

## **Final Report**

# **Nitrous Oxide Emissions from Texas Beef Cattle Feedyards – Upgrade of Varian 3800 Gas Chromatograph to support field research program**

**October 1st, 2009 through December 31st, 2010**

**Principal Investigator:      Kenneth D. Casey Ph.D.  
Research Chemist:            Al Caramanica**

**Texas Cattle Feeders Association**

## PROJECT SCOPE

To develop the capacity for the measurement of greenhouse gases to support an experimental campaign under the Federal Air Quality Initiative into emission mechanisms of greenhouse gases focusing on nitrous oxide (N<sub>2</sub>O) from the feedyard pen surface ('dry-lot').

The initial proposal was to upgrade the existing Varian 3800 – Saturn 2000 – Markes Unity GC-MS-TD system to allow analysis of greenhouse gases. However, a detailed investigation into the feasibility of this approach concluded that the functionality of the existing system would be severely compromised. It was decided instead to purchase a GC system that was equipped and configured specifically to analyze greenhouse gases.

## EQUIPMENT PURCHASED:

A CombiPAL auto-sampler (CTC Analytics AG, Switzerland) was purchased in December of 2009 along with a three channel, Varian 450 Gas Chromatograph (Varian Inc., Walnut Creek, CA) (Figure 1.). The Varian GC was ordered with flame ionization (FID), thermal conductivity (TCD), and electron capture detectors (ECD) for analysis of methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), and nitrous oxide (N<sub>2</sub>O), respectively. The auto-sampler was purchased with the headspace mode option allowing a direct transfer of sample via syringe from its container to the GC, minimizing potential leaks and loss of sample. In addition, a syringe purge option was installed to flush the syringe with helium after an injection of sample to ensure no sample carryover in subsequent injections. Four tray holders along with four vial trays that hold up to 32, 10 ml vials of were also purchased, allowing up to 128 samples to be run consecutively.



Figure 1. Varian 450 GC with CTC CombiPAL Auto-sampler.

**QUALITY ASSURANCE DISCUSSION:**

Initial quality assurance checks of the system show that the instrumentation is very linear in the concentration range that the Air Quality Laboratory is expecting to find in the field. Three calibration standards (Scott Specialty Gases, Plumsteadville, PA) were purchased with the intent to “bracket” the concentrations of methane, carbon dioxide, and nitrous oxide that we are expecting to find in cattle feedlots. The low level standard contains concentrations of the three gases of interest below those found in ambient air, the mid level standard concentrations are closer to ambient, and the high level standard exceeds the concentrations we expect to find (Table 1). Using the CombiPAL auto-sampler, the gas standards are introduced to the GC in the same manner as the field samples, producing a three point calibration curve for each gas of interest (Figure 2.).

**Table 1. Component gas concentrations in the high, mid and low calibration standards.**

Component	Component Gas Concentration (ppm)		
	Low	Mid	High
Carbon Dioxide	200	500	983
Methane	1.0	5.07	9.9
Nitrous Oxide	0.2	1.04	4.95

**GHG GAS CHROMATOGRAPH SYSTEM COST:**

The costing for the Varian 450 greenhouse gas chromatography system as installed is shown in Table 2. The \$6000 funding provided through this project was applied towards the cost of the CTC CombiPAL auto-sampler. The remainder of the system cost was funded from the Federal Air Quality Initiative.

**Table 2. GHG GC Budget**

Item	Cost
Varian 450-GC equipped with FID, TCD and ECD detectors and valves, sample-loops and packed columns for GHG analysis	34,350.10
CombiPAL Auto-Sampler	20,719.82
Galaxie Software and Dell Optiplex 775 Computer	4,829.00
On-Site Installation and Operator Training	2,926.00
<b>TOTAL:</b>	<b>\$62,824.92</b>

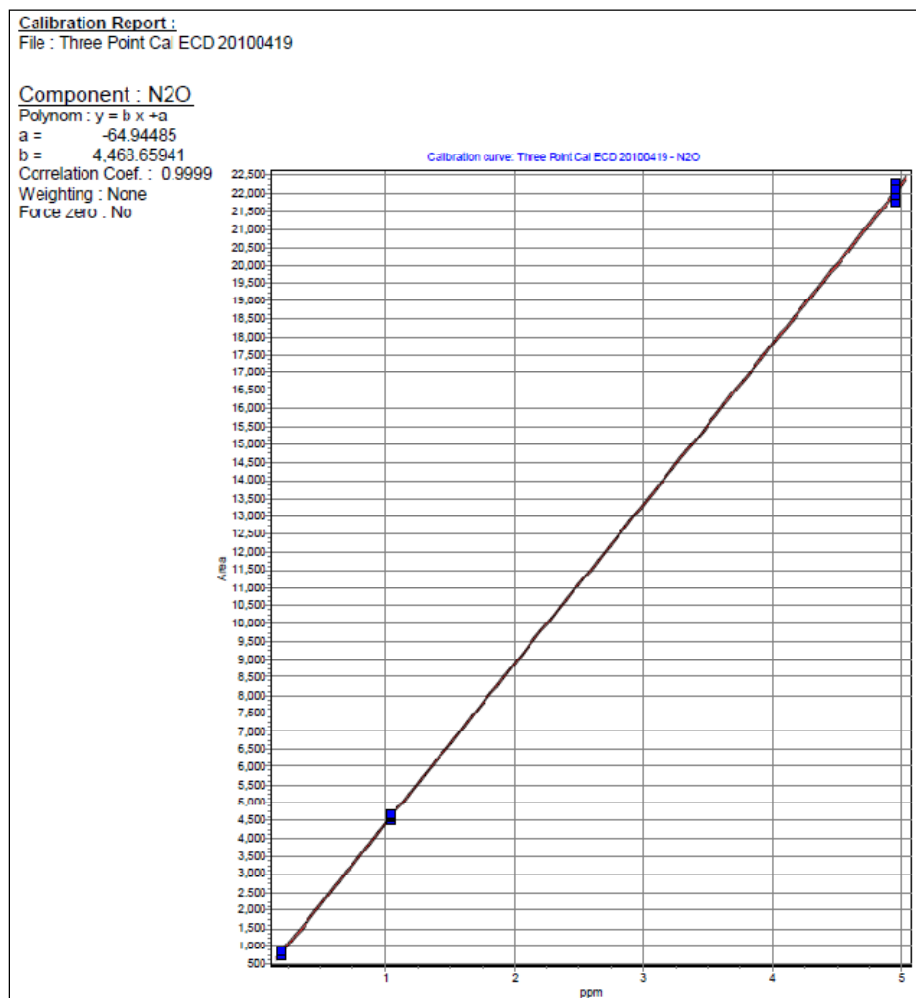


Figure 2. Calibration Curve for Nitrous Oxide on Varian 450 ECD

**Chamber Description:**

Collection of the gases of interest at the feed lots is carried out using non-flow-through, non-steady-state (NFF-NSS) chambers made of eight in., Schedule 40, PVC pipe caps. A skirt of 21 in. diameter, 40 mil shower pan liner is fitted around the external bottom lip of the cap and is weighted down with a length of chain or paver stones to seal against the substrate was first tested in order to keep air exchange at a minimum. The efficacy of the flexible skirt proved variable depending on the pen conditions and the design was changed to a steel rim that is driven into the pen material. A flexible sleeve is used to seal the cap to the base once the cap is in place and the first sample has been collected. Two stainless steel, 0.25 in. to 0.125 in. bulkhead reducing unions (Swagelok, P/N SS-400-61-2) are fitted into opposing sides of the top of the caps. One bulkhead union is fitted with a 0.25 in. stainless steel nut into which a 9.5 mm silicon septa is inserted and serves as the injection port from which samples are taken. A four in. length of 0.125 in. stainless steel tubing is fitted to each union on the interior of the cap. One serves as a sampling tube for the injection port and the other functions as a vent tube to minimize pressure and volume changes during chamber deployment as well as atmospheric turbulence. The volume of each chamber is approximately 4.6 liters.

### Sample Collection:

Prior to sample collection, the sample vials are rigorously vacuumed and purged to ensure that the sampling vials contain no contaminant gases. Sample collection will take place at a pre-determined feedyard with meteorological instrumentation installed. A cattle pen will be chosen for its state of dry or wet substrate, proximity to a meteorological tower, and amount of cattle being held at the time of sampling. Once the sampling chambers have been placed, sampling can commence. A sample is withdrawn from the chamber using a 20 ml disposable syringe fitted with a 1.5 in., 25 gauge luer-lock needle. Twenty (20) ml of sample are withdrawn at time 0, 15 and 30 minutes and injected into 10 ml vials causing an overpressure of the sample container, ensuring no leakage of contaminants into the filled vials. For quality control purposes, two lab blanks and two field blanks are analyzed for every ten samples collected. The lab blanks are prepared with the sample vials, filled with helium and then left in the lab until analysis. The field blanks are also prepared with the sample vials but are vacuumed, taken to the collection area, returned to the laboratory and filled with helium to ensure the packing and transportation of vials was carried out correctly.



Figure 3. Injecting a gas sample collected from the NFF-NSS chamber into an evacuated vial.

### Flux Measurement Determination:

Using the Hutchinson and Mosier (1981) algorithm, allows the researcher to account for a buildup of the analyte concentration in the chamber headspace, which alters the diffusion gradient and resulting flux. However, the three headspace concentration measurements must be made at time periods of equal length, beginning at  $t_0$ (time zero). Concentration measurements at any given sampling should show an increase in the compounds of interest over time if the chamber construction is sound and proper sampling techniques are followed.

$$f_0 = \frac{V(C_1 - C_0)^2}{At_1(2C_1 - C_2 - C_0)} \ln \left[ \frac{C_1 - C_0}{C_2 - C_1} \right], \text{ if } \frac{C_1 - C_0}{C_2 - C_1} > 1$$

where:

$f_0$  = flux at time zero

V = chamber headspace volume (L)

A = soil surface area (m<sup>2</sup>)

$C_0, C_1, C_2$  = chamber headspace gas concentrations (ppm(v)) at time 0, 1, 2, respectively

$t_1$  = interval between gas sampling points (min)

This equation allows the calculation of the flux rate at  $t_0$ (time zero), before the measurement method (NFF\_NSS chamber) begins to influence the flux rate. Under conditions where the flux rate is low, a linear regression can be used to obtain the flux rate as the increase in concentration in the chamber is small enough as to not affect the flux of the gas component of interest.

### References:

Hutchinson, G. L. and A. R. Mosier. 1981. Improved soil cover method for field measurement of nitrous-oxide fluxes. *Soil Science Society of America Journal* 45(2) 311-316.