	13						
11/05/2017	14						
11/06/2017	15	X	20			X	X
11/07/2017	16	X	20			X	X
11/08/2017	17	X	20			X	X
11/09/2017	18	X	20			X	X
11/10/2017	19	X	20			X	X
11/11/2017	20						
11/12/2017	21						
11/13/2017	22	X	20			X	X
11/14/2017	23	X	20			X	X

Date	Day		Add Water (mL)	Apply Fertilizers	Add Water (to bring to weight)	Weigh Columns	Collect Leachate (vacuum suction)
11/15/2017	24	X	20			X	X
11/16/2017	25	X	20			X	X
11/17/2017	26	X	20			X	
11/18/2017	27						
11/19/2017	28						
11/20/2017	29						X
11/21/2017	30						
11/22/2017	31						
11/23/2017	32						
11/24/2017	33						
11/25/2017	34						
11/26/2017	35						
11/27/2017	36	X	20			X	X
11/28/2017	37	X	20			X	X
11/29/2017	38	X	20			X	X
11/30/2017	39	X	20			X	X
12/01/2017	40	X	20			X	X
12/02/2017	41						
12/03/2017	42						
12/04/2017	43	X	20			X	X
12/05/2017	44	X	20			X	X
12/06/2017	45	X	20			X	X
12/07/2017	46	X	20			X	X
12/08/2017	47	X	20			X	X
12/09/2017	48						
12/10/2017	49						
12/11/2017	50	X	20			X	X
12/12/2017	51	X	20			X	X
12/13/2017	52	X	20			X	X
12/14/2017	53	X	20			X	X
12/15/2017	54	X	20			X	X
12/16/2017	55						
12/17/2017	56						
12/18/2017	57	X	20			X	X
12/19/2017	58	X	20			X	X
12/20/2017	59	X	20			X	X
12/21/2017	60	X	20			X	X

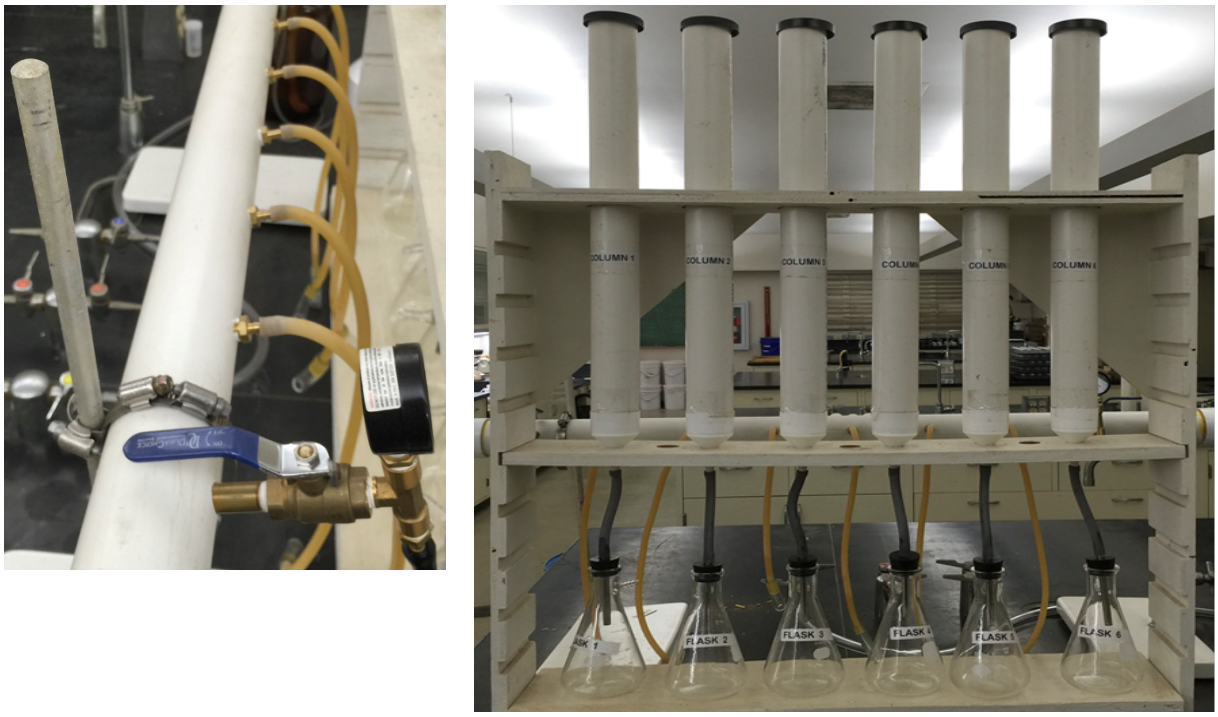

Figure 2. Leaching Column Setup for Comparison of Nutrient Leaching from EEFs and Conventional Fertilizers.

Growing a plant will not be practical in the above columns. However, plants can be grown with wider leaching columns (id of 15 cm and length of 30 cm). Water flow is gravitational for these columns (see Figure 3). The limitations of growing corn to maturity has been discussed in the introduction section. The large columns will help determine NUE and PUE in addition to leaching of N or P. The study with plants should be limited to a single soil, a well-defined irrigation/water regime, and limited to an optimum N rate.

Figure 3. Leaching Column Setup with plants.

5 Release Rate for Coated Fertilizers

5.1 Background and Rationale

The release of nutrients from controlled-release fertilizers though dependent on coating thickness and type of coating is also dictated by soil temperature, soil moisture, and type of soil. *This procedure is recommended once simple water dissolution release studies have identified promising products.* For N water dissolution technique is used, for P the same technique can be used or modified for acidic (pH 4-5) and alkaline (pH 7.5-8.5) solution.

The soil experiment consists of coated N and/or P fertilizer products on a single soil. This can be modified to include more soils and different temperatures. The test products are compared with standard industry products and conventional N or P fertilizers.

5.2 Materials and Method

Soil: The experiment will be conducted on Greenville soil with 4 kg of soil per pot. Soil moisture will be maintained at 75% of field moisture capacity. The moisture content will be checked every day by bringing to initial weight when necessary to make sure that all the pots are kept at the same condition.

Treatments: consist of x different coated products, uncoated fertilizers (urea, TSP, etc), and check.

Incubation Period (10): Samples will be analyzed at the following times: 1, 5, 7, 14, 21, 28, 35, 42, 49, and 56 days after fertilizer application. The sampling intervals may be modified depending on the release rates.

Number of Pots/Soil: x treatments x 4 replications = 4x pots

Fertilizer Application: Each pot will have 10 mesh bags of fertilizer evenly distributed and placed at 7 cm depth. Each mesh bag will have 2 g of product.

Analysis: For each incubation period, a mesh bag from each pot will be removed. The product will be dry cleaned and weighed to calculate the N release by the weight loss method. The fertilizer granules will also be analyzed for total N using the combustion analyzer. A total of 4x N analyses will be conducted per incubation period. *Other analyses will be conducted as per nutrient content of the fertilizer*.

The above procedure can be modified (at higher temperatures, different soil properties) to quantify breakdown of coatings.

6 Quantifying Nitrous Oxide Emission

6.1 Background and Rationale

Among the anthropogenic sources of nitrous oxide, agriculture represents the largest source. N fertilizers both production and consumption contribute to N_2O emission. The environmental impact of N_2O loss from fertilizers is far more critical than economic loss. Emissions of N2O can occur both during nitrification and denitrification processes. Hence, moisture regimes will play critical role in evaluating N_2O emissions from EEFs. Soil properties, such as pH and organic matter content will also influence N_2O emissions. The proposed study therefore needs to include 2-3 soils with different soil pH, organic matter, and texture and moisture content at two levels ((1) always below field capacity moisture content and (2) occasional increases up to saturation or water logging). The EEFs are compared with urea, AS, and UAN and a check without any N application.

6.2 Materials and Method

All N fertilizers are surface applied. Each run includes 15 pots for a maximum of 15 treatments per run (unreplicated). Replications (4) can take place by repeating each run four times. The duration of each run is at least 8 weeks. Several runs will be needed to cover different water regimes and soils.

The pot size is 2 gallons (polyethylene bucket), measuring 24 cm height and 24 cm inner diameter to hold 6-7 kg of soil. The amount of soil is adjusted based on a head space of approximately 10 cm between the top of the soil and the lid. The water amount added to each soil will be based on the field moisture capacity of the soil and calculated to the target amount. The fertilizers will be applied using a constant nitrogen rate. The fertilizers will be applied uniformly to the soil surface for all the treatments.

This is a continuous flow system set up with in-house compressed air flowing through a water reservoir acting as a humidifier to avoid frequent drying of the soil surface. From the reservoir, the air flow will go through a 16-flow meter manifold to control and avoid excess air flowing in different pots. The flow meters will be set to 0.5L/min. Each flow meter is connected to a sealed pot with a head space of approximately 4 liters. The air flows through the headspace in each pot to collect the exchangeable gases then exits the pot in an outflow connection. The outflow from

each pot is connected to a specific 3-way valve solenoid controlled by a datalogger. The solenoids are arranged in a manifold with the airflow coming in from the pots and released to the room (environment) in the de-energized position. When the system is measuring a specific pot, the 3-way valve solenoid becomes active and the airflow goes from the pot to the Picarro analyzer by passing through an automatic flow meter. The airflow of 0.5L/min in each pot is consistently maintained for the duration of the experiment

The Picarro G2058 Gas Concentration analyzer measures N_2O, CH_4, CO_2, NH_3, and H_2O vapor simultaneously. The Picarro system uses a Cavity Ring Down Spectroscopy (CRDS) technology, a highly sensitive optical spectroscopy that measures the absolute optical emission by the samples that will scatter and absorb light.

Figure 4. Picarro G2508 gas analyzer.

6.3 Sampling

For the sampling time, each pot will be measured for four minutes during each hour. Within the four minutes 25 data points will be collected for each pot. For analysis purposes, the program is set up to store only the average of the last 5 measurements that showed to be the most stable during the setting up trials (last 40 seconds of the four minutes interval) allowing the system to stabilize and all the gases from the previous pot to be flushed before the final 5 data points are averaged for analysis. This system will give a snapshot of the gas emitted from each pot (soil plus fertilizer) every hour, 24 hours a day, for the duration of the experiment. All the pots are consistently flushed with in-house compressed air and released to the room, except the pot being measured, allowing for each pot to have the same conditions. We are measuring only the

air sampled during 4 minutes within an hour. This means that for the other 56 minutes the air is released into the room. We will have 24 reading points to represent the release curve from each gas emitted in a day. The program also records the airflow and the temperature. The automated system is set up to run 24 hours per day, 7 days per week.

The 3-way valve manifold is connected by stainless steel tubing connected by 0.25 in Swagelok male tee NPT. Each 3-way valve is connected to a unique pot that is controlled by a Campbell Scientific Loggernet datalogger via a relay controller. The relay controller receives a signal from the datalogger and relays it to the respective valve for energizing and de-energizing. The sequence is followed by the measuring time from each pot (4 min) then moves to the next valve. The system is programmed to stand by until the top of the hour to start the measurement, once the program is initiated.

Figure 5. GHG gas emission analysis setup.

6.4 Issues – Weaknesses and Strengths

The system is limited to 15 chambers (no more than 5 treatments with 3 replications) and can be run continuously for 8-10 weeks. Various wetting and drying cycles can be imposed during the 8-week run. It is not a static chamber approach, so headspace and flowrates are not a major issue, however, emissions within a chamber are diluted with ambient (compressed) air.

7 Quantifying N_20-NO Emission from N Fertilizers under Greenhouse and Field Conditions

Continuous emission measuring system operational at greenhouse and field (Figure 6). For details please see:

Gaihre, Y. K., Satter, M. A., Singh, U., Austin, R., 2014. Operating manual on automated continuous measurement of greenhouse gas emissions. IFDC Technical Bulletin No. T-76. International Fertilizer Development Center, Muscle Shoals, AL 35662 USA. p.82. https://ifdc.org/wp-content/uploads/2020/09/T-76.Op_Manual_on_Auto_Cont_Meas_GHG_Emissions.2015.pdf.

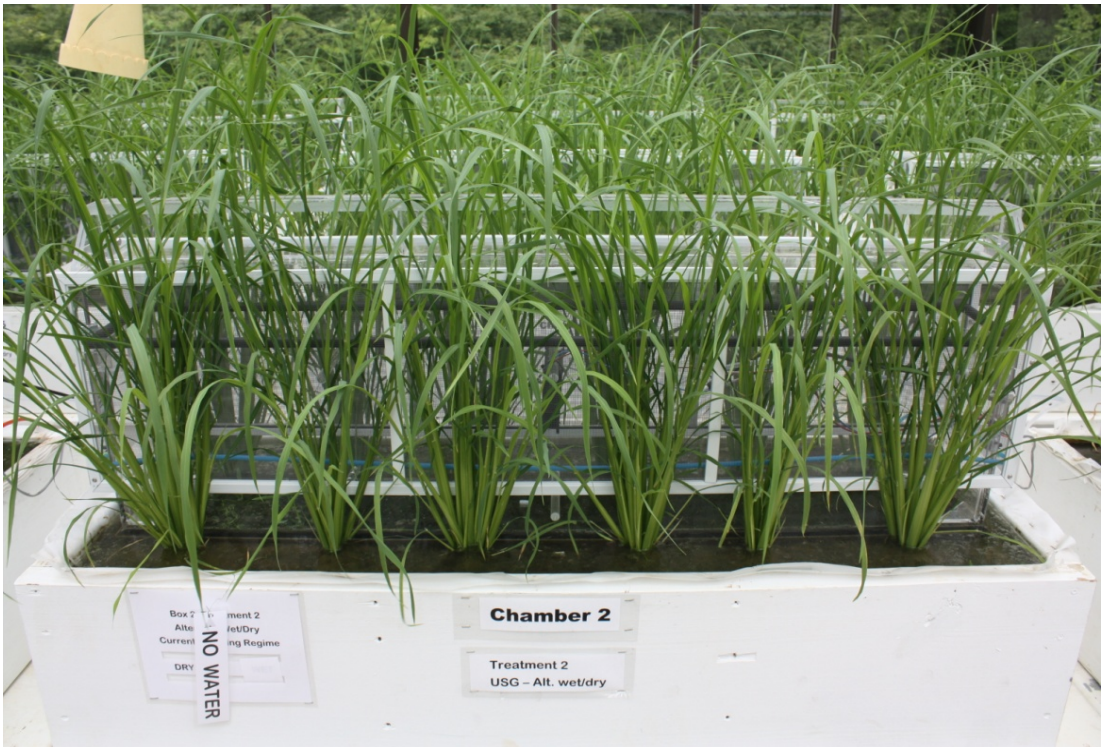

Figure 6. Plexiglas greenhouse gas chambers for continuous monitoring of N2O-NO emission from N fertilizers with flooded rice crop, IFDC Greenhouse, Muscle Shoals, Alabama.

8 Additional P Sorption Tests

Additional tests to quantify potential P losses as runoff or leaching from conventional versus enhanced efficiency P fertilizers can be included in addition to tests conducted under "Quantifying P transformation under soil incubation", "P leaching column", and "P release rate from coated fertilizers".