The Perfluorocarbon Tracer Releases During the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study

Thomas B. Watson

Randy Johnson

National Oceanic and Atmospheric Administration
Air Resources Laboratory
Field Research Division
1750 Foote Drive
Idaho Falls, Idaho
83402

Marc L. Pitchford

National Oceanic and Atmospheric Administration
Air Resources Laboratory
Special Operations Research Division
C/o Desert Research Institute
755 E. Flamingo Road
Las Vegas, NV 89119

Mark Green

Hampden Kuhns,

Vicken Etyemezian

Desert Research Institute
755 E. Flamingo Road
Las Vegas, NV 89119

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Abstract

Since the early eighties, the NOAA/Air Resources Laboratory/Field Research Division (ARL/FRD) has released perfluorocarbon tracers in a number of field programs designed to measure long-range atmospheric transport over regional and continental scales. In the summer of 1999, ARL/FRD participated in a field program designed to understand the long-range transport of visibility-reducing particles from regional sources in the U.S. and Mexico and to quantify the contributions of specific U.S. and Mexican sources (or source regions) possibly responsible for poor visibility at Big Bend National Park. The Big Bend Regional Visibility and Observational (BRAVO) Study field program was conducted over four months, from July through the end of October 1999. Tracer released as part of the BRAVO Study occurred over a four-month period, included three different release schedules to provide time stamping, and required two release systems to be relocated to tag the influence of different sources at the mid-point of the study period. ARL/FRD developed new, automated release systems for the BRAVO Study to accomplish the release in an efficient and cost-effective manner. The design of these systems is described in detail. The systems released the tracer as planned, with only four minor problems resulting from equipment malfunctions. The data recovery rate was 99.6%. The calibration and data analysis methods are described in detail and the data file structure outlined.

1.0 Introduction

During the last 20 years, the NOAA/Air Resources Laboratory/Field Research Division (ARL/FRD) has released perfluorocarbon tracers in a number of field programs designed to measure long-range atmospheric transport over regional and continental scales. Three examples of these projects are:

- Cross Appalachian Tracer Experiment (CAPTEX), 1983 (Ferber, et al, 1986)
- Across North America Tracer Experiment (ANATEX) 1987 (Draxler, et al, 1989)
- Measurement of Haze and Visual Effects (MOHAVE) 1992 (Pitchford, et al, 1998)

This report describes the tracer release system designed to meet the special requirements of a four-month long regional scale transport experiment designed to assess the influence of long-range transport of haze-causing pollutants that impact the Big Bend National Park in Texas.

Big Bend National Park is located in Southwest Texas on the border between the United States and Mexico in the area where the Rio Grande makes a gradual turn to the north (Figure 1). The park has an area of 3240 square kilometers that is primarily desert in a remote, sparsely populated area that is home to many species of wildlife and plants. It is crossed by two mountain ranges and has numerous canyons and other interesting physical features. Big Bend was established as a national park in 1944 and designated as a biosphere reserve in 1976.

In spite of Big Bend's remote location, noticeable changes in the visibility at the park were observed as early as the 1970s. Examples of the effects can be seen in Figures 2 and 3, which show the typical range of conditions possible at Big Bend. As a result of their growing awareness of visibility impacts in national parks and wilderness areas, Congress amended the Clean Air Act in 1977 to include provisions to protect certain of these areas, including Big Bend NP from man-made pollutant impairment of visibility. The National Park Service began an air-monitoring program at Big Bend in 1978 to track air quality levels and better understand the causes of visibility degradation.

In 1996, the Big Bend Air Quality Work Group, a committee with members representing the governments of the United States and Mexico, conducted a limited scale field study in the region (Big Bend Air Quality Work Group, 1999). Membership on the committee consisted of representatives from the Environmental Protection Agency (EPA), the National Park Service (NPS), and

Figure 1: Locations of Big Bend National Park, Carbon I and II Power Plants, Tracer release sites in Eagle Pass, San Antonio, Big Brown, and Houston area

Figure 2: View of Sierra del Carmen in Mexico from Big Bend National Park, August 18, 1999, visual range 156 km.

Figure 3: View of Sierra del Carmen in Mexico from Big Bend National Park, September 1, 1999, visual range 59 km

Procuraduria, Federal de Protección al Ambiente (PROFEPA), a Mexican government agency with environmental monitoring and enforcement responsibilities. The program was conducted in Texas and northern Mexico from September 9 through October 13, 1996. $PM_{2.5}$ and PM_{10} samples were collected and analyzed for chemical composition. There were 19 sampling locations, 10 in Texas and 9 in Mexico. As a result of the study the bi-national work group came to three conclusions, which represent the consensus of the members:

- Relative humidity plays a large role in visibility impairment at Big Bend
- Fine particulate sulfur, primarily in the form of sulfate, is a large component of the haze
- Emissions from sources to the northeast and south appear to have an impact on visibility at Big Bend

The work group recommended a more extensive field program to quantify the contributions of specific sources on the visibility reduction at Big Bend.

Chemical analysis of the preliminary study samples and long term monitoring at the park indicate that approximately 41% of the visibility obscuring haze is composed of sulfate aerosol (Sisler, et al, 1996). Some of the potential sources of this sulfur are coal-fired power plants, petroleum refining, and chemical processing operations.

In Texas the primary sulfur sources are power plants in east and southeast Texas and refineries and industrial plants along the Gulf Coast. A coal deposit, known as the Lignite belt, extends from northeast of Dallas-Ft. Worth to the border area south of San Antonio. There are 22 power plants in this region, located near mines, which use coal from this deposit as their primary fuel. Oil refineries and chemical operations along the Gulf Coast, primarily in the Houston area, are also potential sources of sulfur, which could find its way to Big Bend.

Regional sulfur sources in Mexico that may contribute to the haze at Big Bend are coal-fired power plants, oil refining, oil fired power production, steel production, and other industrial operations. Carbon I and II are power plants with 1200 and 1400 megawatt capacities located approximately 30 km (20 miles) south of the US-Mexico border near the town of Eagle Pass, Texas which is only about 230 km southeast of Big Bend. The Tampico region on the Gulf of Mexico is another potential sulfur source impacting Big Bend. It is a center of oil refining and oil fired power generation. Other, more distant, industrial areas on the Pacific Coast and to the north and south of Mexico City are also potential sources of the sulfate seen in the park.

Researchers at the Desert Research Institute (DRI) analyzed atmospheric transport patterns that result in haze episodes using the Atmospheric Transport and Dispersion model (ATAD) (Heffter, 1980). They correlated visibility impairment, particulate concentration, and levels of chemical constituents at the

park with the trajectories of air masses as determined from the model. Their conclusion from this analysis is that sources to the south contribute most to average visibility degradation at Big Bend, while sources to the east and northeast are responsible for some of the worst episodes of visibility impairment (Green et al, 1999).

2.0 The Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study

Members of bi-national committee formulated plans for the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study as the more extensive follow-up study recommended in the consensus conclusions of the preliminary study report. Two committees were formed to plan and direct the study: a steering committee to make policy decisions and a science committee to design and execute the study.

The representatives of the United States and Mexico on the policy committee were unable to reach agreement on the science plan and the Mexican government chose not to participate in the final field program. As a result of this impasse the U.S. representatives of the steering committee redesigned the study to limit its monitoring activities solely within the U. S.

A subcommittee of non-governmental organizations was formed that consisted of representatives from industry and environmental group to advise the steering and scientific committees. Organizations participating in BRAVO Study include:

- Environmental Protection Agency (EPA)
- United States National Park Service (NPS)
- Texas Natural Resources Conservation Commission (TNRCC)
- National Oceanic and Atmospheric Administration (NOAA)
- Department of Energy, Brookhaven National Laboratory
- University Of Nevada, Desert Research Institute (DRI)
- ENSR, an environmental contractor
- University of California, Davis
- Colorado State University, Cooperative Institute for Research in
- the Atmosphere
- Electric Power Research Institute
- Environmental Defense Fund

The goals established for the BRAVO Study include:

- Determination of the chemical constituents of fine particles responsible for regional hazes that affect Big Bend;
- Determination of the effects of meteorology including moisture from the Gulf of Mexico on visibility-reducing particles; and

- Evaluation and improvements in the accuracy of atmospheric models and source attribution methods through the use of atmospheric tracer and updated source emission profiles.

The plan developed for the BRAVO Study is based upon the information developed by the preliminary study, routine monitoring at Big Bend, regional meteorological data and emissions inventories for the U.S. and Mexico. Experience gained in other source attribution studies such as the recently completed Project MOHAVE was also applied to the design of the BRAVO Study.

Particulate sulfate contributes most to visibility impairment at Big Bend; thus sources of SO_2 are of particular interest to BRAVO. Particulate carbon (elemental and organic) also contributes substantially to haze at Big Bend; the aerosol monitoring program was designed to reveal more information regarding sources of carbonaceous aerosol at Big Bend.

On the average, visibility at Big Bend is most impaired during the May to September period. However, in October transport from the northeast is sometimes associated with very poor visibility. A four-month field program from July through October 1999 was selected to maximize the number of occurrences of flow from two regions of particular interest: northeast Mexico and eastern Texas. Backtrajectory analysis showed that this four month period would maximize the number of occurrences of flow from the significant source areas for SO_2 that are closest to Big Bend National Park. These periods would also be expected to experience many episodes of transport from large SO_2 sources in central Mexico and would likely result in one or more cases of transport from large SO_2 source regions in the eastern U.S.

The use of tracers in Project MOHAVE showed that the current state of atmospheric transport and dispersion modeling in complex terrain is not accurate enough to draw reliable conclusions regarding source-receptor relationships on a day-by-day basis (Pitchford *et. al.,* 1999, Green and Tombach, 2000). This result argued for the release of artificial tracers for use in direct attribution methods such as TAGIT (Kuhns et al. 1999a), to help evaluate and calibrate transport and dispersion models, and for use in receptor based models. The tracer program design and especially the tracer release is the primary subject of this report discussed in much greater detail in subsequent sections.

The principal receptor-monitoring site was established in Big Bend, which also served as the primary location to address many of the outstanding technical issues raised by the preliminary study. This site was heavily instrumented with gas phase and particulate air quality samplers and instruments measuring atmospheric optical properties. A number of high time resolution air quality instruments were deployed here to measure high sensitivity gas phase SO_2, particulate sulfate, organic carbon, and particulate nitrate. Other monitoring at this site included 24-hour carbonaceous aerosol sampling and for detailed

speciation of selected samples by GSMS; and high time resolution gas phase nitric acid, gas phase ammonia, and gas phase hydrogen peroxides. Various real time particle size measurement and atmospheric optical devices were also deployed at the K-Bar Ranch site including three transmissometers over various site paths, ambient and RH controlled nephelometers, 5 automated 35 mm cameras each taking three color photos a day, aethelometer, and a photoacoustic light absorption instrument.

Previous studies also demonstrated the utility of a large network of particulate monitoring sites and chemical analysis of the filter samples. Several analysis methods utilize this spatially resolved aerosol data. The BRAVO Study design includes a network of 37 aerosol-monitoring sites (Figure 4). There were 18 sites where 24-hour samples of SO_2 and tracer were collected to establish a gradient for use with the spatial analysis attribution methods, as well as other modeling methods. These sites were located with approximately 100 km spatial separation. There were 6 sites in the Big Bend area, where six-hour integrated samples of $PM_{2.5}$, SO_2, and tracer were collected (Figure 5). The increased sampling frequency was intended to provide greater resolution around the principal receptor site.

Upper air measurements that supplement routine weather observation in the region were made by radar wind profilers at 10 locations (4 specifically for BRAVO) to help evaluate and calibrate wind field models for input to air quality models.

Receptor modeling will be used to help identify the influence of different emission sources. Some receptor models require source characterization data. A program of sampling and chemical analysis of emission sources of interest was conducted by the Desert Research Institute to supplement source characterization information in the literature. Sources characterized include motor vehicles, biomass burning, specific coal fired power plants, cement kilns, refineries, carbon black production facilities, and cooking sources. DRI employed a dilution sampling system to collect stack samples from hot sources, such as the power plants, to cool and dilute the effluent. This reproduces the dilution and cooling in the atmosphere so that the particulate fraction collected corresponds to the ambient particles produced by the sources (Zielinska et al, 1998). The X-ray fluorescence analytical technique was used to identify 40 elements in samples. Sulfate, nitrate, and ammonium ions were characterized by ion chromatography and organic and elemental carbon by thermal desorption methods.

An independent quality assurance audit program was designed and implemented by ENSR for all quantitative measurements. Features of this program include review of all written protocols for all sampling, analysis, and measurements; on-site audits of procedures, including particulate and tracer

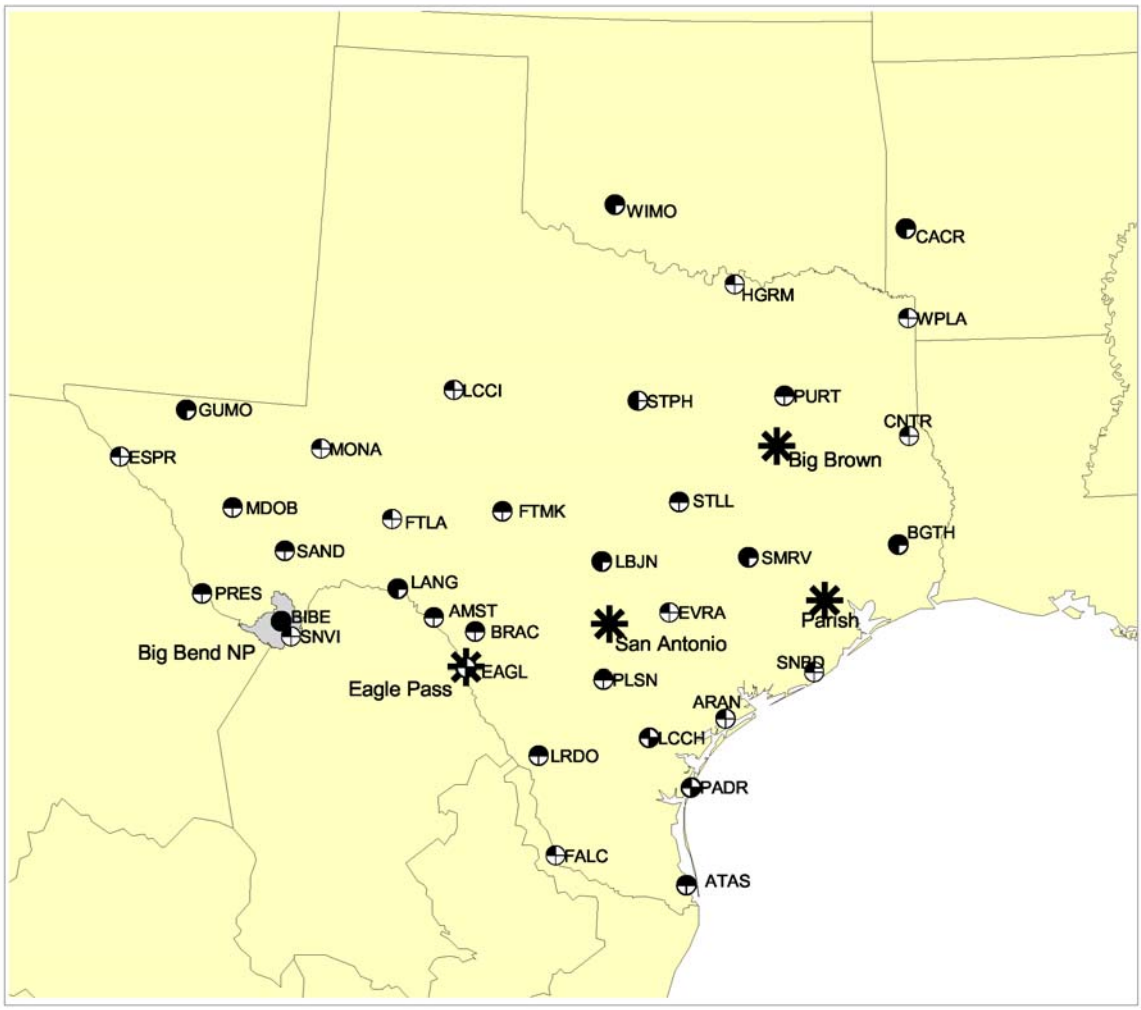

Figure 4: Locations and measurements made at sites where 24-hour integrated tracer samples were collected.

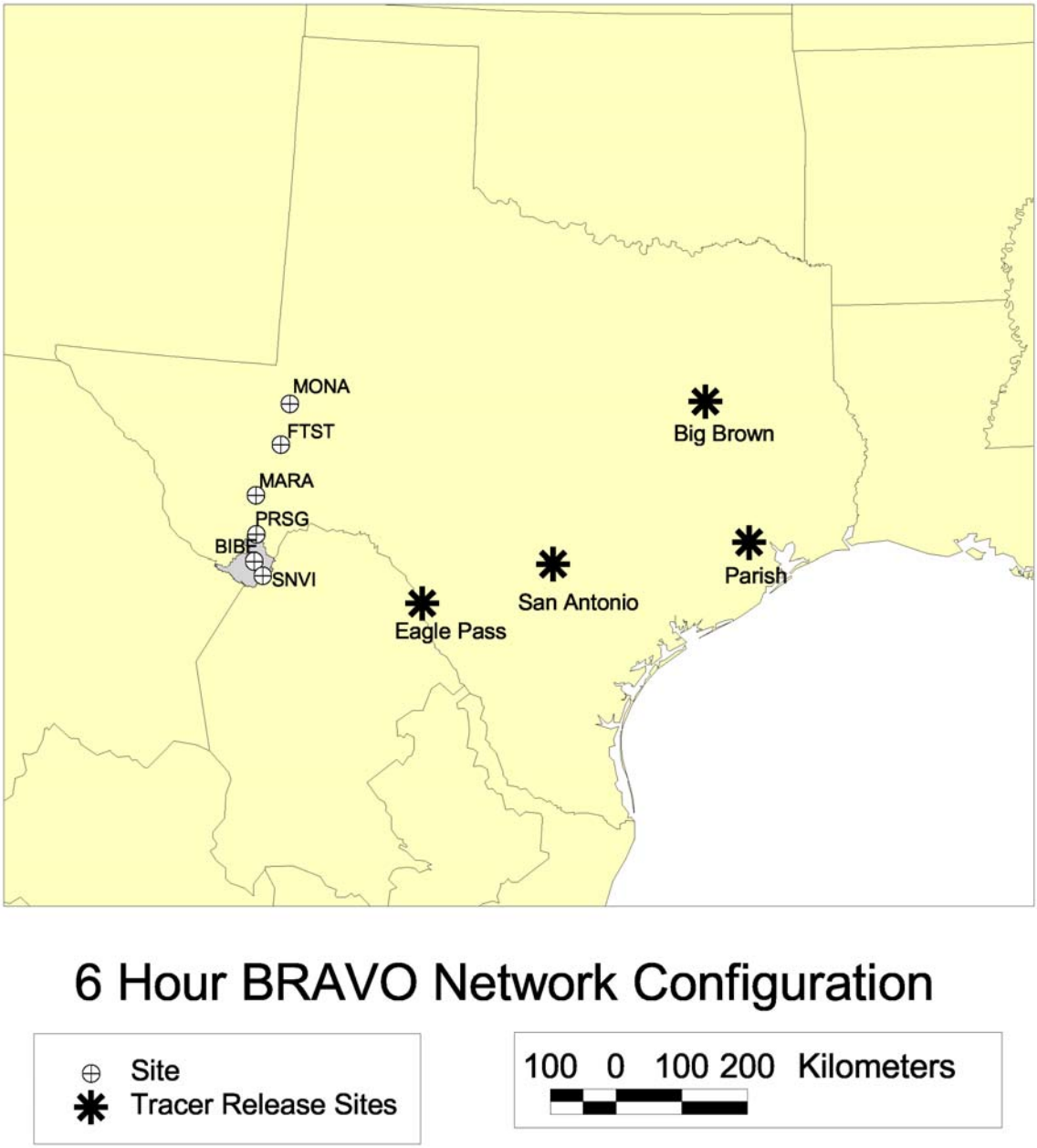

Figure 5: Locations and measurements made at sites where 6-hour integrated tracer samples were collected.

sampling, tracer release, and tracer analysis; and monitoring of data processing and archiving.

3.0 Perfluorocarbon Tracer Program

Artificial tracers used in the BRAVO study are a class of compounds known as perfluorocarbons. These compounds are fully fluorinated hydrocarbons. The predominance of fluorine in these compounds gives them properties which a make them ideal tracers; they have low atmospheric background levels; they are inert and do not decompose in the troposphere - the atmospheric lifetime of this class of compounds is on the order of three thousand years; and they are easily detectable at low levels using electron capture chromatography. The specific compounds used in BRAVO and their detection limits for concentrations due to study release are given in Table 1.

Table 1: Perfluorocarbon compounds used in BRAVO, their background levels and estimated detection limits for identification of above background concentrations due to study release.

Unit	BRAVO Tracer Designation	IUPAC[1] Chemical Designation	Estimated Background[2] (parts in 10^{15})	Estimated Detection Limit[3] above background (parts in 10^{15})
Unit 1	oPDCH	Perfluoro-1,2-dimethylcyclohexane	1.00	0.18
Units 2 and 5	PDCB	1,1,2,2,3,4-hexafluoro-3,4-bis(trifluoro-methyl) cyclobutane	1.4	0.21
Units 3 and 6	PTCH	Perfluoro-1,3,5-trimethylcyclohexane	0.15	0.07
Unit 4	iPPCH	perfluoro-iso-propylcyclo-hexane	0.10	0.04

1. International Union of Pure and Applied Chemistry
2. (Dietz, R. private communication)
3. 3 X standard deviation of background variability

3.1 Release Plan

The tracer releases were designed in two phases to take advantage of the seasonal flow regimes. The first phase was a characterization of southeasterly flows and was designed to provide information on transport, dispersion, and transport time for the Carbon I & II power plants. The restriction of the study to U. S. release sites in Eagle Pass, 30 km from the power plants in Mexico, required creativity in the use of tracer to approximate transport from Carbon I and II. Time-resolved tracer data was necessary to determine the transport time from the Eagle Pass/Carbon I and II area to BBNP. This transport time is necessary to make estimates of SO_2 to sulfate conversion. It was also necessary to differentiate between emissions released during the day and those released at night. The SO_2 to sulfate conversion is a photochemical process and has a distinct diurnal cycle. There are different transport mechanisms in a well-mixed boundary layer, which generally occurs during the day, and stable, stratified conditions, which occur most often at night. In addition, it was expected that daytime releases during well-mixed conditions would more closely mimic releases from the power plants than nighttime releases during stable conditions with increased vertical wind shear. The tracer release was designed so that the perfluorocarbons detected in the analysis of the samples would provide information to:

- provide a measure of dispersion
- distinguish between well mixed and stratified conditions (day vs. night)
- determine the day of the release
- provide unambiguous results

The second experimental phase was the continuous release of four tracers at four different locations. The purpose of these releases was to characterize transport and dispersion from sources that may be transported from areas in Texas northeast of the park.

3.2 Phase 1 Release

Three tracers were used at the Eagle Pass site to meet the timing requirements: one tracer was released continuously to quantify dispersion; one was released every day for 12 hours, from 8:00 Central Daylight Time (CDT) to 20:00 CDT, to identify daytime periods and provide for timing information; and one tracer was released for 24 hours every other day to provide a release day marker and a second time stamp (Table 2). The releases at Eagle Pass were made from the top of a 107 m (350 feet) tall tower, to simulate the releases from the Carbon I and Carbon II Power Plant stacks. There was also one tracer released continuously from the Big Brown Power Plant. Big Brown is located at the northern end of the Lignite Belt near Fairfield, Texas (Figure 1) and operated by Texas Utilities. The tracer was introduced into the exhaust duct just before the point where the duct enters the stack.

Table 2: Phase 1 tracer release rates and schedule

Location	Unit	Tracer	Release rate (g min^{-1})	Release schedule
Eagle Pass	1	oPDCH	2.6	Continuous 7/5/99-11/1/99
Eagle Pass	2	PDCB	8.75	08:00 to 08:00 alternate days 7/5/99-9/13/99
Eagle Pass	3	PTCH	3.0	08:00 to 20:00 daily 7/5/99-9/13/99
Big Brown	4	iPPCH	1.5	Continuous 7/9/99-11/1/99

3.3 Phase 2

Phase 2 of the study was designed to characterize the easterly flow from source regions in the Lignite Belt and Gulf Coast area. Two of the tracer release systems used during Phase I at Eagle Pass, Units 2 and 3, were moved. Unit 2 was moved to the San Antonio area and was re-designated Unit 5. Unit 3 was moved to the Houston area and was re-designated Unit 6. Releases from Units 5 and 6 were continuous throughout the remainder of the program. Unit 1 remained at Eagle Pass releasing continuously as in Phase 1. Unit 4 remained at Big Brown releasing continuously, as in Phase 1. The San Antonio release system was located at an air quality monitoring station run by the utility company, City Public Service. The site was inside the beltway and was chosen to represent the San Antonio area source. The release in the Houston area was made from the Parish power plant, operated by Reliant Energy, located about 64 km southwest of Houston. Tracer was introduced into the stack of Boiler 7 through a sampling port at the 100 ft. level. Release rates and locations are listed in Table 3.

Table 3: Phase 2 tracer release rates and schedule.

Location	Unit	Tracer	Release Rate (g min^{-1})	Release Schedule
Eagle Pass	1	oPDCH	2.6	continuous 7/5/99-11/1/99
San Antonio	5	PDCB	7.4	continuous 9/17/99 – 11/1/99
Houston	6	PTCH	1.9	Continuous 9/17/99 – 11/1/99
Big Brown	4	iPPCH	1.5	Continuous 7/9/99 – 11/1/99

3.4 Tracer Sampling and Analysis

A programmable sampler was used to collect 1 hour, 6-hour, and 24-hour integrated samples on adsorbent cartridges at 25 locations (1 1-hour site, 6 6-hour sites, 18 24-hour sites). Samples were shipped to the DOE laboratory at Brookhaven where they were analyzed using gas chromatography with electron capture detection. A sophisticated analytical protocol requiring thermal desorption of the samples, followed by cryo-focusing, a two column separation method, and drying and catalytic reaction steps was required (Draxler et al, 1991) for the analysis.

4.0 Tracer Release System

In past programs, ARL/FRD technicians were required to continuously monitor tracer releases. The release rates were manually controlled. Data were recorded by hand. This was inefficient and expensive because it required two or three shifts and housing a staff of technicians near each release site. The releases in BRAVO occurred over a four-month period, included three different release schedules to provide time stamping, and required two systems to be moved in the middle of the experiment. BRAVO required a new approach to tracer release. Automated systems were designed specifically for this program to accomplish the release in an efficient and cost-effective manner.

The operation of the system is based on programs executed by a Campbell Scientific, Inc., CR23X data logger. The microprocessor in the CR23X runs a program that controls data collection and storage and executes self-diagnostic routines to evaluate and compare data from a number of sensors monitoring the performance of the system. An alarm sequence, which results in a phone call to the FRD Idaho Falls office, is triggered if any operational limits are exceeded.

The release systems were completely automated and able to operate unattended. However, a local operator was recruited to visit the systems once a day and visually inspect the equipment and record tank levels and pressures. The local operators were also available to make adjustments to the systems and help correct minor problems. The PFC tanks were designed with sufficient capacity to hold the tracer supply necessary for the duration of the experiment. It was necessary to fill the tanks only once. This limited fugitive emissions to one period at the beginning of the study. Data was acquired once a day via telephone lines. Systems were built with redundant pumps and heater elements and were housed in air conditioned, weatherproof metal cabinets (Figure 6).

4.1 PFC Handling Components

The components of the release systems are shown schematically in Figure 7. There are two PFC tanks; a large supply tank that holds the bulk of the tracer and a smaller metering tank with finer mass resolution from which the PFC is released and the rate metered. Both tanks are suspended from load cells that continuously monitor weight and are sealed and pressurized with 5 to 10 psi of compressed air. Tank headspace pressure and differential pressure are measured. The differential pressure is measured between the top and bottom of each tank. The pressure measured between the top and the bottom of the tank is another method to calculate PFC weight. A metering pump is used to move the PFC from the metering tank to the vaporizer. The load cell output was used in conjunction with the metering pump to provide an accurate measure of release rate. Metering pumps were calibrated before the experiment and using the experimental data as described below.

Figure 6: Release system in weather-proof cabinet.

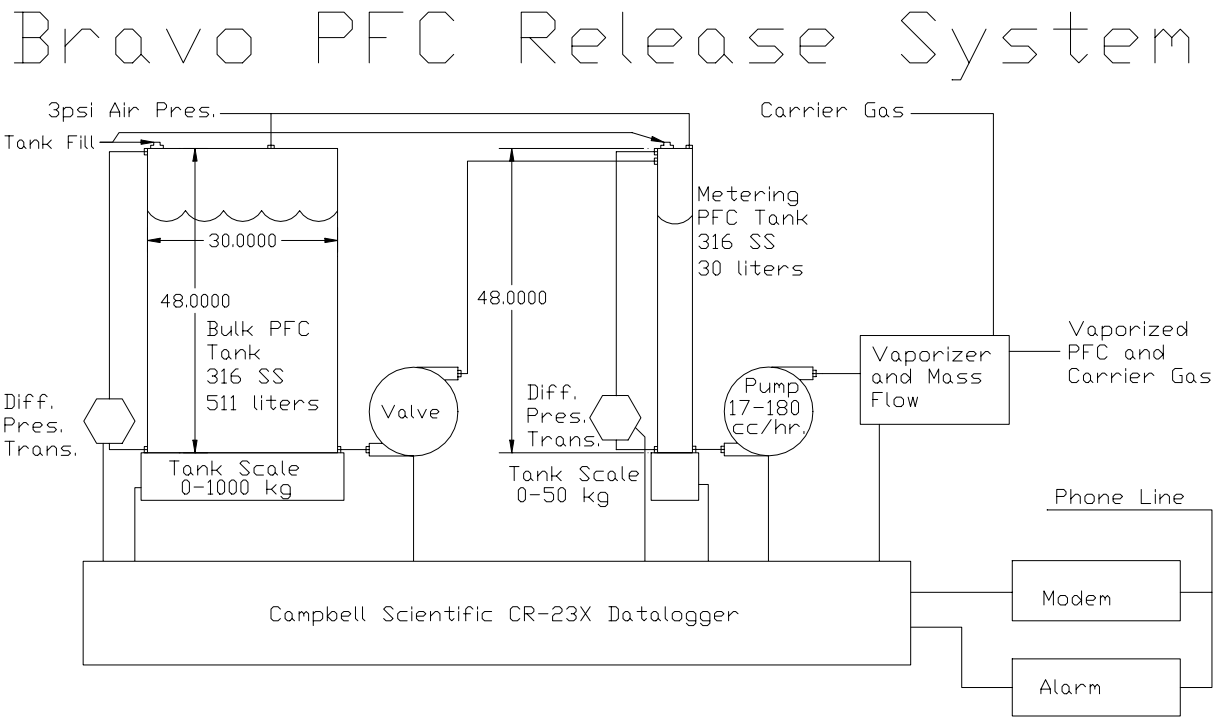

Figure 7: Schematic drawing of release system components

There were two pumps in each system to provide a backup in case of a pump failure. Each pump was operated for 24 hours on alternate days.

The PFCs are liquid at ambient temperature. They must be vaporized before release. Vaporization was accomplished in an aluminum block with two power resistors attached to the outside acting as heating elements. One power resistor provided sufficient heat to vaporize the PFC. The second resistor was a spare. The PFC flowing from the metering pump was introduced into the central cavity of the block through the side. The blocks were maintained at constant temperature by changing current supplied to the power resistor. The power used by the vaporizer was monitored and is proportional to PFC flow rate. This relationship was determined in the laboratory and used as one of the parameters examined during self-diagnostic comparisons. A compressor supplied a flow of air past a one inch opening in the top of the block. This air acted as carrier gas to dilute the vaporized PFC so it would not condense in the delivery lines and to transport the PFC to the stack or to the top of the tower. The carrier gas flow rate was approximately 30 lpm providing a dilution factor of over 10,000:1.

4.2 Data Acquisition and Monitoring

A Campbell Scientific, CR23X data logger was used to collect and process the data from the release system. The data acquisition rate was 8 Hz. These data were averaged every 5 minutes and stored as a record. One-hour averages were collected and stored as well. Some of the important parameters recorded were:

- Time and date
- Supply tank weight
- Metering tank weight
- Supply tank head space pressure
- Metering tank head space pressure
- Differential pressure of both tanks
- Metering pump RPM
- Vaporizer current
- Carrier air flow rate

The CR23X was programmed to compare parameters such as the differential pressure, mass change of the metering tank, and vaporizer power consumption. If discrepancies were detected, it would call the NOAA Idaho Falls office and play a recorded message. The data logger transferred the data from each system once a day over telephone lines in response to a request from a computer in the Idaho Falls office. Data were examined daily. Operational parameters of all systems were checked by hand and data were plotted, posted on our website (www.noaa.inel.gov/recentprojects/bravo), and backed up and archived.

4.3 Operation Cycle

A cycle of events automatically occurred during the tracer release beginning with filling the metering tank. When the metering tank weight was reduced to 20% of capacity as indicated by the load cell, a valve opened and the smaller tank was filled with PFC from the main tank. During this transfer, the metering pump continued to supply 1.5 to 8 cc PFC per minute to the vaporizer. Every 24 hours, at midnight, the pump currently working was shut down and the other pump placed in service. Diagnostic parameters were monitored continuously. The conditions that could trigger an alarm were:

- Tank headspace pressure outside of limits
- Differential pressure of supply tank outside of limits during transfer
- Differential pressure of metering tank outside of limits during normal release
- During transfer from supply tank, weight change of supply tank and metering tank do not agree or are outside limits
- Metering tank falls below 20% capacity
- Weight change of metering tank outside of limits
- Metering pump RPM outside of limits
- Current of vaporizer outside limits
- Carrier flow outside of limits

4.4 Calibration

All the load cells used in the release systems were purchased specifically for BRAVO. They were calibrated by the manufacturer before shipping and returned for re-calibration after the program was over. All calibrations were traceable to NIST standards. Pre and post test results are listed in Table 4. All changes were less than 0.2%.

Table 4. Pre-test and post-test load cell calibration results

	Load Cell S/N	Pre-test $kgmV^{-1}$	Post-test $kgmV^{-1}$	Change $kgmV^{-1}$	% change
Unit 1					
supply	102675	114.796	114.728	0.07	0.06
metering	D47614	3.8075	3.8126	0.005	0.13
Units 2 and 5					
supply	102777	114.51	114.43	0.08	0.07
metering	D47609	2.982	2.973	0.01	0.3
Units 3 and 6					
supply	D55308	56.84	56.91	0.07	0.1
metering	D61170	2.979	2.983	0.004	0.13
Unit 2					
supply	D55315	57.362	57.362	0.0	0.0
metering	D61147	2.983	2.986	0.003	0.1

4.5 Load Cell Noise

The manufacturer's specifications state the error of the load cell measurements as +/- 0.002% of full scale. This is equivalent to 1800 g for the main tank, which has a full-scale capacity of 2000 lb (907.18 kg), and 45 g for the metering tank load cell, which has a full-scale capacity of 50 lb (22.68 kg). The release rates ranged from 1.5 to 8 g min^{-1}. The five-minute differences between load cell readings are at or below the noise level. There is additional noise in the load cell signals from vibrations caused by the pumps and air conditioning units. The fill cycles, although they occurred for only one or two five-minute averaging periods every several days, prevented continuous determination of release rates from the load cell data. Therefore, release rates and uncertainty limits were established using the pump rpm measurements calibrated using 24-hour load cell readings.

4.6 Metering Pump Calibration

A calibration factor for each pump was determined in post processing. The time periods used in calculations were 24 hours in the case of continuous releases and total time a pump was operating during a release cycle in the case of the timing releases. The total PFC mass released and the total number of pump revolutions in the period were calculated. The mass was divided by the number of revolutions of the metering pump to determine a calibration factor with units of grams per revolution.

$$C_{cal} = \frac{\Delta \text{ total PFC mass}}{\text{total number of pump revs}} \qquad (1)$$

The calibration factor for each period was then multiplied by the 5-minute average rpm values in that period to calculate the 5-minute release rates. Table 5 lists the mean and standard deviation for the 5-minute release rates calculated for the entire test period for each unit.

$$\text{release rate} = C_{cal} \text{ X rpm} \qquad (2)$$

Confidence limits in individual 5-minute release rates are, very conservatively, estimated from the standard deviation of the mean 5-minute release for each unit for the entire test. The highest relative standard deviation of the mean release rate for any unit was 6%. Plots of 5-minute release rates for each unit are given in Appendix B.

Table 5: Mean release rates and related statistics calculated from 5-minute averaged pump rpm values and calculated calibration factors.

Unit #	R, mean release rate ($g\ min^{-1}$)	σ, standard deviation ($g\ min^{-1}$)	σ/R, coefficient of variation	$\sigma/N^{1/2}$, ($g\ min^{-1}$)	2 X ($\sigma/N^{1/2}$) ($g\ min^{-1}$)	N, number of points
1	2.6	0.1	0.04	7×10^{-4}	1.3×10^{-3}	33,864
2	8.5	0.2	0.03	2×10^{-3}	5×10^{-3}	8,586
3	2.75	0.14	0.05	1.4×10^{-3}	3×10^{-3}	9,900
4	1.5	0.009	0.006	5.4×10^{-4}	1×10^{-3}	29,693
5	7.3	0.45	0.06	4×10^{-3}	8×10^{-3}	11,872
6	1.9	0.1	0.05	1×10^{-3}	2×10^{-3}	10,614

- σ/R is the relative standard deviation of the mean or the variance.
- $\sigma/N^{1/2}$ is the standard deviation of the mean.

- 2 X ($\sigma/N^{1/2}$) is two times the standard deviation of the mean or the 95% confidence limit.

5.0 Release System Performance

There were relatively few problems with the release process. On two occasions there were interruptions caused by power outages at the Eagle Pass site. Tripped circuit breakers caused the Unit 2 compressor to shutdown twice and Unit 5 to shut down once. The exact reason for this problem was never determined. The compressor failures present a potential problem in the analysis of the data from the tracer samples. When the compressors failed, there was no carrier airflow. The PFC, however, continued to be released and vaporized. When the compressor restarted, we do not know what happened to the PFC accumulated in the vaporizer or release lines. Analysis of samples attributed to impacts from these periods should have interesting tracer data. It is possible that compressor failures could lead to additional time stamping in the samples.

The Eagle Pass systems were originally scheduled to be shut down and moved on September 1. The systems were filled with enough PFC to last for the scheduled time. However, the Phase 1 release was extended through September 13, at the request of the scientific planning committee. Near the end of this time PFC was running low in Units 2 and 3. A supplemental PFC fill was carried out on September 6. Unit 2 release rate was cut in half on September 3 to nominally 4 g min^{-1} and returned the previous level of 8 g min^{-1} on September 9.

A third type of problem occurred at Eagle Pass when temperatures dropped suddenly October 17-19. The release rate dropped along with the temperatures. The problem was resolved by having the local operator put a space heater in the cabinet.

There was a loss of 504 five-minute data records from Unit 5 during the period from September 21 through September 23. The hourly averaged data from this period was not lost, however, and indicated that the release rate was unchanged during this period. This is the only period when data from any of the units is missing. The total number of 5-minute data records recorded during BRAVO was 129,636. The data recovery rate was 99.6%.

Plant shutdowns occurred at the Big Brown and Parish plants during the test. In those cases, the release systems were taken off line. Problems and shutdowns for each unit are summarized in Appendix A.

6.0 Data Reporting

The data are tabulated in separate files, each containing the data for one of the six units. Each unit has two files, one containing hourly averages, the other 5-minute averages. Each file contains comma-delimited records following the reporting protocol outlined by Kuhns, et al 1999b. A summary table and description of the data records is presented in Table 6.

Files are named by unit and averaging time:

- Unitx_h.dat is one-hour data
- Unitx_5m.dat is 5-minute data
- x is the unit number.

Table 6: Data records.

SITE	POC	Date	Start Time	Duration	Size Or Elev	Param1 Val	Param1 Unc	Param1 Flag Code

Site designations for Tracer release locations are designated using the following codes:

BBPP	Big Brown Power Plant
EAGL	Eagle Pass, Texas
PRSH	Parish Power Plant
SNAN	San Antonio, Texas

POC designates parameter occurrence code. When more than one instrument per site is reported it is used to distinguish between instruments. For Phase One in Eagle Pass, POC 1, 2, or 3 indicate the corresponding release units.

Duration is 5 in the case of 5-minute averaged files and 60 in the case of one-hour averaged files.

Parameter uncertainties, designated in column 8, are filled with NA in the release data. Uncertainties are given in Table 5.

Error flags used in the data set are

000	good data
888	missing data
777	plant shutdown
666	compressor failure

7.0 Preliminary Results of Analysis of Tracer Samples

At the time of composition of this document, the tracer analysis had not been completed. Preliminary analysis of samples has shown that the timing tracers were being seen at sites in and around BBNP. Figure 8 shows an example from the Big Bend site. All three tracers released from Eagle Pass during Phase 1 were detected.

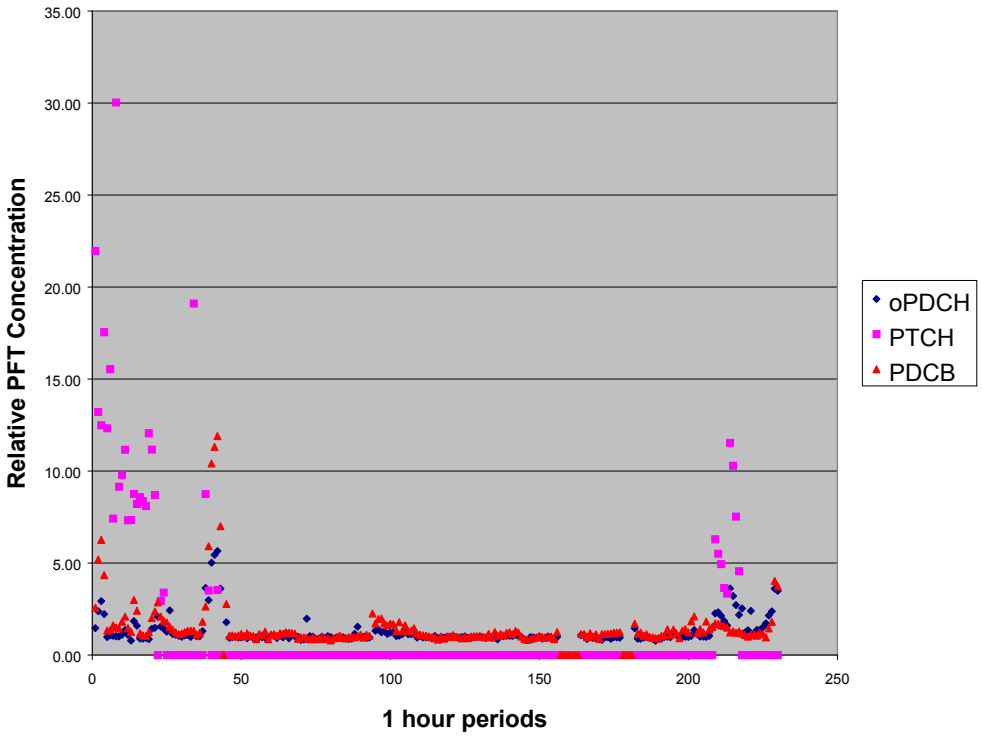

Figure 8: Results of the analysis of one-hour samples collected at the Big Bend site from July 8 through August 3, 1999. All three of the tracers released from Eagle Pass were detected.

8.0 References

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Appendix A: Data Statistics by Release Unit

Table A1: Unit 1, operation dates and dates and times of problems.

Start date (mm/dd/yy)	End date (mm/dd/yy)	Total days	Total records
7/5/99	11/1/99	119	33,916

Problems	Date (mm/dd/yy)	Start time	End time
Power outage	7/6/99	8:30	10:00
Power outage	9/1/99	10:55	13:30

Unit 2

Start date (mm/dd/yy)	End date (mm/dd/yy)	Total days	Total records
7/5/99	9/13/99	71	19,942

Problems	Date (mm/dd/yy)	Start time	End time
Compressor failure	8/13/99	10:00	17:00
Compressor failure	8/14/99	10:55	13:30
Power outage	9/1/99	10:55	13:30
Release rate reduced to 4 g min^{-1}	9/3/99	17:00	
Release rate returned to 8 g min^{-1}	9/9/99	8:00	

Unit 3

Start date (mm/dd/yy)	End date (mm/dd/yy)	Total days	Total records
7/5/99	9/13/99	71	19,333

Problems	Date (mm/dd/yy)	Start time	End time
Power outage	9/1/99	10:55	13:30

Unit 4

Start day (mm/dd/yy)	End day (mm/dd/yy)	Total days	Total records
7/5/99	11/1/99	119	32,651

Problems	Start date (mm/dd/yy)	Start time	End date (mm/dd/yy)	End time
Tracer refill	7/26/99	12:00		
Plant shutdown	8/15/99	18:00	8/17/99	8:00
Plant shutdown	10/8/99		10/16/99	

Unit 5

Start day (mm/dd/yy)	End day (mm/dd/yy)	Total days	Total records
9/17/99	11/01/99	71	12,843

Problems	Start date (mm/dd/yy)	Start time	End day (mm/dd/yy)	End time
Missing data	9/21/99	17:00	9/23/99	10:55
Compressor failure	10/10/99	23:00	10/12/99	14:00

Unit 6

Start day (mm/dd/yy)	End day (mm/dd/yy)	Total days	Total records
9/17/99	10/25/99	39	10,951

Problems	Start date (mm/dd/yy)	Start time	End day (mm/dd/yy)	End time
Compressor failure	10/18/99	16:00	10/19/99	11:00

Appendix B: Plots of 5 minute Release rates by unit

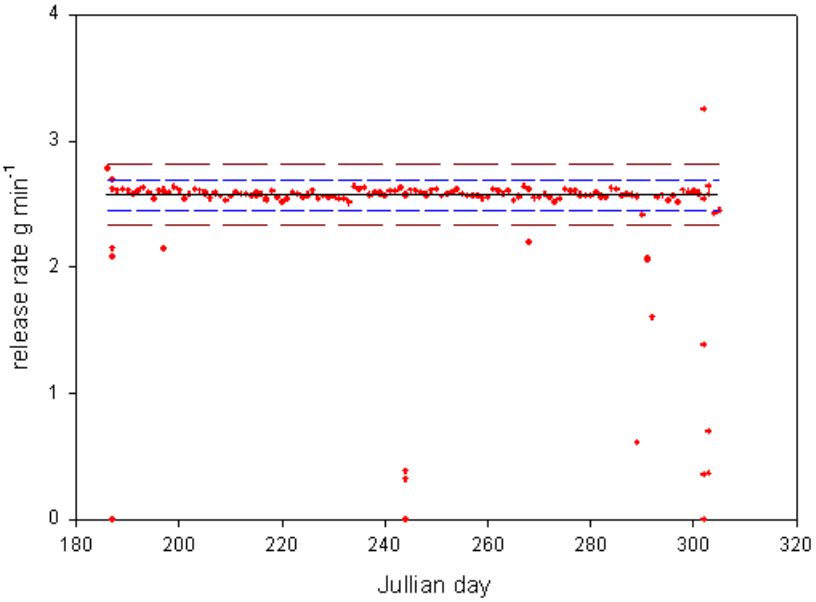

Figure B1: Eagle Pass, Unit 1, 5-minute release rate mean, and +/- 1 and 2 standard deviations. Mean = 2.6. Standard deviation = 0.1.

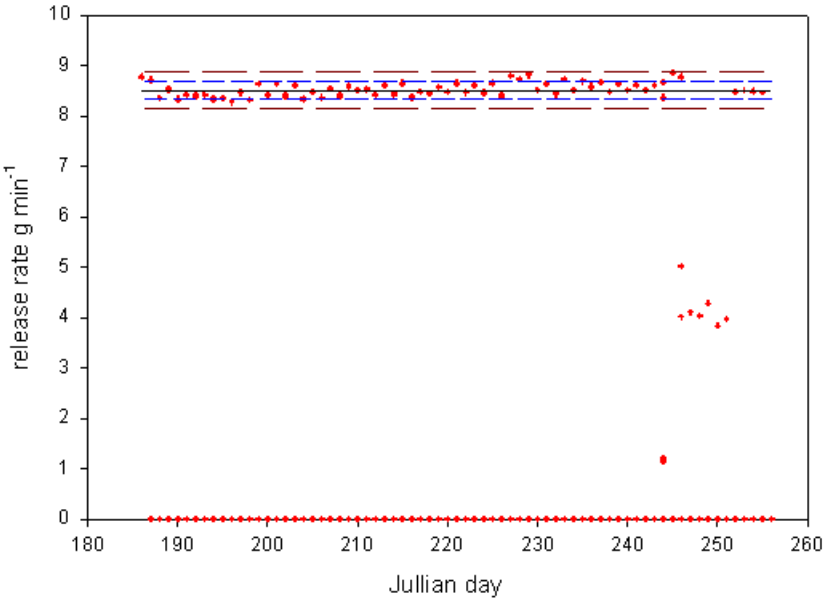

Figure B2: Eagle Pass, Unit 2, 5-minute release rate mean, and +/- 1 and 2 standard deviations. Mean = 8.5. Standard deviation = 0.2.

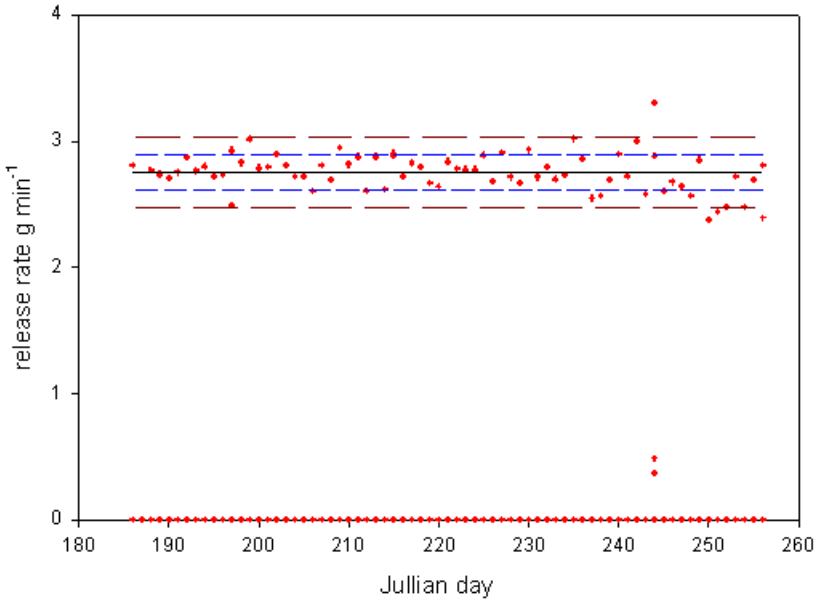

Figure B3: Eagle Pass, Unit 3, 5-minute release rate mean, and +/- 1 and 2 standard deviations. Mean = 2.75. Standard deviation = 0.14.

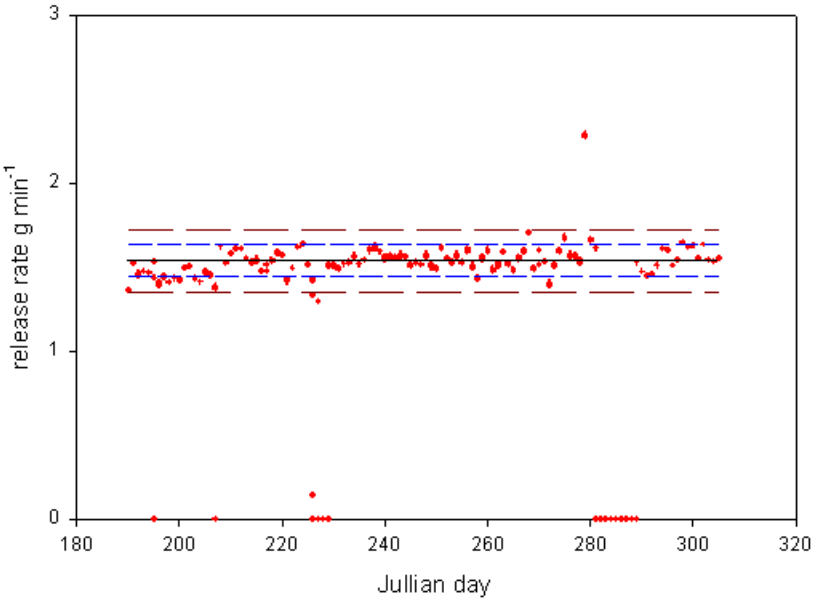

Figure B4: Big Brown, Unit 4, 5-minute release rate mean, and +/- 1 and 2 standard deviations. Mean = 1.5. Standard deviation = 0.009.

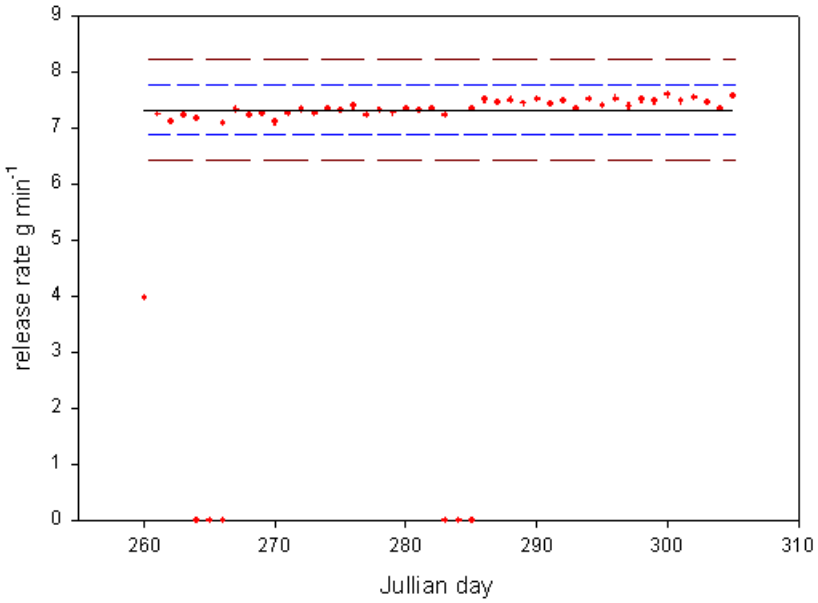

Figure B5: San Antonio, Unit 5, 5-minute release rate mean, and +/- 1 and 2 standard deviations. Mean = 7.3. Standard deviation = 0.045.

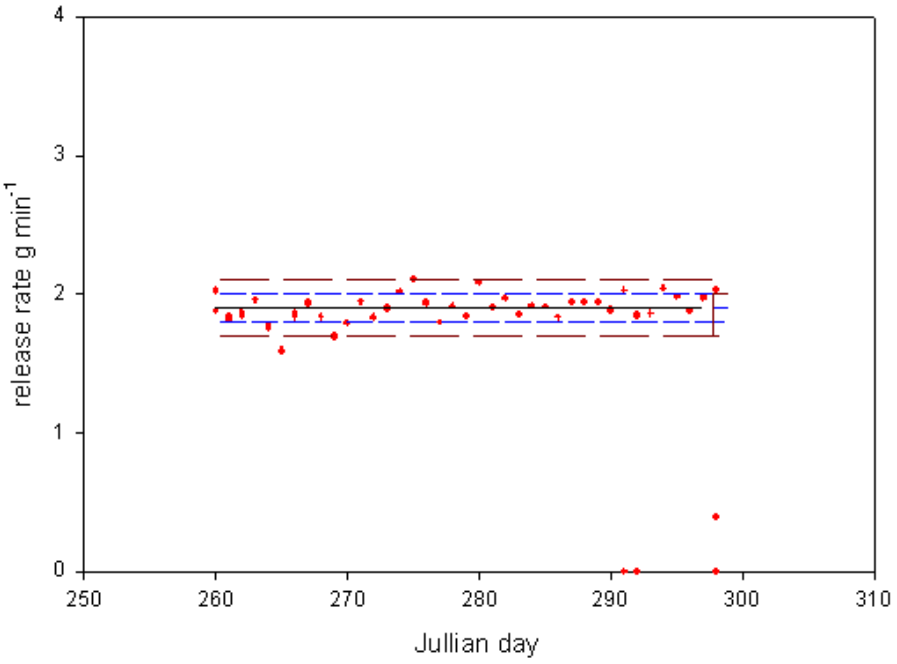

Figure B6: Houston area, Unit 6, 5-minute release rate mean, and +/- 1 and 2 standard deviations. Mean = 1.9. Standard deviation = 0.1.