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**Simultaneous soil flux measurements of five gases -- $N_2O$, $CH_4$, $CO_2$, $NH_3$, and $H_2O$ -- with the Picarro G2508**

The fluxes of $N_2O$, $CH_4$, $CO_2$, $NH_3$, and $H_2O$ from soil were measured at the same time with a static soil chamber and the new Picarro G2508. The system was shown to provide repeatable measurements and able to follow the dynamic fluxes produced in a simple laboratory soil sample.

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**Abstract:**

Picarro has developed a new analyzer capable of simultaneously measuring five gases: $N_2O$, $CH_4$, $CO_2$, $NH_3$, and $H_2O$. This paper demonstrates the ability of this analyzer to measure soil fluxes when connected to a static chamber as part of a closed system. The experiments took place in a laboratory on a soil sample. The first set of chamber tests on dry soil were designed to demonstrate repeatability and showed rate-of-rise variation that was comparable to the standard error calculated for the slopes. The system was able to measure a $CH_4$ rate-of-rise of 0.17 ppb/min with a $1\sigma$ uncertainty of +/- 0.016 ppb/min. The second set of tests simulated a rain event. Following the addition of water to the soil, the flux rates showed quite different trends for each of the measured gases. $N_2O$ emission rate triples immediately and continues to rise over the next hour. $CH_4$ emission immediately spiked, but then decreased toward the emission rates of the dry soil. $CO_2$ emission was initially suppressed but recovered by the end of 2 hours. $NH_3$ and water vapor content increased. The new Picarro G2508 analyzer was able to provide repeatable, statistically significant soil flux rate-of-rise measurements for $N_2O$, $CH_4$, $CO_2$, $NH_3$, and $H_2O$.

**Introduction:**

The exchange of greenhouse gases between the soil and atmosphere is a major step in the global nitrogen, water, and carbon cycles. The nitrogen cycle is particularly difficult to quantify, in part because of the lack of high quality instruments that are capable of operating in the field.

$N_2O$ is particularly important. It is the fourth most prevalent greenhouse gas (after $H_2O$, $CO_2$ and $CH_4$) and accounts for 6% of the global warming effect, having ~300 times more global warming potential molecule-for-molecule than $CO_2$ over a 100 year period [1]. $N_2O$ is also reported to be the largest ozone-depleting species from man-made sources[2]. One important source of $N_2O$ is

agricultural soil, where it is produced as a result of fertilization [3]. The global nitrogen budget is not as well understood as is the carbon or water budgets. Measurements of the exchange of nitrogen between soil and the atmosphere help to quantify these key steps in the nitrogen cycle.

Picarro has recently developed a new analyzer, the Picarro G2508, that simultaneously measures the five most common gases exchanged between soil and the atmosphere: $N_2O$, $CH_4$, $CO_2$, $H_2O$, and $NH_3$. The first four are the most significant greenhouse gases. $NH_3$ is a very important molecule to track as large quantities of $NH_3$ are released following fertilization. 47 million kilograms of ammonia-based fertilizers were applied to soil worldwide in 2011 [4]. By measuring these gases simultaneously, the rate-of-rises of the five gases are automatically synchronized. The analyzer completes a measurement in < 8 seconds, so it is capable of measuring very fast soil flux dynamics. This is especially helpful in characterizing the non-linearity in a rate-of-rise. Since the analyzer measures $H_2O$, and $NH_3$, the analyzer is able to account for the cross-influence of these molecules on $N_2O$, $CO_2$ and $CH_4$ and reports the dry mole fraction of each of these species. The corrections for the presence of water vapor are determined using the same methodologies as described in Rella, et al. [5] This analyzer allows researchers to get immediate results to optimize the experiment and obtain the best data the first time.

The analyzer is housed within the Picarro G2000 platform, which has a long track record of successful field deployments. The G2000 platform meets mil-spec requirements for shock and vibration. It provides stable results over a large ambient temperature range of 10-35 $^{\circ}$C, humidities up to 99%, and varying ambient pressures from 300 to 1000 Torr. The analyzer is less than 28kg, so it is easy to transport. The analyzer has a built in Windows XP based computer. With an internet connection, researchers can control the analyzer remotely, as well as download data automatically.

The purpose of this study is to demonstrate the capability of the new G2508 to measure soil fluxes. The set up is simple. The analyzer is connected to a static chamber as a closed system. We test both the repeatability of the measurements as well as the ability of the system to follow dynamic flux rates.

**Experimental Details**:

The objective of the experiment was to produce a dataset that would be clearly interpretable for those in the soil research community. We wanted to demonstrate the capabilities of the G2508 as part of a closed system with a static soil chamber. We worked in a tightly controlled laboratory environment to isolate instrument error from dynamic field conditions. Accordingly, we used a simple static soil flux chamber apparatus operated as a closed system (Figure 1). The soil sample consisted of ~2 kg of potting soil mixed with ~100 g of manure placed in a plastic container (Figure 2b) to a depth of 5cm. A 10cm collar was placed in the soil to a depth of 3cm. The G2508 analyzer was equipped with a newly developed low-leak diaphragm pump (leak rate <0.1 standard cubic centimeters per minute [sccm]). The pump and analyzer were then connected to a 10cm diameter soil chamber (Figure 2a). The chamber inlet consists of a perforated tube bent into a crescent through which the gas from the analyzer re-enters the chamber. When the chamber was closed, the crescent inlet was positioned ~5cm above the soil surface. The outlet is at the top of the chamber. The flow through the system was ~275 sccm. Stainless steel flexible tubing and VCR connectors with silver coated nickel gaskets were used for all the connections. The total internal volume was 495 ml. The total response time was on the order of two minutes.
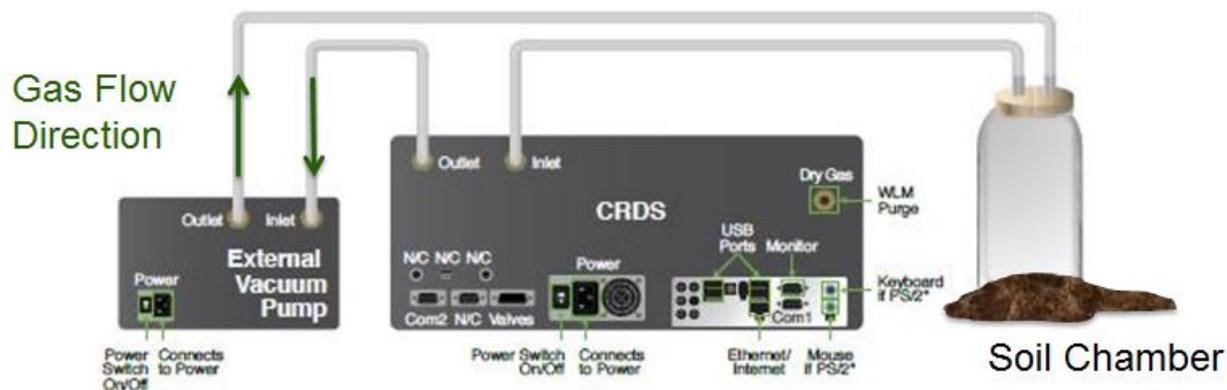
**Figures 1**: The experimental apparatus operated as a closed system. Gas emitted from the soil is captured by the soil chamber. It then flows to the G2508 cavity ringdown spectrometer (CRDS) where the gas concentrations are measured. The gas is drawn through the system by the low-leak external vacuum pump. The gas exiting the pump returns to the soil chamber.

The first set of five chamber test experiments were designed to show the repeatability of the measured fluxes. The soil was relatively dry at the beginning of the experiment with the ambient air containing 0.65% water vapor (~45% relative humidity at ~20$^{\circ}$C) Over the course of 2 hours, the chamber was placed over the collar 5 times, and the concentrations of the five gases were monitored. The duration of each chamber test was no less than 15 minutes. The chamber was open for a minimum of 6 minutes between each test.

The second set of five chamber tests were designed to show the result of a rain event. To simulate this, water was added to the soil sample. Within 2 minutes, the chamber was placed on the collar for 12 minutes. This was repeated four additional times with duration between 14 and 18 mintues. Like the dry soil tests, the chamber was open for a minimum of 6 minutes between each test. Adding water to the sample caused large changes in the flux of all five gases

For each chamber test , the rate-of-rise was calculated by averaging one-minute bins of the analyzer output. The starting point was identified as the time at which the $H_2O$ concentration rose from the baseline. A line was fit to the first 12 minutes of this data to arrive at a slope, a 1$\sigma$ standard error of the slope, and the correlation coefficient, $R^2$. In some cases, the rate-of-rise was clearly non-linear. For these cases, the standard error of the slope is larger and $R^2$ is <0.99. Accordingly, a non-linear functional form should be used to model the data, but this wwas no within the scope of this analysis as there are several models in use by the soil flux community.

One can see that the initial data concentration is not always the same for each chamber test. This is due to variations in ambient gas concentration at the instant the chamber was closed. This is especially true for $CO_2$. Many people work in the lab in which these experiments were conducted, so the background levels do vary depending on the number of people in the lab and their proximity to the experiment.
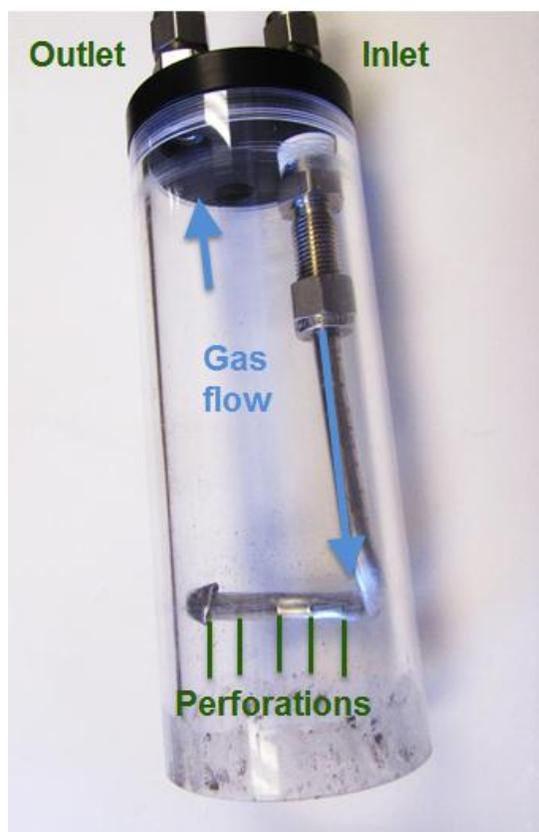
**Figures 2**: a) The static chamber. The arrows show the perforations in the crescent shaped end of the inlet tube. The gas then flows up, through the outlet, and to the analyzer, through the pump, and back to the chamber. b) The soil sample with the collar in place.

## Results:

The results of the tests are shown in Table 1a and 1b as well as Figures 3-5. The first set of five chamber tests on dry soil (Table 1a) showed very repeatable results with the variation in the rate-of-rise being comparable to the standard error calculated for the slope. The second set of five tests following the addition of water to the soil (Table 1b) showed quite different trends for each of the measured gases. $N_2O$ emission rate triples immediately and continues to rise over the next hour. $CH_4$ emission immediately spiked, but then decreased toward the emission rates of the dry soil. $CO_2$ emission was initially suppressed but recovered by the end of 2 hours. $NH_3$ concentration was higher. As one would expect, the water vapor content increased.

| Dry soil test | Time min | $CO_2$ ppm/min (dry mole fraction) | $N_2O$ ppb/min (dry mole fraction) | $CH_4$ ppb/min (dry mole fraction) |
|---|---|---|---|---|
| 1 | -125 | **30.4** +\- 1.14 ($R^2$ = 0.986) | **5.16** +\- 0.082 ($R^2$ = 0.997) | **0.210** +\- 0.017 ($R^2$ = 0.940) |
| 2 | -97 | **35.1** +\- 1.63 ($R^2$ = 0.979) | **5.43** +\- 0.121 ($R^2$ = 0.995) | **0.207** +\- 0.016 ($R^2$ = 0.943) |
| 3 | -73 | **35.5** +\- 1.58 ($R^2$ = 0.981) | **5.27** +\- 0.149 ($R^2$ = 0.992) | **0.088** +\- 0.017 ($R^2$ = 0.740) |
| 4 | -44 | **34.5** +\- 1.37 ($R^2$ = 0.985) | **5.33** +\- 0.124 ($R^2$ = 0.995) | **0.210** +\- 0.016 ($R^2$ = 0.947) |
| 5 | -23 | **37.6** +\- 1.65 ($R^2$ = 0.981) | **5.47** +\- 0.098 ($R^2$ = 0.997) | **0.158** +\- 0.015 ($R^2$ = 0.913) |
| Average | | **34.6** +\- 1.47 | **5.3** +\- 0.12 | **0.17** +\- 0.016 |
| Repeatability | | **2.65** | **0.127** | **0.053** |

**Table 1a**: The slope of the rate-of-rise for $CO_2$, $N_2O$, and $CH_4$ emitted from dry soil. The time shown is relative to the addition of water to the soil. The uncertainty is the $1\sigma$ standard error of the slope. The repeatability is the $1\sigma$ standard deviation of the 5 rates for dry soil.

| Wet soil test | Time min | $CO_2$ ppm/min (dry mole fraction) | $N_2O$ ppb/min (dry mole fraction) | $CH_4$ ppb/min (dry mole fraction) |
|---|---|---|---|---|
| 1 | +2 | **14.3** +\- 0.13 ($R^2$ = 0.999) | **17.64** +\- 0.319 ($R^2$ = 0.997) | **23.69** +\- 0.943 ($R^2$ = 0.984) |
| 2 | +20 | **20.7** +\- 0.25 ($R^2$ = 0.999) | **19.54** +\- 0.217 ($R^2$ = 0.999) | **9.37** +\- 0.148 ($R^2$ = 0.998) |
| 3 | +40 | **25.7** +\- 0.48 ($R^2$ = 0.996) | **21.88** +\- 0.238 ($R^2$ = 0.999) | **5.20** +\- 0.051 ($R^2$ = 0.999) |
| 4 | +62 | **30.4** +\- 0.59 ($R^2$ = 0.996) | **25.44** +\- 0.193 ($R^2$ = 0.999) | **3.76** +\- 0.051 ($R^2$ = 0.998) |
| 5 | +100 | **34.8** +\- 0.70 ($R^2$ = 0.996) | **28.99** +\- 0.202 ($R^2$ = 1.000) | **2.30** +\- 0.040 ($R^2$ = 0.997) |

**Table 1b**: The slope of the rate-of-rise for $CO_2$, $N_2O$, and $CH_4$ emitted from wet soil. The time shown is relative to the addition of water to the soil. The uncertainty is the $1\sigma$ standard error of the slope.
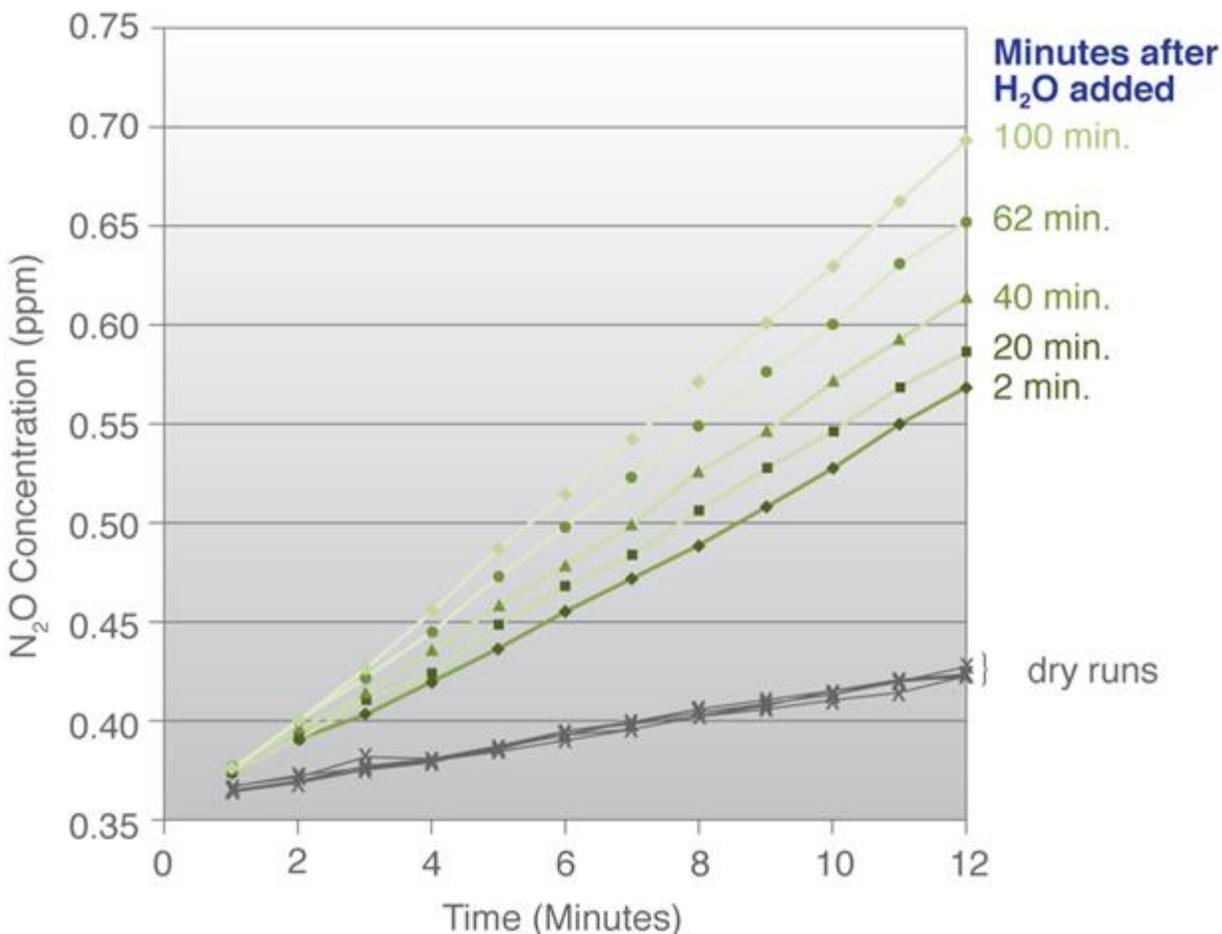
**Figure 3**: $N_2O$ rate-of-rise data. The chamber tests with dry soil conditions are shown in gray. The chamber tests following the addition of water are shown in green. The start time of the chamber tests relative to the time of watering is shown on the right.

**$N_2O$**

The repeatability of the $N_2O$ rate-of-rise of dry soil was quite consistent with an average rise of 5.3 +/-0.12 ppb/min. The uncertainty is the $1\sigma$ standard error of the slope. The variations in the slopes of all five runs were comparable to the calculated standard errors. The $R^2$ values were all >0.99 as the slopes were very linear at these low concentrations (Figure 3).

After adding water to the soil, the flux of $N_2O$ immediately tripled and was over 5 times higher after 100 minutes (Table 1b and Figure 3). While the $R^2$ values continue to be >0.99, a slight positive curvature can be seen in the rate of rise, which indicates that the flux rate is increasing during each chamber test. Clearly, this is the case as one can see the increase between chamber tests. One could either model this effect or perform much shorter chamber tests, which is possible as the analyzer records a set of data faster than every 8 seconds.
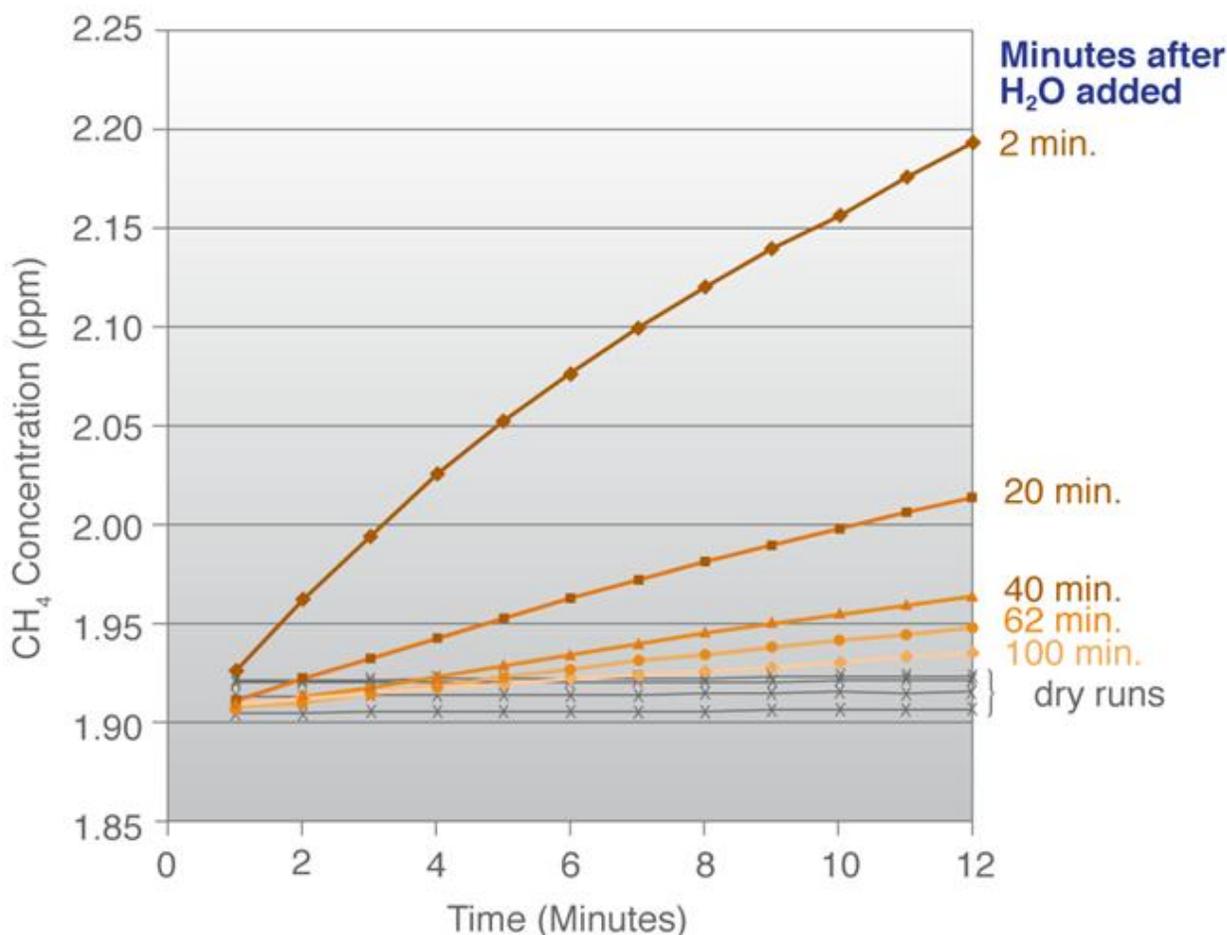
**Figure 4**: $CH_4$ rate-of-rise data. The chamber tests with dry soil conditions are shown in gray. The chamber tests following the addition of water are shown in orange. The start time of the chamber tests relative to the time of watering is shown on the right.

**$CH_4$**

The repeatability of the $CH_4$ rate-of-rise of dry soil was good considering that the measured rate was very low, averaging 0.17 +/-0.016 ppb/min (Table 1a and Figure 4). The $R^2$ values were not close to 1 due to the signal-to-noise at the low flux rates. Nonetheless, the small positive rate-of-rise values are clearly significant statistically as the rises are ~10x the 1$\sigma$ standard error for the slope.

The water correction that is a standard part of Picarro analyzers was particularly important in this case. Without the correction, the $CH_4$ concentrations appeared to decrease during each of the dry soil chamber tests with an average change of -0.3 ppb/min. During each test, the water vapor concentration increased rapidly. This will have an effect on the raw measurements of the spectroscopic lines for $CH_4$ (and $N_2O$ and $CO_2$). Once the spectroscopic effects of water vapor were accounted for, the actual source behavior of the system was clear. Accounting for the

effect of water vapor properly is critical in distinguishing sink from source behavior at these low flux rates.

It is possible, however, that this rate-of-rise is not entirely soil flux. Separately, we measured the outgassing of the pump, which has elastomer membranes. We measure an outgassing rate of ~ 0.1 ppb/min in a 24-hour test. As this is similar to the measured rate of the chamber system, some portion of this flux rate is due to outgassing at the pump. Our characterization of the leak and outgassing behavior of our Closed System Measurement Package is underway and will be the subject of a future applications note. Nonetheless, the soil flux rate is clearly quite small, and quite different than the fluxes that follow.

After adding water, the soil flux of $CH_4$ immediately increases by over 100x but then decreases over the following 2 hours. Nonetheless, 100minutes later is was still 10x of the dry value. While the $R^2$ values were all >0.98, the data do show a clear negative curvature. While there are certainly cases where this can arise at high gas concentrations where the back diffusion can result in a slowing rate-of-rise, here the concentration of $CH_4$ is only 2.2 ppm at the maximum concentration. In this case, it is likely that the emission from the soil is decreasing over the course of the first chamber test. This is confirmed by the next four chamber tests, which showed decreasing $CH_4$ soil flux rates, although these rates were consistently higher than the dry soil rate. It appears that adding water to the soil produced an immediate increase in the $CH_4$ soil flux rate which lasted only a few minutes.
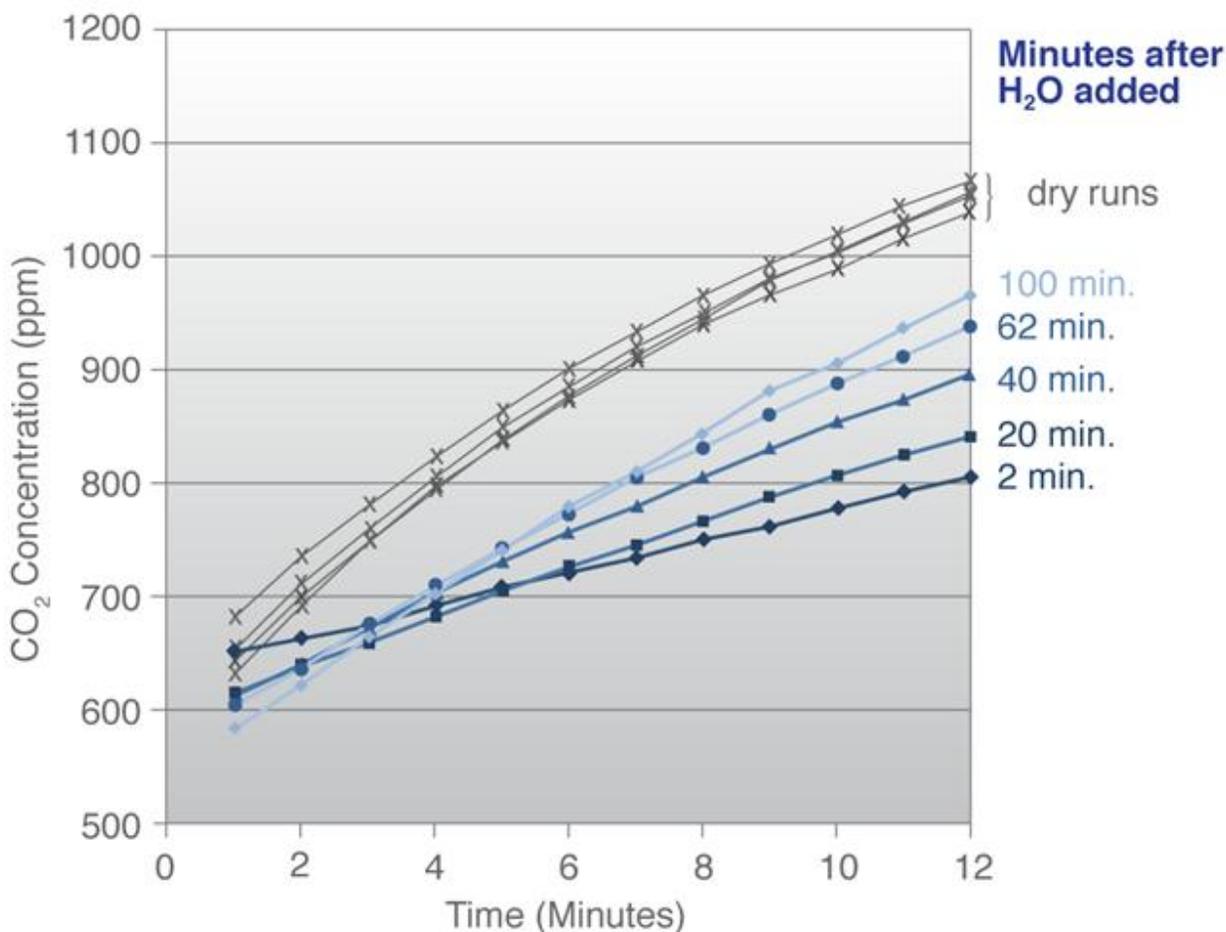
**Figure 5**: $CO_2$ rate-of-rise data. The chamber tests with dry soil conditions are shown in gray. The chamber tests following the addition of water are shown in blue. The start time of the chamber tests relative to the time of watering is shown on the right.

## $CO_2$

The repeatability of the $CO_2$ rate-of-rise of dry soil was consistent with an average rise of 34.6 +/-1.47 ppm/min (Table 1a and Figure 5). The variations in the slopes for 4 of the 5 runs were comparable to the calculated standard errors. The $R^2$ values were ~0.98 as the data showed negative curvature. The concentrations of these chamber tests exceeded 1000ppm, which is 2.5 times normal ambient concentrations. It is likely that this high concentration of $CO_2$ reduced the flux by shifting the equilibrium.

Adding water suppressed the soil flux of $CO_2$. The soil flux of $CO_2$ immediately afterward was less than half of the dry value. Over the following 2 hours, the $CO_2$ soil flux recovered to the dry value. The $R^2$ values improved to >0.99 as the data were more linear than the dry rate-of-rise data. The suppression of the $CO_2$ flux may have been caused by the absorption of $CO_2$ by the water. Once the water was saturated, the previous $CO_2$ flux was re-established.
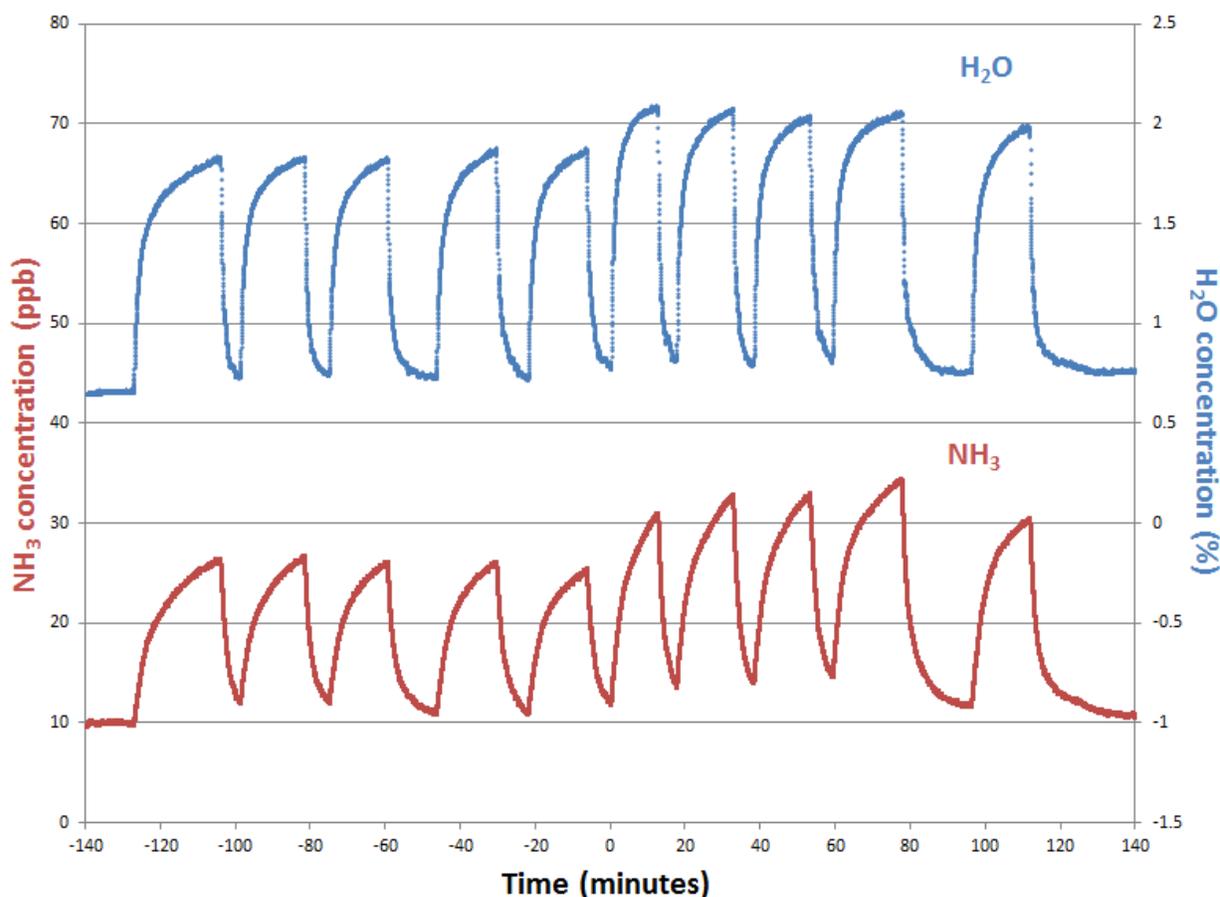
**Figure 6**: 10 chamber tests for $NH_3$ and $H_2O$. Water was added at time=0. $NH_3$ is shown in red, and $H_2O$ is shown in blue.

### $NH_3$ and $H_2O$

The rate-of-rise data for $NH_3$ and $H_2O$ are more difficult to interpret than that of $N_2O$, $CH_4$, or $CO_2$. The responses of $H_2O$ and $NH_3$ are limited by the adsorption of these species to the surfaces of the experimental apparatus. While the analyzer will accurately measure the concentration of $NH_3$ and $H_2O$ within the cavity, calculating the actual flux of $NH_3$ and $H_2O$ from the soil from these measurements will require de-convoluting the adsorption dynamics within the system from the soil flux rate. Figure 6 shows the concentrations of $NH_3$ and $H_2O$ in all ten chamber tests. The rates-of-rise are clearly non-linear. When the chamber is removed and ambient gas flushes the system, these gases are slow to purge from the measurement cavity. A simple way to quantify the change with the addition of water is to note the concentrations of both gases after the chamber has been on the collar for 12 minutes. This concentration may correlate with the ultimate saturation concentration. For $NH_3$, the average concentration after 12 minutes was 24.4 ppb for dry soil and 30.9 ppb for wet soil. Similarly, the $H_2O$ concentration was 1.78% for dry soil and 2.01% for wet soil. Clearly, using this data will require more sophisticated modeling and instrument calibration than one would use for the other gases, but the relative change in soil flux of $NH_3$ and $H_2O$ is clear and invites further quantitative analysis.

## Conclusions:

The new Picarro G2508 analyzer was able to provide repeatable, statistically significant soil flux rate-of-rise measurements for $N_2O$, $CH_4$, or $CO_2$. The analyzer also provided detailed information on the soil flux of $NH_3$ and $H_2O$. It was able to reveal details dynamics of the soil flux after a simulated rain event. The analyzer successfully operated as part of a closed system.

## References:

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