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J. R. Bowyer,

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1998.

CONC. MEASUREMENTS
NMBC OK BUT VELOCITY
MEAS. NOT VALID

L-2

NCDENR

NORTH CAROLINA DEPARTMENT OF
ENVIRONMENT AND NATURAL RESOURCES

# Final Report

(Revised)

Ron,
Could you put this emission rate of $4.39 \times 10^{-5}$ g/sec into some kind of perspective? Are there data for filling stations, for example against which this value may be compared?

Yours,
[illegible] x1183

NC Department of Environment and Natural Resources
Division of Air Quality, Toxics Protection Branch

Raleigh, North Carolina

# A Study to Determine an Emission Rate of Benzene from Asphalt Load-out

**ATAST #98026**

**Final Report**

by

James R. Bowyer, Ph.D.

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**NC Department of Environment and Natural Resources**
**Division of Air Quality, Toxics Protection Branch**

# A Study to Determine an Emission Rate of Benzene from Asphalt Load-out

**ATAST #98026**

## Final Report

(Revised)

**Abstract**
This study was conducted to obtain a better measure of the emission rate of benzene from asphalt trucks during the load-out process. Canister grab samples were collected during the load-out directly from the truck bed within a 1-minute sampling time. At the time of the sampling, other information was gathered including meteorological data, temperatures (sample, asphalt, and ambient), emission velocities, photographic documentation, and site position data.

The samples were subsequently returned to the Division of Air Quality's Toxics Protection Branch (TPB) Laboratory for analysis by GC/MS according to EPA Compendium Method TO-14 (Determination of Volatile Organic Compounds in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography). From these samples, benzene concentrations were quantified; and the mean benzene concentration was found to be 2.471 ± 1.782 ppbv (7.894 ± 5.694 $\mu g/m^3$) at a 99.5% confidence level [n=12, standard deviation = 1.988 ppbv (6.350 $\mu g/m^3$)].

These values were then used in conjunction with the emission velocity measurements (mean = 0.51 m/sec) to determine an emissions rate for benzene from asphalt load-out into any size vehicle [4.03 $\mu g/m^2 sec$ (4.03 x $10^{-6}$ $g/m^2 sec$)] and for the average asphalt truck (10.9$m^2$) of 4.39 x $10^{-5}$ g/sec.

**Acknowledgements**
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The regional office staff who were instrumental in finding the sampling sites and assisting in the sample and data collection, Chuck Dewey and Donny Redmond (Raleigh Regional Office) and Angela Bell, Troy Harrison, Steve Maynard, and Marjorie Meares (Asheville Regional Office).

Christie Barbee, Executive Director of the Carolina Asphalt Pavement Association, who provided helpful information on asphalt and assistance in finding sampling sites.

The asphalt plant managers and site personnel for allowing us to sample during their normal operations and their cooperation in providing information in a timely manner, Don Schell (Rea Construction), Bill Lindsey (APAC Carolina), Richard Stillwell (East Burke Asphalt), and Phil Adams (S.T. Wooten).

Thanks also go to other members of the TPB for their assistance in preparations and moral support. Thanks are also given to Tom Anderson, Air Quality Analysis Branch, for his assistance during the study plan design phase and Lee Daniel for editorial comment.

## Introduction

This investigation was initiated based on citizen concerns over asphalt emissions and the Division of Air Quality's (DAQ) need for more data on which to base an emission factor for benzene during asphalt load-out. There were a variety of concerns raised by citizens over emissions from asphalt plants such as arsenic, cadmium, and formaldehyde[1]. Also of concern were source points associated with asphalt plants other than load-out operations such as stacks, silos, and heaters.[1] This investigation focused only on the emissions of benzene during asphalt load-out. This is based on the initial inquiry into load-out emissions conducted by the Toxics Protection Branch (TPB) of DAQ which suggested that the lowest AAL and most readily quantifiable of the volatile emissions during load-out was benzene[2]; and on data reported in an EPA document entitled "Evaluation of Emissions from Paving Asphalts"[3] which stated:

> VOC [volatile organic compound] analysis showed statistically significant amounts of benzene emitted from both types of asphalt studied. None of the other 55 volatile compounds targeted for quantitative analysis was observed in statistically significant concentrations. A wide variety of volatile compounds, not specifically targeted for quantitative analysis, was also seen in various samples although no consistent set of compounds could be established.

A proposed study plan was written which outlined the reason for the study, the equipment needed, the specific procedures for sampling, the tasks assigned to each team member, and the analytical procedure to be used. The study plan is given in Appendix A. This report will present the findings of this investigation and results of calculations of an emission factor for benzene from asphalt load-out.

## Sites and Equipment

*Site Selection:* Grab samples were collected at 5 locations distributed across the state (2-Mountains, 3-Piedmont, Figure 1). Initially, it was hoped that one of the sites would be in the coastal region but time constraints made this impossible. The executive director of the Carolina Asphalt Pavement Association, Christie Barbee, and the NC DENR, DAQ Regional offices in Asheville and Raleigh, NC were requested to provide names and locations of asphalt companies that would be amenable to assisting in the study. Of the 5 sites visited (see Table 1), Ms. Barbee identified two and the regional offices identified the others. All of the facilities were drum mix plants; and although one (East Burke Asphalt) was represented as a continuous feed plant, it appeared to have the same drum mixing and conveying system as all the other drum plants. The reasoning and criteria for choosing these particular sites are discussed in the Results and Discussion section.

*Site Mapping:* At each site, a Global Position System (GPS) was used to derive a site map. This map includes the approximate open area boundaries, the sampling locations, meteorological station, and various structures at the facility. The GPS data was also used to plot the facility location within the state. Figure 1. A site map of each facility is given in Appendix B.

Also as part of the site mapping, a digital camera was used to provide photographic documentation of various aspects of the site, the sampling procedure, the met station, and general layout of the facility.

**Figure 1 - Geographic Positions of Sampling Sites in North Carolina**

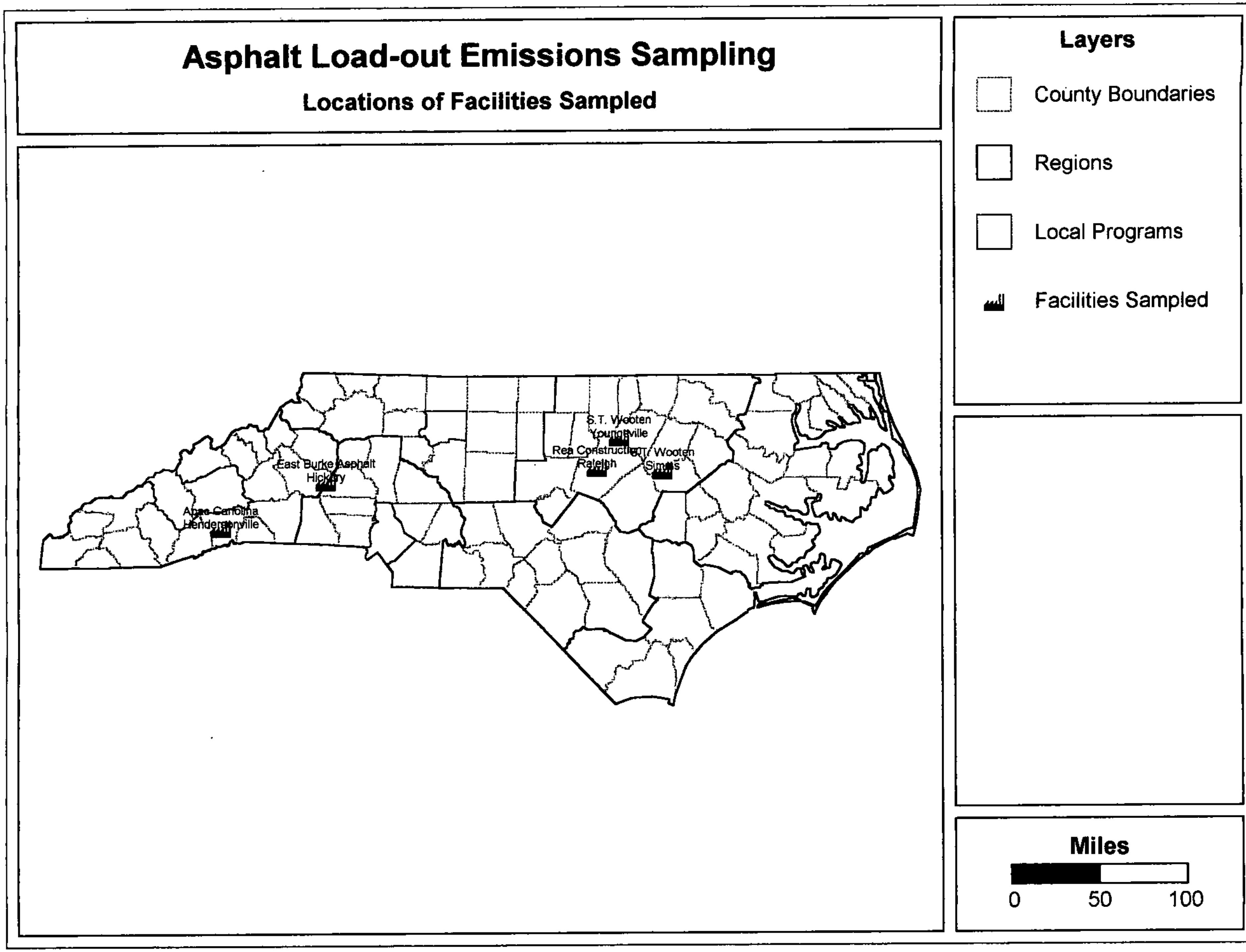


**Table 1: Sampling Site Information**

| Company (ID) | Location | Region | Plant Type | Asphalt Type[4] |
|---|---|---|---|---|
| Rea Construction (RC) | Raleigh, NC | Raleigh | Drum plant | I-2<br>AntiStrip additive<br>[*PG6522*] |
| APAC Carolina (AC) | Hendersonville, NC | Asheville | Drum plant | I-2<br>[*PG6422*] |
| East Burke Asphalt (EB) | Hickory, NC<br>(Drexel, NC) | Asheville | Continuous feed<br>(drum plant) | I-2 |
| S.T. Wooten (SW) | Sims, NC | Raleigh | Drum plant | I-2 |
| S.T. Wooten (WY) | Youngsville, NC | Raleigh | Drum plant | I-2<br>AntiStrip additive |

Brackets [ ] indicate the *liquid* asphalt type used for I-2 as indicated by the company.

*Meteorological Station:* At each site, a meteorological station (met station) was set up and a data logger automatically recorded met conditions during the time of the sampling visit (Plate 1). The conditions monitored were ambient temperature, wind speed, wind direction, solar radiation, and solar flux. All measurements were logged at a rate of one measurement every second and averaged to give a 1, 5, and 10 minute average for each of the conditions. The maximum wind velocity within a 10 minute period was also logged. The 1-minute wind speed and direction data were later plotted to give wind rose graphs. The 1-minute data points for ambient temperature, solar radiation, and solar flux at each site was also compiled and plotted to give profiles of each. Other general meteorological conditions such as cloud cover and apparent humidity were also noted on a data sheet during the sampling events. These wind roses, temperature profiles, and general met conditions are presented in Appendix C.

*Sampling Apparatuses:* Samples of load-out emissions were collected via grab sampling using a sampling apparatus constructed in-house. (Plate 2). The emissions sampling train consisted of a stainless steel funnel, 12ft of 1/4in OD 3/16" ID Teflon™ tubing, and one 6-L SUMMA™ stainless steel canister. The sampling apparatus also consisted of a Type-K thermocouple for measuring the temperature of the sampled emissions and a digital thermal anemometer for measuring the emissions' velocities during sampling. These various parts of the sampling apparatus were attached to an extendable pole to easily reach over and into the bed of the trucks during load-out thus minimizing risk to personnel.

A second apparatus was constructed in-house and consisted of an extension pole and a type-K thermocouple (Plate 3). This apparatus was used to measure the temperature of the asphalt just after load-out. A third thermocouple was used to measure the ambient temperature at the silo load-out site.

Temperature readings at the sampling site were recorded automatically using these three type-K thermocouples connected to a data logger during each sampling visit (Plate 4). The temperatures logged were reference temperature, sampling site temperature, sample temperature (described above), and asphalt temperature. *Note: the sample temperature refers to the emissions not to the asphalt itself.* The reference temperature was obtained from an internal thermistor supplied by the data logger manufacturer (Campbell Scientific, Provo, UT). Temperature profiles were plotted from the logged data from these three thermocouples and are provided in Appendix D.

*Sample Analysis:* The samples were analyzed by GC/MS according to EPA Compendium Method TO-14 (Determination of Volatile Organic Compounds in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography similar to that used in the Paw Creek study[4]. The GC/MS system consisted of a Varian GC (Model 3400) with a 60 m DB-1 chromatographic column, a NuTech cryogenic preconcentrator (Model 3550A), a Nafion Dryer water management system, a Finnigan Magnum series ion trap mass spectrometer, and a Gateway 2000 computer system with Finnigan work station software (Magnum System 3.0) for data collection and output. System parameters and conditions are listed below in the Procedures section below.

**Procedures**

*Glossary terms:*

1. Scribe: team member who was responsible for recording and transferring information.
2. Handler: team member who was responsible for handling the sampling apparatuses and collecting the samples.
3. Photographer: team member who was responsible for taking photographs and documenting their descriptions.
4. Mapper: team member who was responsible for using the GPS for site maps and documenting the description of the points taken.

Upon arriving at the site, a team member contacted the site manager, discussed the sampling routine, and obtained pertinent information on the chemical/physical characteristics of the asphalt, output of the plant, truck load-out procedures and weights, etc. Some of this information was noted on a field data sheet. This team member then reported back to the rest of the team any items of interest such as safety issues, operation areas, and restricted areas.

During preparations for sampling at the load-out area by the Scribe and the Handler, the other team members set up the met station, conducted a site survey, and took photographs. Details of the tasks involved with each of the positions listed above and the procedures used for this study are given below.

*Met Station:* Upon arrival, team members looked for an appropriate place to set up the met station and obtained permission to do so from the plant manager. The met station would then be erected, the appropriate connections made, and the data logger started. The Photographer and Mapper then proceeded with their respective duties.

*Photographic Documentation:* The Photographer was allowed to take photos of anything they felt was important to document the site, the sampling procedure, and/or other operations at the site. The following tasks and procedures were used by this team member.

- The digital camera was used in the low-resolution mode (640 x 480 pixels)
- The Photo Documentation Data Sheet #3 was used to document the following information.

Photo # = the order that the pictures were taken
Location = where taking pictures from, examples: silo, sampling site, or met station.
Example: Standing at the met station, I am looking directly at silo #1453.
Description = describe what is in picture like "sampling assembly" or "load-out procedure"

- All aspects of the sampling procedure and site were documented as needed.
- The dimensions of two load-out truck beds were measured and recorded on the Field Data Sheet #3 at the APAC Carolina Plant, Hendersonville, NC. These two trucks were the same general size as all the trucks that were sampled during this study.

Once the sampling visit was concluded the photographer turned over any data sheets with photo numbers and descriptions to the team leader. The photos were later downloaded from the camera to a computer for documentation purposes.

*Site Mapping:* Once the met station was in place, the Mapper began conducting the GPS site survey at various points. The choice of points was at the discretion of the Mapper. The main positions to be plotted were the area boundaries, met station, silo, and control building. In some cases the Mapper's experience with the GPS indicated to them that the proximity of the control building to the silo would make differentiating their positions impossible. In these cases, the control building was not plotted but was later placed on the site map in proximity to the plotted silo position. The following is a generalized procedure used in collecting the GPS survey data.

- The Mapper would try to locate visible boundary markers or as close to them as possible and begin the site survey at one of these points.
- The GPS was allowed to collect between 180 and 200 data points from the satellites in one file name for eventual differential correction.
- The site location, description, and file name were recorded on a data sheet.
- Other points at the site such as the silo, met station, and others were mapped in a similar way.

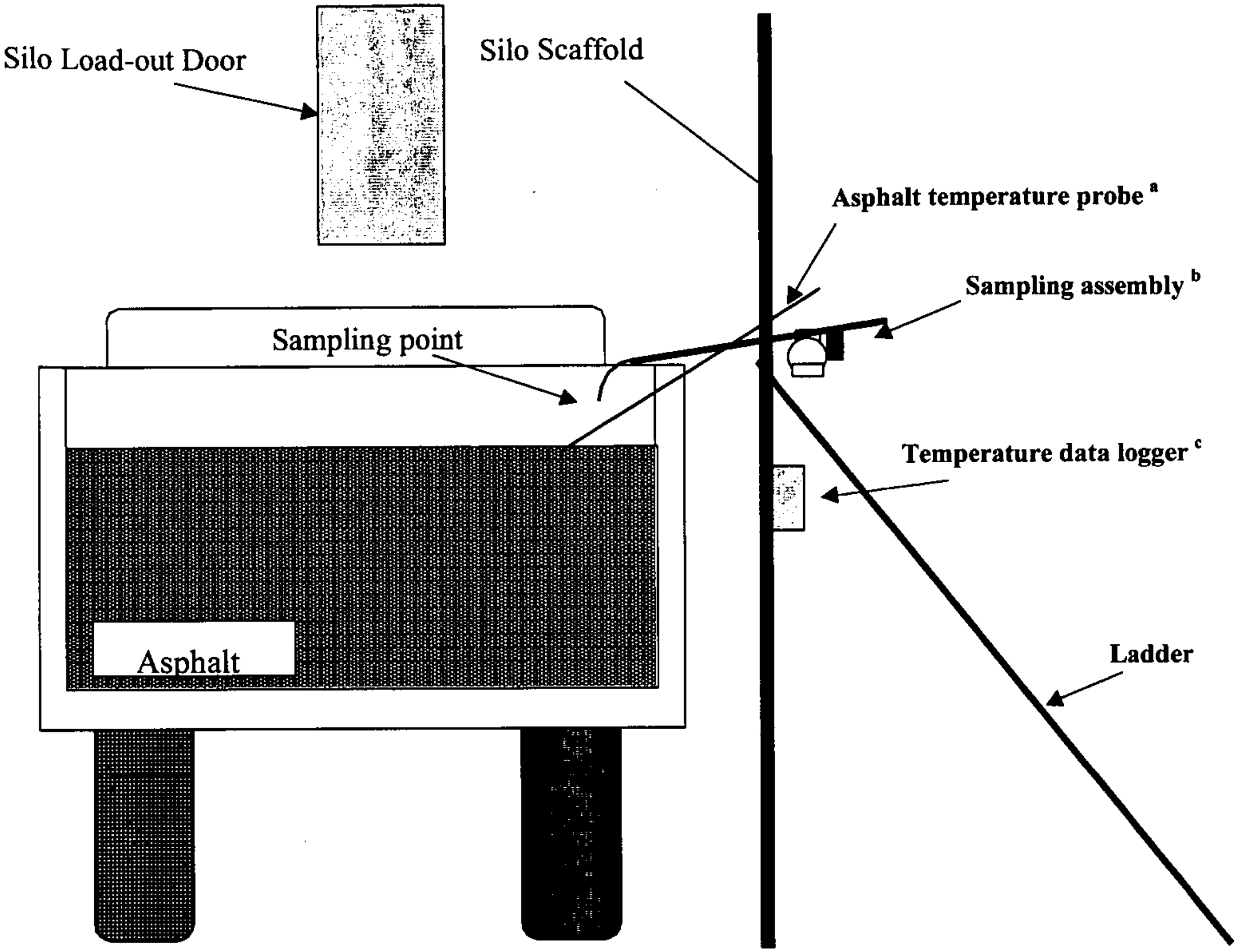
At the end of the sampling visit the data sheet was returned to the team leader. This data sheet and the GPS were later given to a TPB staff member to download the data. This data was then differentially corrected and used to produce site maps for each facility. See Appendix B.

*Sampling:* Sampling of the emissions from the asphalt load-out were basically carried out by the Scribe and the Handler at the asphalt silo. Figure 2 illustrates the basic orientation of the sampling area components. The Scribe and Handler had the following task.
The Scribe:

- Directed the truck driver and other facility personnel as to what they needed to do such as when to start the load-out and when it was okay to leave at the conclusion of sampling.
- Collected and recorded information on the Field Data Sheet. Some of this information came from other team members and plant personnel such as load-out weights.
- Recorded various necessary Chain of Custody (COC) items such as COC seal numbers, canister numbers, and sample numbers on the Field Data Sheet.
- Recorded any changes to the procedure and/or equipment.
- Recorded any pertinent comments or notes.
- Observed and recorded the time the Handler opened the canister and signaled the Handler when to close the canister.

At the conclusion of sampling visit, the Scribe returned the data sheets to the team leader and informed the team leader of any glaring abnormalities.

Figure 2: Diagram of Sampling at Asphalt Silo




a. Asphalt temperature probe consists of a support pole and thermocouple wired to the data logger.
b. Sampling assembly consists of a support pole, thermocouple wired to the data logger, canister, thermal anemometer, and sample line.
c. Temperature data logger is connected to three thermocouples (wires not shown in diagram for clarity). The three monitored temperatures are asphalt after load-out, sampling probe inlet, and sampling site air.

Sampler Handler:

- Collected sample and took asphalt temperatures as described below and relayed any problems or other pertinent information to the Scribe.
- Used thermal anemometer to determine emissions' velocities from the asphalt and relayed this information to the Scribe.
- Replaced sampling line and canister for the next sampling event.

At the end of the sampling visit, the Handler would make sure all the equipment and apparatuses were dismantled, cleaned, and stored. They would also assist in properly labeling and sealing canisters to assure Chain of Custody.

The following is the general procedure followed by the Scribe and Handler in collecting the grab samples. Five (5) grab samples were collected from 5 different trucks at each site. An upwind fence-line grab sample was also collected at each site.

1. The Scribe instructed the driver to do as he normally would for loading but not to leave until given a signal.
2. The Handler got in position (Plate 5) to collect sample by placing the end of the sampling apparatus over and into the bed of the truck. The funnel was placed so that it was 6"-8" out over and 6"-8" down inside the truck bed.
3. The Handler would then signal the silo operator to begin loading. (Plate 6)
4. As the asphalt was falling into the truck, the Handler would open the valve on the canister to draw sample into the can. (Plate 7)
5. During the 1 minute sampling time (noted by Scribe), the Handler would take an anemometer reading and report the maximum value obtained within the 1 minute to the Scribe.(Plates 8-9)
6. At the end of 1 minute, the Scribe would signal the Handler to close the valve.
7. The valve was closed and the apparatus was handed to the Scribe. (Plate 10)
8. The Handler then extended the asphalt temperature probe over the asphalt and placed the thermocouple in the asphalt for approximately 1-3 minutes. (Plate 11)
9. The probe was retracted and the driver signaled to leave.
10. The Scribe would then signal the silo operator to mark the truck information for later retrieval.
11. The canister was then disconnected from the sampling apparatus, sealed with a COC seal, and labeled.
12. A new sampling line and canister were then attached and the Handler prepared for the next truck load-out.
13. Various sampling information was recorded on data sheet.
14. Other information was also recorded on the data sheet. See study plan in Appendix A.

Upwind, fence-line samples were collected in the following manner.

1. The Mapper was sent to a position upwind and at the fence-line with a 6-L canister.
2. The canister was held at head height and opened for 1-minute then closed.
3. It was returned to the Scribe who labeled and COC sealed.

Once the sampling was completed (usually within 2 hours), truck load-out information was retrieved from the silo operator and the information transferred to the data sheet. Collected data files from the met station and temperature data loggers were then downloaded to a laptop computer for later data reduction and compilation.

*Sample Analysis:* Sample analysis was conducted by the Toxics Protection Branch Laboratory at the Air Quality Lab facility. The instrumentation was as described above. The GC was run with a oven temperature program beginning at 40°C for 5 minutes, ramped at 5°C/min to 135°C, then ramped at 1°/min to 149°C, then at 20°C/min to 205°C and held for 9.2 min. The injection system had an injector temperature of 200°C and a transfer line temperature of 240°C. The MS was run in the electron ionization (EI) mode with a mass range set for 35 to 260 amu with 80 count peak threshold and 0.9 sec/ scan.

Benzene concentrations were quantified based on 5-point calibration curves (0.2, 0.5, 1.0, 3.0, 10.0 ppbv) with a correlation coefficients of >0.98. This passes established quality assurance for the method of analysis. The low end of the calibration curve was established based on 0.2 ppbv being the lowest concentration at which a reproducibly accurate standard could be made. Reported values that lie outside the curve boundaries, i.e. <0.2 or > 10.0 ppbv were reported as estimated values. As in the Paw Creek Study, a Reportable Level of 0.1 ppbv was established for this study. Although this value is outside the calibration curve boundaries, it represents a level at which the instrumentation can reliably report concentrations (based on a minimum detectable level that is at least two orders of magnitude lower than the reportable limit). Therefore benzene concentrations which lie between 0.1 and 0.2 ppbv were included in the calculation of the mean benzene concentration. Benzene concentrations that were below the reportable level (BRL) of 0.1 ppbv were labeled as such but were not considered in the calculations. Values that were considerably above the range of the majority of points were statistically tested as being outliers using two widely used independent methods, the Dixon Test and the Grubbs Test[6-11]. Those values that met the criteria for being outliers according to these tests were not included in the data set and are marked as such in Table 2. Discussion of the reasoning behind the exclusion of outlying data points is included in the Results and Discussion section. The mean and standard deviation were then calculated. The mean benzene concentration was then used to calculate an emission factor for benzene during asphalt load-out. The results of the quantification are listed in the Results and Discussion section (Table 2) and sample calculations are given in Appendix E.

**Results and Discussion**

*Site Selection:* The rational for the regional distribution of sites was to take into account possible variations in the asphalt or its emissions at load-out due to differences in formulations. That is, it was initially surmised that in different geographic regions, asphalt formulations may have differed due to the requirements of the road surface and the climatic and driving conditions experienced in that area. This was found not to be the case to any great extent based on a conversation with Ms. Christie Barbee, Executive Director of the Carolina Asphalt Pavements Association.[4] Ms. Barbee indicated that I-2 and PG6422 asphalt designations (see Table 1) were closely related, i.e. I-2 is the general term for a "generic" hot mix asphalt produced in North Carolina and PG6422 is the liquid asphalt used in producing most of this mix. She further indicated that one designation (PG6522) was not a designation for asphalt and was probably PG6422 that had been misidentified. Also, the additive LOF6500 product is an anti-strip additive that is generally added to all asphalt mixes as an aggregate bonding enhancer.[4] Therefore based on this information, the only seeming major differences in the asphalts that were sampled were the size of the aggregates. All of the asphalt plants were producing I-2 with various sized aggregate. Also, based on this information, it would seem, the study was not affected by not having a coastal sampling site.

In an attempt to minimize sources of variability, sites were chosen which used virgin materials in the production of the asphalt. Asphalt facilities using Recycled Asphalt Paving (RAP) were avoided as to minimize the introduction of a component that had the potential to increase composition variability.

*Site Mapping:* The GPS system was used to establish a site map for the facility in the general open area of the working plant. No attempt was made to find and plot the actual location of the property boundaries. These site maps (Appendix B) were made to document orientations of various points on the site and illustrate where samples were taken in relationship to those points and wind direction. One should refer to these site maps when looking at the meteorological data. Photographs taken as part of the site mapping are used in this report to illustrate particular points. The other photos will be archived as documentation of the study.

*Meteorological Data:* Although the meteorological data is not used in this report to aid in calculating an emission factor, it is an important consideration if one were to do modeling of the site. Therefore relevant data was collected during the sampling period and will be filed if needed at a later date. Graphical representations of these data are presented as general information in Appendix C.

*Sampling:* In an effort to obtain representative samples of asphalt emissions, 5 grab samples of load-out emissions were taken at each asphalt plant. These were generally from 5 sequential load-outs, not 5 from the same truck. By doing this, effects on collection due to variations such as filling rate and/or truck bed dimensions would be minimized by averaging the values obtained. Also, anything unusual or anomalous about a particular truck and/or its contents such as unknown previous payload or use, would be confined to an anomalous sample from that truck rather than skewing the results from the entire sampling visit, such as would be the case if only one truck were sampled 5 times. If seemingly anomalous measurements were obtained from one truck then the results could be statistically tested as an outlying point and omitted from the data set. This was believed to be the case in two samples and is discussed later in this section.

Grab sampling was conducted because it was the best method for obtaining a representative sample within the physical and temporal constraints of the load-out process. Since the emissions occur: 1) from a confined area, the truck bed, 2) at irregular intervals, and 3) for relatively short periods (load-out of a truck can occur in as little as 3-5 minutes), time integrated sampling would be impractical in terms of both equipment operation and sample collection time. Conversely, grab samples could be collected manually within the short time of the event (3-4 minutes) and directly from the source of the emission during the event. To achieve this proximal position to the source of the emissions, the sampling assembly's sampling port could be positioned inside, and lower than, the top edge of the truck bed. By doing so, it was felt that dilution of the emissions due to mixing would be minimized.

Additionally, since the sampling did not begin until the load-out was underway, it was reasonably assumed that the hot asphalt and its emissions would quickly displace the ambient air in the empty truck bed, and fill the airspace with an atmosphere created almost entirely by the load-out. And although the emissions were rising due to the increased buoyancy caused by the heat from the asphalt, the collection point would be well within the rising plume and in a zone that was not expected to have significant mixing with air outside the truck bed. See Figure 2 and Plates 5-11.

Because the emissions plume from the load-out would be expected to dissipate as the loading stopped and the asphalt cooled in the truck, every effort was made to collect samples at the same relative time during the load-out procedure so that any effects of mixing and/or dilution with time was minimized.

In addition to the grab samples collected during load-out, one fence-line grab sample was also collected at each site. These samples were collected to give an indication of the benzene level in the surrounding air mass at the time of the sampling. The fence-line benzene concentrations were not subtracted from the load-out samples because it was assumed that the load-out samples were collected directly from an environment that was minimally impacted by the ambient air as discussed earlier.

*Sampling Site Temperature Measurements:* In an attempt to further characterize the environment from which the emissions were sampled and under what conditions, three separate temperatures were recorded at the asphalt sampling site (silo). These three temperatures were silo ambient temperature, sample temperature, and asphalt temperature. The profiles for these temperatures are given in Appendix D. The temperature spikes are due to placing the probes into the sampling zone and then removing them. From these profiles one can see that the temperature of the sampled emissions are considerably lower than the temperature of the asphalt itself and is usually between 90°F and 130°F. The asphalt temperature range was from 175°F to 290°F.

*Velocity Measurements:* The anemometer was used to measure velocities during sampling. Additional readings were taken as other trucks were loaded (no sample taken) in order to obtain more values for a more representative average. The average velocity was 0.51 $\pm$ 0.09 m/s at a 99.5% confidence level (n=34, standard deviation = 0.20). These measurements were assumed to represent the velocity of the emissions from asphalt and were used in the calculation of the emission factor along with the average benzene concentration. The calculation of the confidence interval is included in Appendix E - Calculations.

*Analysis and Results:* The results of the analyses are presented below in Table 2.

As stated earlier, there were two values that appeared to lie well outside the range of the other sample data. The most plausible explanation for this was a transient secondary source of benzene that is not specifically related to asphalt emissions during load-out and was not directly observed to be attributable to any specific cause or source. In such cases, where the data set is relatively small and a justification for rejection of the data point(s) is not obvious, it is scientifically valid to use statistical means to determine the validity of rejecting or retaining suspected outliers. It is especially important with a small data set to reject any outlier in order to obtain a better measure of the mean and standard deviations and in this study, a better estimation of the benzene emission factor. A good argument for dealing with outliers can be found in a National Bureau of Standards Publication (NBS) which states in part[11]:

> When a measurement is far-removed from the great majority of a set of measurements of a quantity, and thus possibly reflects a gross error, the question of whether that measurement should have a full vote, a diminished vote, or no vote in the final average - and in the determination of precision - is a very difficult question to answer completely in general terms. If on investigation, a trustworthy explanation of the discrepancy is found, common sense dictates that the value concerned should be excluded from the final average and from the estimate of precision, since these presumably are intended to apply to the unadulterated system. If, on the other hand, no explanation for the apparent anomalousness [sic] is found, then common sense would seem to indicate that it should be included in computing

the final average and the estimate of precision. Experienced investigators differ in this matter. Some, e.g., J.W. Bessel, would always include it. Others would be inclined to exclude it, on the grounds that it is better to exclude a possible "good" measurement than to include a possibly "bad" one. The argument for exclusion is that *when a "good" measurement is excluded* we simply lose some of the relevant information, with consequent decrease in precision and the introduction of some bias (both being theoretically computable); whereas, *when a truly anomalous measurement is included* it vitiates our results, biasing both the final average and the estimate of precision by unknown, and generally unknowable, amounts.

Therefore in order to ensure that only scientifically valid points were included in the emission factor calculation, two widely used statistical methods for determining outliers were employed, the Dixon Test and the Grubbs Test. Normally either of these methods would be sufficient to ensure the reliability of data inclusion or rejection; but in the interest of ensuring that these two points were indeed outliers, both were employed here. Explanations and calculations are given in Appendix E.

From these calculations it was found that these points did meet the criteria as outliers of the data set and as such were not included in the calculation of either the mean or the standard deviation. The values that were used for calculation of the mean and standard deviation were those values that were neither below the reportable level nor the two outliers. The benzene concentration mean was 2.471 ± 1.782 ppbv (7.894 ± 5.694 $\mu g/m^3$) at a 99.5% confidence level [n=12, standard deviation = 1.988 ppbv (6.350 $\mu g/m^3$)].

The emission factor was calculated with the units of $g/m^2sec$ so that it can be applied to any size vehicle or container to calculate a final emission rate in g/sec. Using the average emission velocity (n=34) of 0.51 m/sec and the mean benzene concentration above, the emission factor was calculated to be 4.03 $\mu g/m^2sec$ (4.03 x $10^{-6}$ $g/m^2sec$). By way of comparison, the EPA report "Evaluation of Emissions from Paving Asphalts"[3] estimated the emission rate for benzene from AC10 without Rubber vs. Facility Blank to be $\leq$ 0.95 $\mu g/m^2sec$. This number was based on a controlled set of experiments for a given amount of asphalt packed into a heater block.

An emission factor in units of g/sec can now be calculated knowing the dimensions of the vehicle's container and multiplying the emission factor above by the area of the container. In this study, two truck beds were measured that represented the average size and configuration of the dump trucks used for asphalt load-out (7'2"W x 16'9"L and 7'5"W x 15'4"L). Using the average area calculated from these measurements ($10.9m^2$), the benzene emission factor for an average asphalt truck during load-out is calculated to be 4.39 x $10^{-5}$ g/sec.

**Table 2: Results of Canister Analyses (all sample numbers begin with the ATAST # 98026)**

| Sample # | Benzene Conc (ppbv) Trip Blanks | Sample # | Benzene Conc (ppbv) Upwind Samples | Sample # | Benzene Conc (ppbv) Load-out Samples |
|---|---|---|---|---|---|
| RC00 | BRL | RC01 | 0.406 | RC02 | BRL |
| AC00 | BRL | AC06 | 0.431 | RC03 | BRL |
| EB00 | BRL | EB01 | 0.619 | RC04 | BRL |
| SW00 | BRL | SW06 | 0.204 | RC05 | 3.328 |
| WY00 | BRL | WY06 | 0.251 | RC06 | 508.83* |
| **Average** | BRL | **Average** | **0.382** | AC01 | BRL |
| | | **Std. Dev.** | **0.164** | AC02 | BRL |
| | | | | AC03 | BRL |
| | BRL = Below Reportable Limit of 0.1 ppbv | | | AC04 | BRL |
| | | | | AC05 | 1.252 |
| | | | | EB02 | 67.261* |
| | | | | EB03 | 0.515 |
| | | | | EB04 | 4.190 |
| | | | | EB05 | 0.678 |
| | | | | EB06 | BRL |
| | | | | SW01 | 0.195 |
| | | | | SW02 | BRL |
| | | | | SW03 | BRL |
| | | | | SW04 | BRL |
| | | | | SW05 | 1.734 |
| | | | | WY01 | 2.625 |
| | | | | WY02 | 6.657 |
| | | | | WY03 | 5.005 |
| | | | | WY04 | 2.222 |
| | | | | WY05 | 1.252 |
| **Average without Outliers* & BRLs at a confidence level of 99.5%** n= 12, std. dev. = 1.988 ppbv (6.350 μg/m$^3$) | | | | | **2.471 ± 1.782 ppbv** (7.894 ± 5.694 μg/m$^3$) |

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## Appendix Section

## Appendix A - Proposed Study Plan for Collection of Data to Support a Determination of an Emission Rate of Benzene from Asphalt Load-out (ATAST #98026)

**Introduction:** The reason for this investigation is based on citizen concerns over asphalt emissions and to give the Division of Air Quality (DAQ) more data on which to base an emission factor for benzene during asphalt load-out. Citizens have raised concerns over emissions from asphalt plants such as arsenic, cadmium, and formaldehyde[1]. Also of concern are source points associated with asphalt plants other than load-out operations such as stacks, silos, and heaters.[1] This investigation will focus only on the emissions of benzene during asphalt load-out. This is based on the initial inquiry into load-out emissions conducted by the Toxics Protection Branch (TPB) of DAQ which suggested that the lowest AAL and most readily quantifiable of the volatile emissions during load-out was benzene[2]; and on data reported in an EPA document entitled "Evaluation of Emissions from Paving Asphalts"[3] which stated:

> VOC [volatile organic compound] analysis showed statistically significant amounts of benzene emitted from both types of asphalt studied. None of the other 55 volatile compounds targeted for quantitative analysis was observed in statistically significant concentrations. A wide variety of volatile compounds, not specifically targeted for quantitative analysis, was also seen in various samples although no consistent set of compounds could be established.

In general, the sampling will occur at 5 sites across the state (2-Mountains, 2-Piedmont, and 1-Coastal) via grab sampling (5 samples at load-out site and 1 at the fence-line, upwind of the site). The rational for this regional distribution of sites is to take into account possible variations in the asphalt or its emissions at load-out due to geographic considerations. That is, in different geographic regions, asphalt formulations may differ due to the requirements of the road surface and the climatic and driving conditions experienced in that area. Additionally, having more than one site in a region may assist in determining variability in a given region and how much that variation might be. To help further characterize variability, 5 grab samples of load-out emissions will be taken. These will be 5 consecutive load-outs, not 5 from the same truck. The emissions plume from the load-out would be expected to dissipate as the loading stopped (filled truck) and the asphalt cooled in the truck. Therefore every effort will be made to collect samples at the same relative time during the load-out procedure so that the effects of mixing and/or dilution with time may be minimized. For each site visited, these 5 values will be used to give a range and average level of benzene. The total number of samples expected to be taken will be 25 and will be used to give a range and average value for the 5 sites.

To help further minimize variations, sites will be chosen which use virgin materials in the production of the asphalt. Asphalt facilities using Recycled Asphalt Paving (RAP) will be avoided as to minimize the introduction of a component that has the potential to increase the composition variability.

Grab sampling will be conducted because it is the best method for obtaining a representative sample within the physical and temporal constraints of the load-out process. Since the emissions occurs: 1) from a confined area, the truck bed, 2) at irregular intervals, and 3) for relatively short periods (load-out of a truck can occur in as little as 1-3 minutes), time integrated sampling would be impractical in terms of both equipment operation and sample collection time. Grab samples can be collected manually within the short time of the event (1-3 minutes) and directly from the source of the emission during the event. The sampling assembly's sampling port will be positioned inside, and lower than, the top edge of the truck bed to minimize possible dilution of the emissions during load-out due to mixing. Since the sampling will not begin until the loading is underway, it is reasonable to assume that the hot asphalt and its emissions will quickly displace the ambient air in the empty truck bed, and will fill the airspace with an atmosphere created almost entirely by the load-out. And although the emissions will be rising due to the increased buoyancy caused by the heat from the asphalt, the collection point will be within the rising plume but in a zone that will **not** be expected to have significant mixing with air outside the truck bed. See Figure 1. Photographs will be taken of the approximate sampling point, as safety allows, either prior, during, or just after load-out.

The velocity of these emissions will also be measured; and will be used in conjunction with the measured concentration of the benzene in the load-out emissions to calculate an emission factor for benzene during load-out. This calculation is based on the following assumptions:

1) the velocity of the benzene and the load-out emissions are the same
2) the velocity of the emissions during load-out is in the same range of velocities as those immediately after load-out and
3) the concentration of benzene in the emissions during load-out at the sampling point is representative of the entire emission volume.

These are reasonable assumptions given the facts that: 1) the benzene component is an integral part of the emission; 2) the time interval between load-out sampling and velocity measurement is only a minute or two (not enough time for the asphalt to cool and the emission's velocity to change considerably); and 3) the sample is collected during the load-out and proximity of the sample collection point to the emission point mitigates the effects of dilution or partitioning of the emissions. This calculation is illustrated by a units analysis in the Emissions Factor Calculation section of this Study Plan.

A meteorological station will be deployed at the site and will take data every one minute for the entire sampling site visit. Sampling times and met data times will be closely correlated. The data will include temperature, solar radiation, solar flux, wind speed, and wind direction. Percent cloud cover will also be noted on the data sheet during each sampling event. The relative position of the meteorology station to the sampling sites will be noted and recorded on a site map that will be composed from GPS data taken during the site visit. Site mapping information will be noted on a separate data sheet. See data sheet #2.

Because emissions can vary with temperature, temperatures at various sampling points will also be taken concurrent with sampling. Temperatures at points 2-4 below will be logged automatically and continuously every one minute via a data logger set up at the sampling site. The following temperatures will be collected, as safety will allow:

| | |
|---|---|
| 1. Ambient temperature | meteorological station |
| 2. Sampling site temperature | at sampling site |
| 3. Sample temperature | at end of probe line |
| 4. Asphalt temperature | on the surface at the end of load-out sampling |

**Sampling Plan:**

***Compound of Interest:*** Benzene

***Time Frame:*** Sampling is expected to take a full day at each location.

***Team size:*** 4 members of the TPB staff and 1 member from the Regional office.

***Equipment / Supplies:***
SUMMA canisters (7 per site) & requisite sampling lines-all certified as clean.[4]
Extension ladder
A-frame ladder
Bungee cords
Safety Equipment
- Air purifying respirator with HEPA/activated charcoal cartridges.
- Gloves
- Goggles
- Boots
- Hard hat
- Hearing protection (as needed)
- Safety harnesses (as needed)
- Coveralls (as deemed necessary)

Thermal anemometer
Temperature data logger
Global Position System (GPS)
Compass
Camera
Tie off cord
Tape measure
Meteorology station
Chain of Custody (COC) seals
Data sheets (sampling, site mapping, photographic, chain of custody)
KimWipes and Methanol for temperature probe cleaning

***Task Assignments:*** The following are the staff assignments for the site visits. Assignments will be rotated amongst team members as needed. One team member will handle the GPS assignment for the day. If this assignment is completed before the end of the day, that team member will then assist the sampling team.

*ALL Team Members:*
- ♦ Assist in setting up the met station, sampling station, and temperature data logger.
- ♦ Assist in labeling, placing under COC, and handling samples as they are taken.
- ♦ Report pertinent information to the Scribe for recording.
- ♦ Be familiar with each task.
- ♦ Insure that signals are worked out between Scribe/Timer and Sampler Handler for sample canister opening and closing, etc.
- ♦ Assist in taking measurements such as sampling heights and truck bed dimension.

*Scribe/Timer:*
*<u>As the Scribe:</u>*
- ♦ Direct the truck driver and other facility personnel as to what they may need to do such as:
  -holding the truck after load-out for temperatures to be measured
  -requesting that the ignition be turned off during load-out.

- ♦ Record all information required on the Field Data Sheet. Some of this information may come from other team members on similar data sheets. This will be necessary especially in the case of obtaining the asphalt wt. because the truck weigh-out area may not be readily accessible to the scribe. A Regional staff member may be assisting with this aspect.

- Use of the Field Data Sheet (specific section notes):

  1. **Met conditions**: Cloud cover should be noted for each sampling event on the line provided next to the %. Example: 0% 1, 3,4,6 10% 2,5,7.

  2. **Sample ID** numbers will be as follows:
     98026XXX## = [ATAST investigation#][Facility name abbr.][Sample#] Example:
     98026BAC01 = ATAST #, Big Asphalt Company, first sample

  3. **Truck #**: An identifier for finding the load-out weight from scales if possible.

  4. **Asphalt wt**: Weight obtained from load-out scale.

  5. **Truck information**: Obtained from Photographer.

- Record any changes to the procedure and/or equipment.

- Record any pertinent comments or notes.

- Obtain other data for the Field Data sheet from other personnel such as asphalt wt.

*As the Timer:*

- Synchronize a watch with a sweep hand to the met station data logger and temperature data logger clocks.

- Observe the initial load-out to determine the best time to begin the sample, confer with other observers, and note the time agreed upon.

- Work out start and stop signals with the sampler handler.

- Accurately record times of sample taking start and stop.

➢ Post-Sampling Responsibilities:
  1. Return data sheets in order to the team leader.
  2. Inform the team leader of any glaring abnormalities (should already be noted)
  3. Record data from other team members to complete their data sheets.
  4. Sign and date the data sheet at the lower right corner of each sheet.

*Sampler Handler:*

- Take sample and asphalt temperature as described in sampling plan section.
  Specific considerations:
  1. Extend the sampler probe over and into the bed of the truck, making sure that the end of the probe is below the level of the top edge of the bed.
  2. Open and close the valve on the canister when directed by the Timer.
  3. Open the valve completely during sampling.
  4. Relay any problems or other pertinent information to the Timer/scribe for noting.

- Take temperature of asphalt: After taking the sample and the load-out is complete, take the temperature of the surface of the asphalt by lowering the temperature probe to the surface for 3-5 minutes.

- Use thermal anemometer to determine velocity of rise of heat from the asphalt. Relay to Scribe the information.

➢ Post-Sampling Responsibilities:
  1. Make sure that the sampling probes are cleaned and stored properly.
  2. Canisters are all properly labeled and COC sealed.
  3. Dismantle with assistance the sampling equipment.

*Photographer:*
- Use the higher capacity digital camera in the low-resolution mode (~120 pictures).

- Use date and time imprint on the photos.

- Use Photo Documentation Data Sheet #3 to document the requisite information.
  Photo # = the order that the pictures were taken
  Location = where taking pictures from, examples: silo, sampling site, or met station.
  Example: Standing at the met station, I am looking directly at silo #1453.
  Description = describe what is in picture like "sampling assembly" or "load-out procedure"

- Document all aspects of the sampling procedure and site as needed.
  Specific considerations but not limited to these:
  1. Met station with respect to other sites.
  2. Sampling sites with respect to other points.
  3. Truck load-out.
  4. Sampling port position like it will be during sampling.
  5. Height and distance measurements being taken.
  6. Sampling at the fence-line.

- Measure and record on a Field Data Sheet the dimensions of a load-out truck.
  Note where the exhaust exits, though during sampling the trucks should not be running.

➢ Post-Sampling Responsibilities:
  1. Download the photos into computer so that it will be ready for the next sampling trip.
  2. Return data sheets to team leader, signed and dated in the lower right corner of each sheet.
  3. If requested by the team leader, compile a short narrative of each picture.
  4. Assist GPS site maker with recollection of site features if needed.

*GPS map maker:*
- Fill out the top of the GPS data sheet as needed and begin site survey.

- Establish the property boundary corners (as much as feasible), noting any discrepancies between site boundaries and points taken as boundaries.
  Example: Area near a river or swampy area that is not accessible, take a position as close as possible and note discrepancy.

- ♦ Use lower storage digital camera for any needed site photos to backup notes on the data sheet, such as swampy areas or inaccessible areas.

- ♦ On the data sheet:
  1. Identify by name, the location of the position being taken. If there are multiple sites (e.g. silos, building, sheds) that could be described similarly, look for some identifying markings or signs that will clearly describe it once the site map is made.
  2. Record the file name (number) given to each position and stored in the GPS.
  3. Record pertinent notes such as described above in "establishing the boundaries of site".

- ♦ Use digital camera to document site especially when positions were not taken of the actual boundaries (see above). Use photo documentation sheet in addition to the GPS data sheet and follow instructions as necessary given for the photographer assignment.

- ➤ Post-Sampling Responsibilities:
  1. Sign and date each data sheet in the lower right corner.
  2. Download any photos from the camera
  3. Return GPS and data sheets to engineer for site plotting.
  4. Engineer will download data to the GPS site plotting software and plot site map.
  5. Engineer will provide site map and data sheets to team leader with requisite site keys. Appropriate site key data will be left to the discretion of the engineer.

*Regional Staff Person:*

- ♦ Obtain process information and record on a Field Data sheet.
  1. Asphalt Information to include type and other pertinent information (if it won't fit in the space provided use the back in the notes/comments box)
  2. Find out average amounts of asphalt per day (production) and per truck..
  3. Record the sampled truck # and if weighs going out, record wt of asphalt in truck.

- ➤ Post-Sampling Responsibilities:
  1. Sign, date, and return data sheets to the Scribe for transcription of data needed to complete the Scribes data sheets.

***Sampling Sites:*** The samples will be taken at 5 locations to be determined by agreement with asphalt producers and will be in various locations in the state (2-Mountains, 2-Piedmont, 1-Coastal).

***Initial Site Reconnaissance and Set Up:*** Upon arriving at the site, a team member will contact the site manager and discuss the sampling routine and obtain pertinent information on the chemical/physical characteristics of the asphalt, output of the plant, truck load-out procedures and weights, etc. Some of this information will be noted on a field data sheet. The team member will then report back to the rest of the team, any items of interest such as safety issues, operation areas, and restricted areas.

The meteorological station (met station) will be deployed. Preferable position would be between the sampling site and the tentative upwind fence-line, sampling site. The times on the met station data logger and the temperature data logger will be noted in the procedure modification section for referencing the two stations. The met station will be at a 6-meter height. General climatic conditions (cloudy, sunny, rain, etc.) will be noted as will the % cloud cover. The conditions at the time of the sampling will also be noted. During the site visit and sampling, the field data sheet will be completed with all relevant information. See attached data sheet #1.

Once the met station is in place. Sampling personnel will watch at least one load-out to determine the best placement of the equipment to gain access to the truck bed during load-out and determine if any modifications of the equipment or procedure will be necessary. *Especially important will be determining the start sampling time.* Note will be taken of any modifications that are made so that they may be incorporated into a sampling plan modification for subsequent sampling site use and the final report.

While part of the team is conducting the sampling, another member will use the GPS (global positioning system) to establish a site map that will include the location of major buildings, silos, scaffoldings, tanks, burners, etc. and the approximate property boundaries (corners) to establish a site map of the facility. The position of the sampling site, met station, and fence-line grab sample will also be located and plotted on this site map. The GPS system can be used to differentially correct a position and get that position to within a few feet (2-3) of its actual location. This technique will be used to develop the site map. A GPS site mapping data sheet will be used. See attached data sheet #2.

Photographic documentation of the site, sampling, and other pertinent information will be conducted following the guidelines outlined in the Tasks section of this study plan.

***Sample Collection:*** Samples will be collected in clean certified SUMMA canisters via grab sampling. Generally, grab sampling is defined as taking an evacuated canister (approximately 27mmHg), placing it in the zone to be sampled, opening the canister, allowing it to remain open for a given amount of time to come to ambient pressure, and closing the canister. (A sampling probe line will be constructed such that it will extend a given distance horizontally over the edge of the truck bed and vertically down into the bed so as to avoid mixing.)
The following sample collection scheme will be used in this study.

<u>Grab samples</u> will be taken as follows:
1. Safety equipment will be donned as necessary.
2. A ladder will be put in position at about the horizontal midpoint of the truck bed such that the sampling probe can be extended over and into the bed of the truck during load-out.
3. **Sampling probe** consisting of the extension pole, sample line, thermal anemometer, canister, and temperature probe will be assembled and positioned near the sampling point.
4. The asphalt temperature probe will be assembled and also positioned near the sampling point.
5. When the truck comes under the shoot, the driver will be requested to turn off the ignition.
6. The probe will then be extended over the bed to a predetermined position. The inlet will be positioned so that it is below the top edge of the truck bed but will not be in contact with the asphalt as it is loaded. Figure 1.
7. A few second (3-5) after the load-out begins, the Timer will signal the Sampler Handler to open the canister and will note the time from the temperature data logger.
8. At the end of one minutes, the Timer will signal the Handler to close the canister and will note the time.
9. The velocity of the air from the asphalt in the truck bed will be measured with the thermal anemometer and the reading relayed to the Scribe.
10. The sampling probe will then be retracted.

11. The **asphalt probe** will then be lowered to the surface of the asphalt or as close as possible, allowed to remain there for at least 1-2 minutes.
12. After the sample has been taken, it will be sealed and labeled with COC for transport back to the lab.
13. The sample line will be changed and the sampling assembly reassembled.
14. The temperature probes will be cleaned with methanol and air-dried.
15. If possible, 5 consecutive load-out truck samples will be taken at each site.

A fence-line sample will be taken as follows during or immediately after the third sampling event at the load-out location as follows:

1. A location upwind at the fenceline of the facility will be identified.
2. From this location a grab sample will be obtained that will represent the ambient air that is entering the site.
3. The grab sample will be taken while holding the canister at a height approximately that of those taken at the load-out area. (Use of a 6 or 8 rung stepladder may be necessary.) The canister will be opened, remain open for 1 minute, and then closed, sealed and labeled for transport to the lab.

**Sample Analysis:**

Sample analysis will be conducted at the Toxics Protection Branch laboratory at the Air Quality lab facility. The analysis will be by GC/MS under a modified TO-14 method similar to that used in the Paw Creek study[4]. Benzene will be quantitated and reported. File identification names will be in a form that closely matches the Sample ID numbers rather than the canister number. Canister number will be noted as appropriate in the data file.

**Emission Factor Calculation:**

An emission factor for benzene at load-out will be calculated using the measured emissions velocity and the quantitated concentration of benzene collected during asphalt load-out. The calculation of the emissions factor will be demonstrated below by a units analysis and is based on the assumptions presented earlier in the Introduction section of this Study Plan. The measured velocity will have units of meters/sec (m/sec). The quantitated benzene concentrations from the analyzed samples will be reported in ppb which have *units* of $\mu g/m^3$. By multiplying these together, one obtains an emission factor in the units of $\mu g/m^2 \cdot sec$. This value will allow calculation of an emission factor with units of $\mu g/sec$ that can ultimately be used in modeling for load-out of any vehicle if the area of the vehicle's asphalt container is known. Calculations shown below:

Velocity = m/sec
Benzene concentration = ppb (units of $\mu g/m^3$)
Emission Factor per unit area = (Velocity)(Concentration) = $(m/sec)(\mu g/m^3) = \mu g/m^2 \cdot sec$

Area of vehicle container = $m^2$
Emission Factor for any vehicle container area = (Emission Factor / unit area)(area)
$= (\mu g/m^2 \cdot sec)(m^2) = \mu g/sec$

## Appendix B - Site Maps

The following pages are site maps for the 5 sites that were visited and samples taken in accordance with the procedure described in the Procedures section of this report. These site maps were derived from the GPS data obtained during each site visit with the exception of Apac Carolina. This site map was constructed using a survey map obtained from the Asheville Regional office. The site was reproduced on approximately the same scale as the other maps and labeled according to information obtained during the site visit and photographs.

The names and mailing addresses for each company is given below:

Rea Construction
5801 Chapel Hill Rd.
Raleigh, NC 27606

Apac Carolina
P.O. Box 6939
Asheville, NC 28816

East Burke Asphalt
Drexel, NC

S.T. Wooten
P.O. Box 2408
Wilson, NC 27895

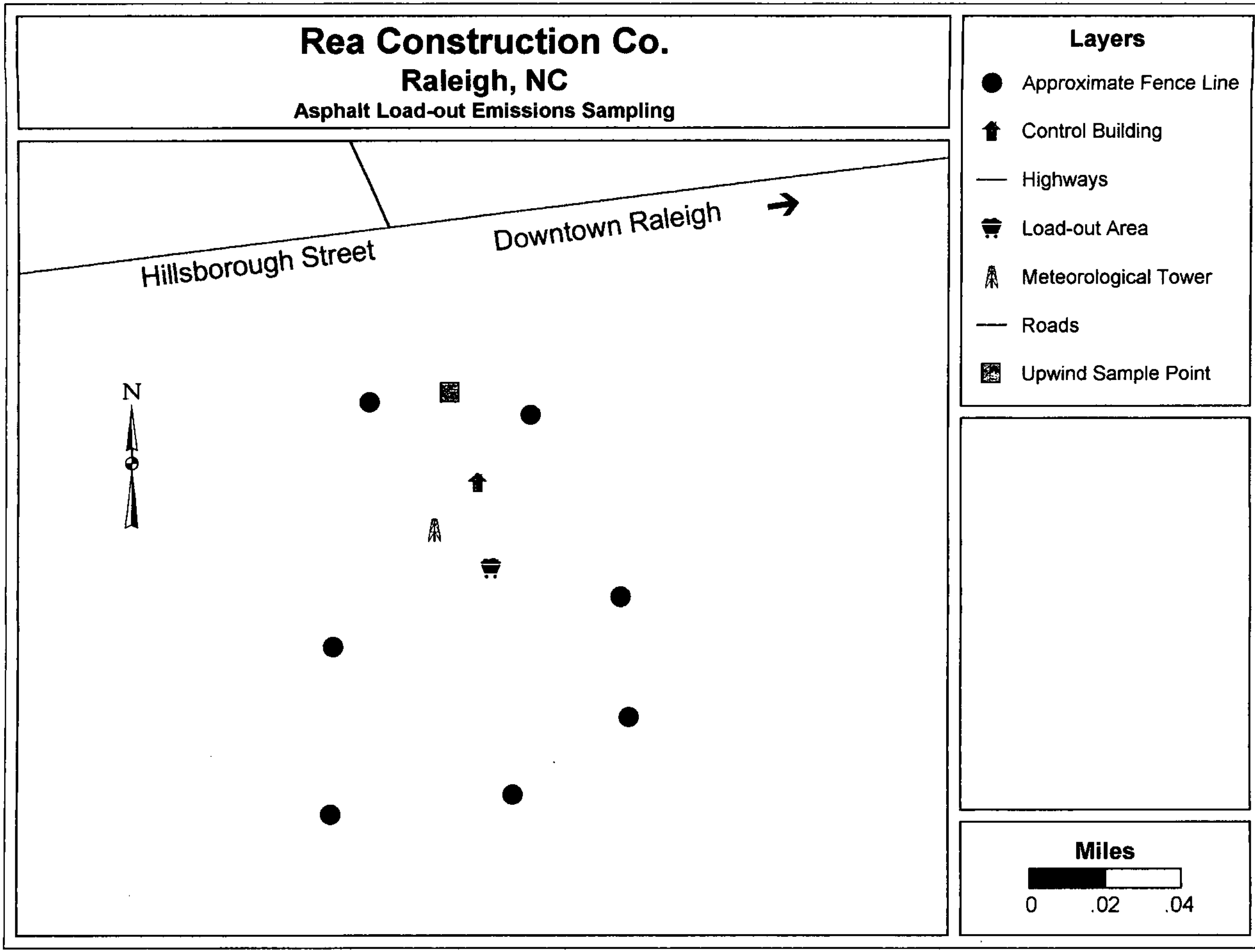

Rea Construction Co.
Raleigh, NC
Asphalt Load-out Emissions Sampling
Hillsborough Street
Downtown Raleigh
N
Layers
Approximate Fence Line
Control Building
Highways
Load-out Area
Meteorological Tower
Roads
Upwind Sample Point
Miles
0
.02
.04

Figure B.1

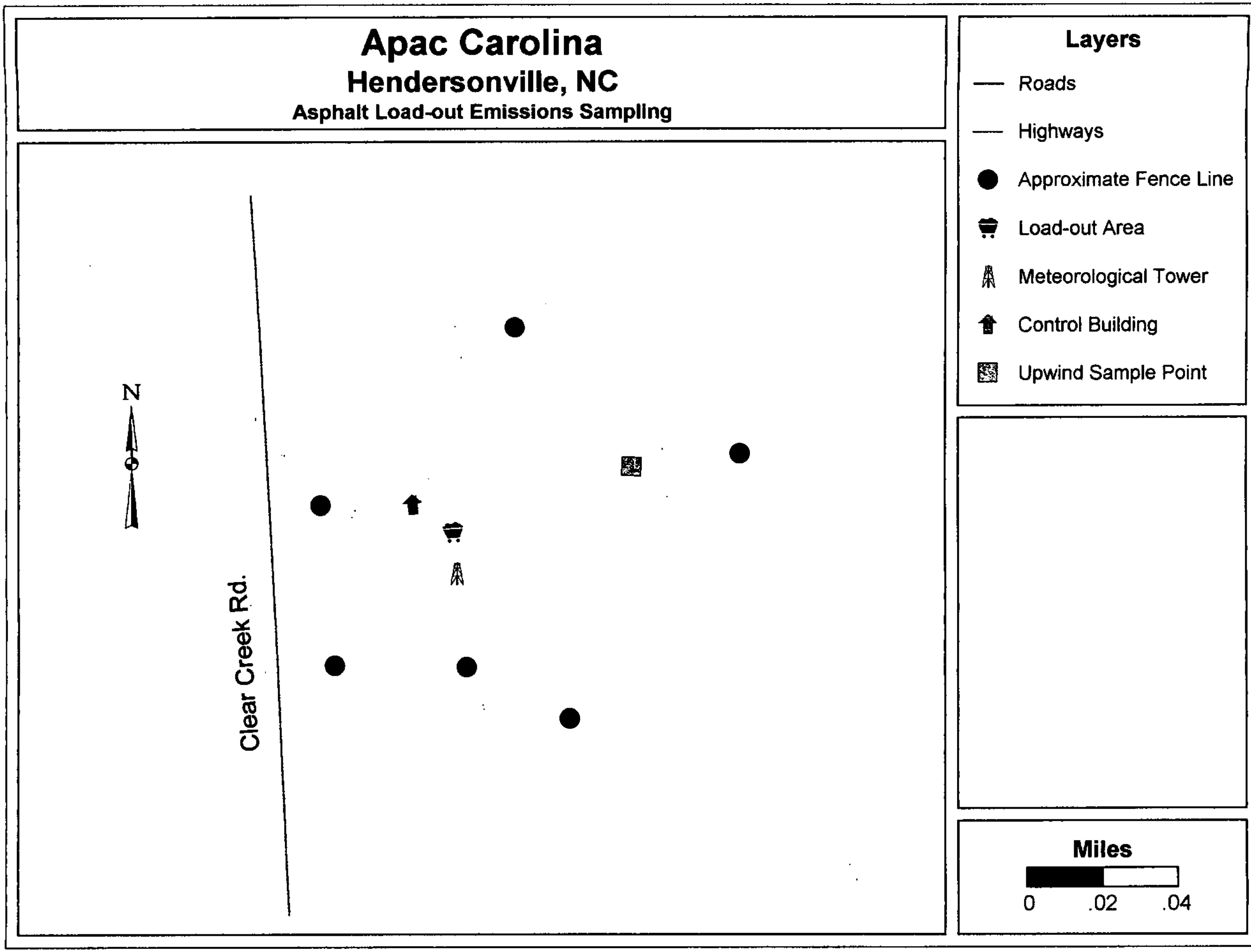

Apac Carolina
Hendersonville, NC
Asphalt Load-out Emissions Sampling
Layers
Roads
Highways
Approximate Fence Line
Load-out Area
Meteorological Tower
Control Building
Upwind Sample Point
N
Clear Creek Rd.
Miles
0
.02
.04

Figure B.2

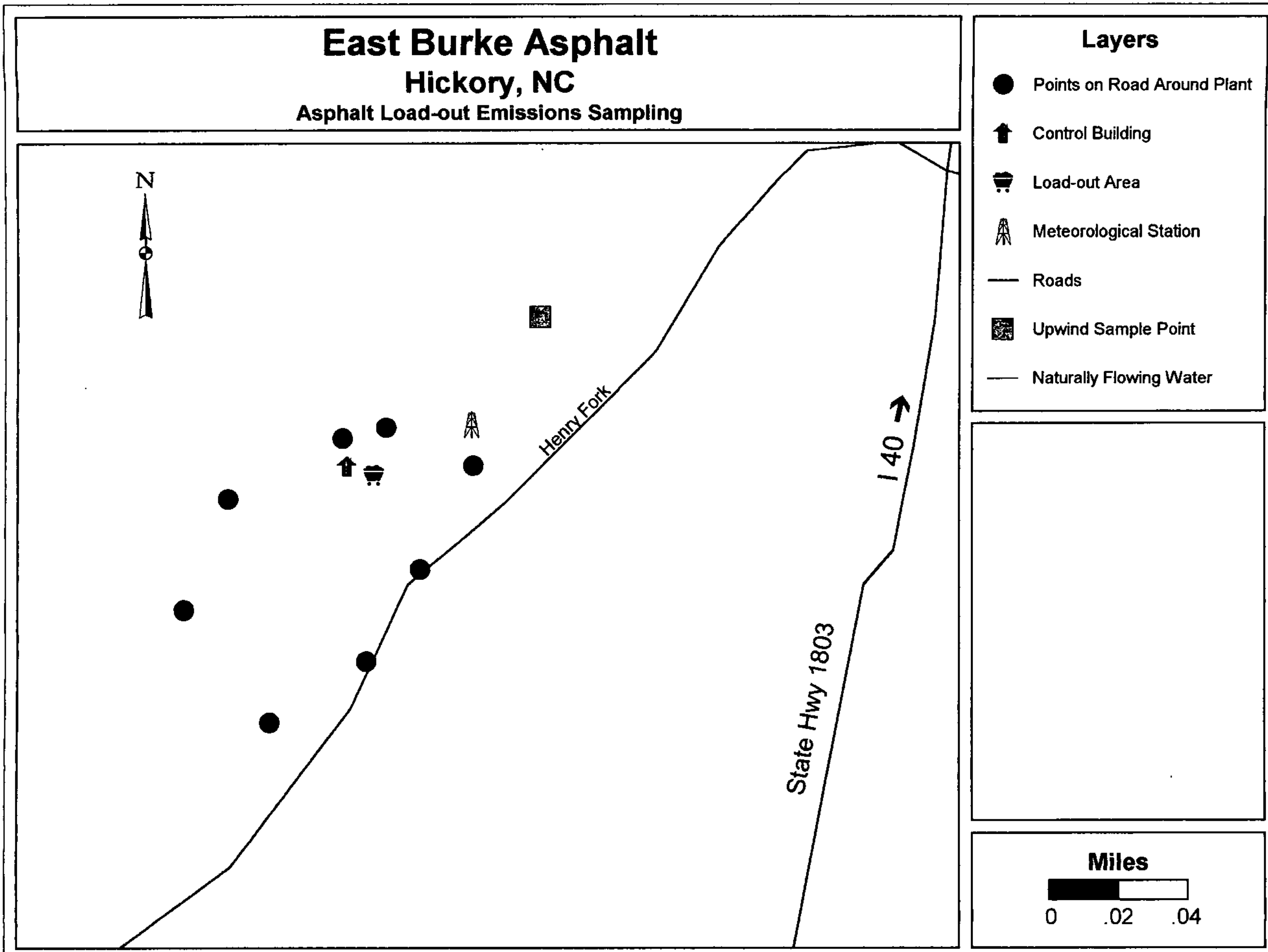

East Burke Asphalt
Hickory, NC
Asphalt Load-out Emissions Sampling
N
Henry Fork
I 40
State Hwy 1803
Layers
Points on Road Around Plant
Control Building
Load-out Area
Meteorological Station
Roads
Upwind Sample Point
Naturally Flowing Water
Miles
0
.02
.04

Figure B.3

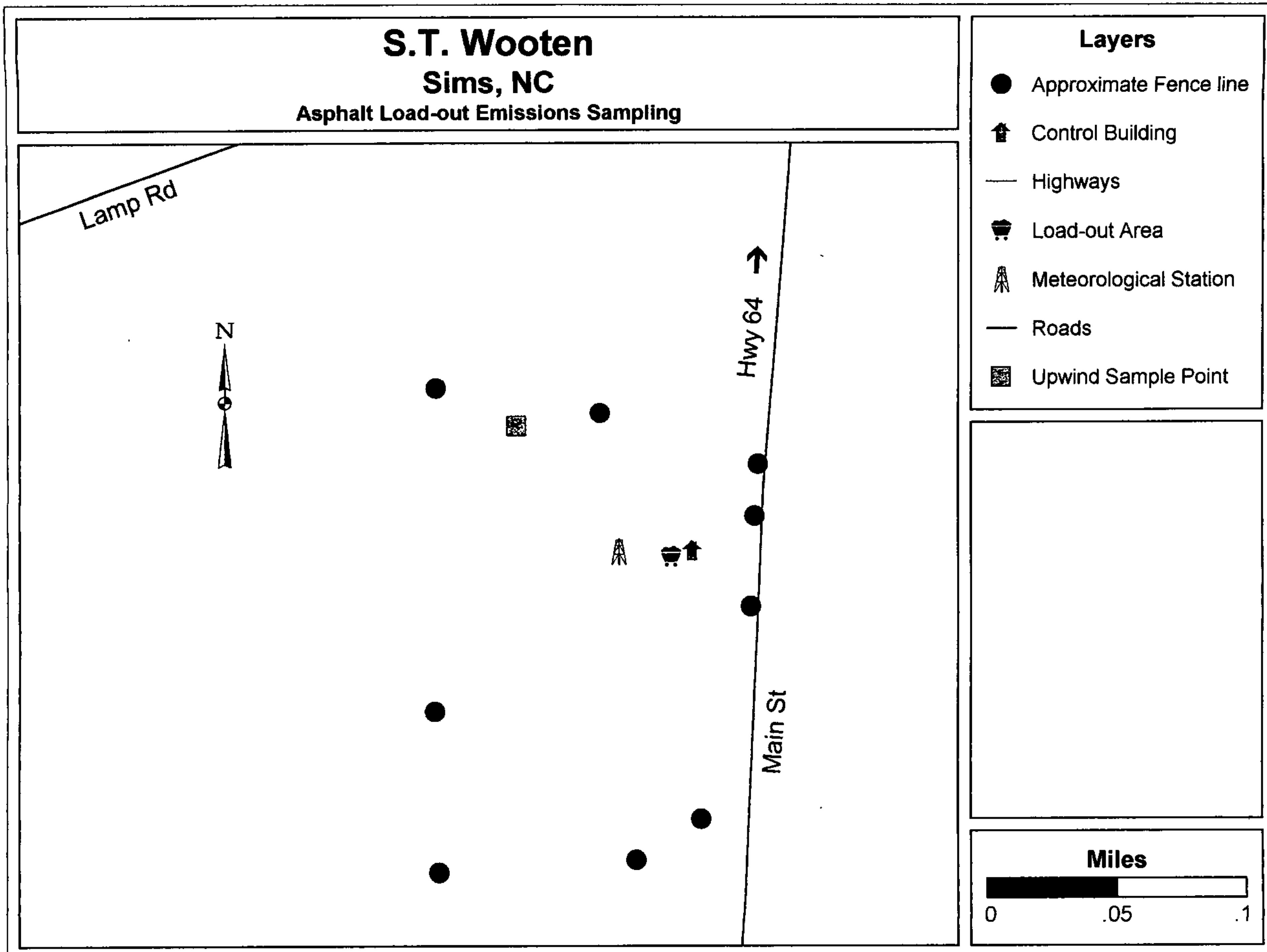

S.T. Wooten
Sims, NC
Asphalt Load-out Emissions Sampling
Lamp Rd
N
Hwy 64
Main St
Layers
Approximate Fence line
Control Building
Highways
Load-out Area
Meteorological Station
Roads
Upwind Sample Point
Miles
0
.05
.1

Figure B.4

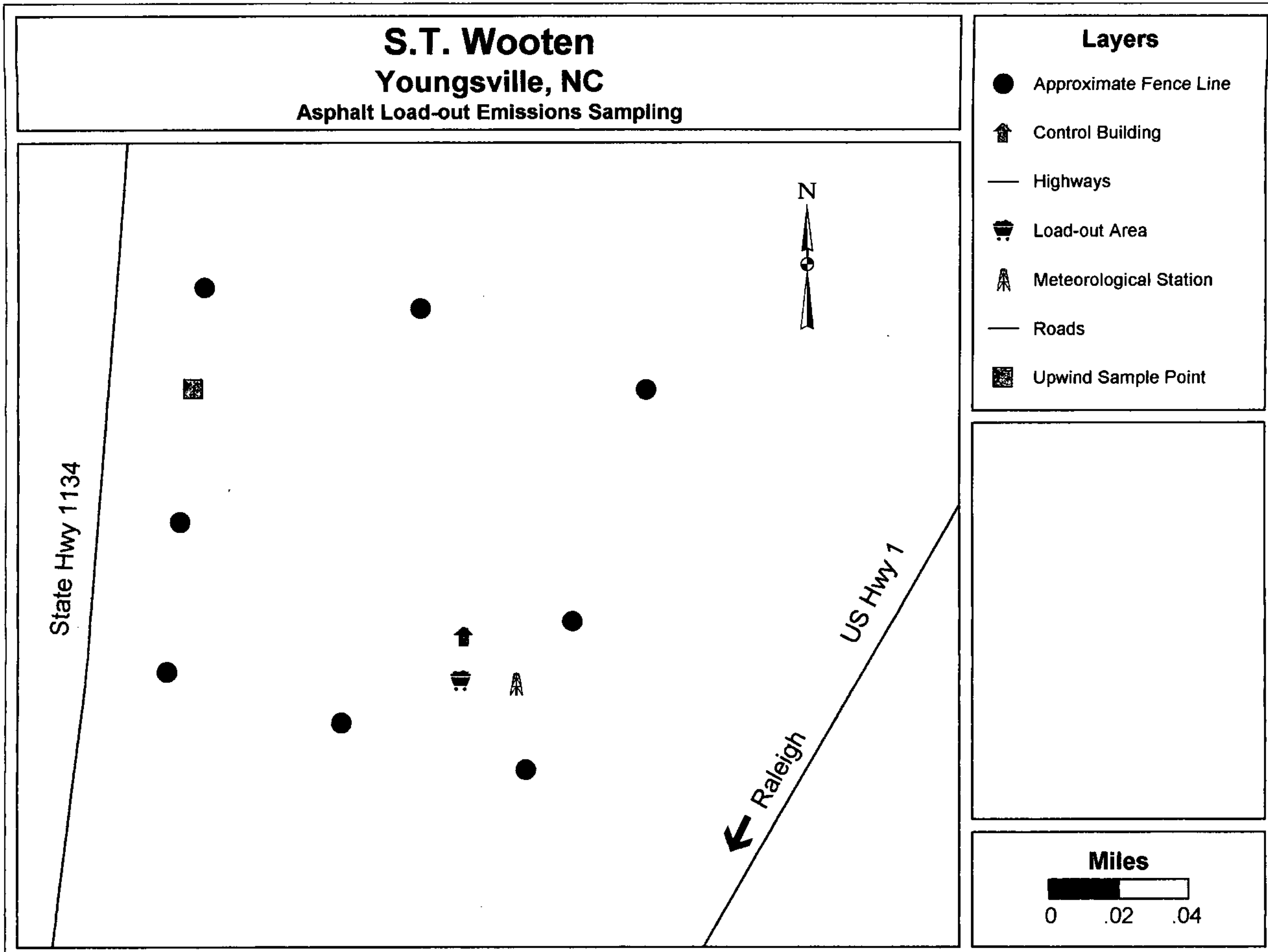

S.T. Wooten
Youngsville, NC
Asphalt Load-out Emissions Sampling
N
State Hwy 1134
US Hwy 1
Raleigh
Layers
Approximate Fence Line
Control Building
Highways
Load-out Area
Meteorological Station
Roads
Upwind Sample Point
Miles
0
.02
.04

Figure B.5

# Appendix C - Meteorological Data

The following are the meteorological data presented as wind roses, temperature profiles of the ambient temperature, and solar radiation profiles (radiation and flux) for the dates and times of each sampling visit. The data was compiled from the meteorological data logger for one-minute intervals.

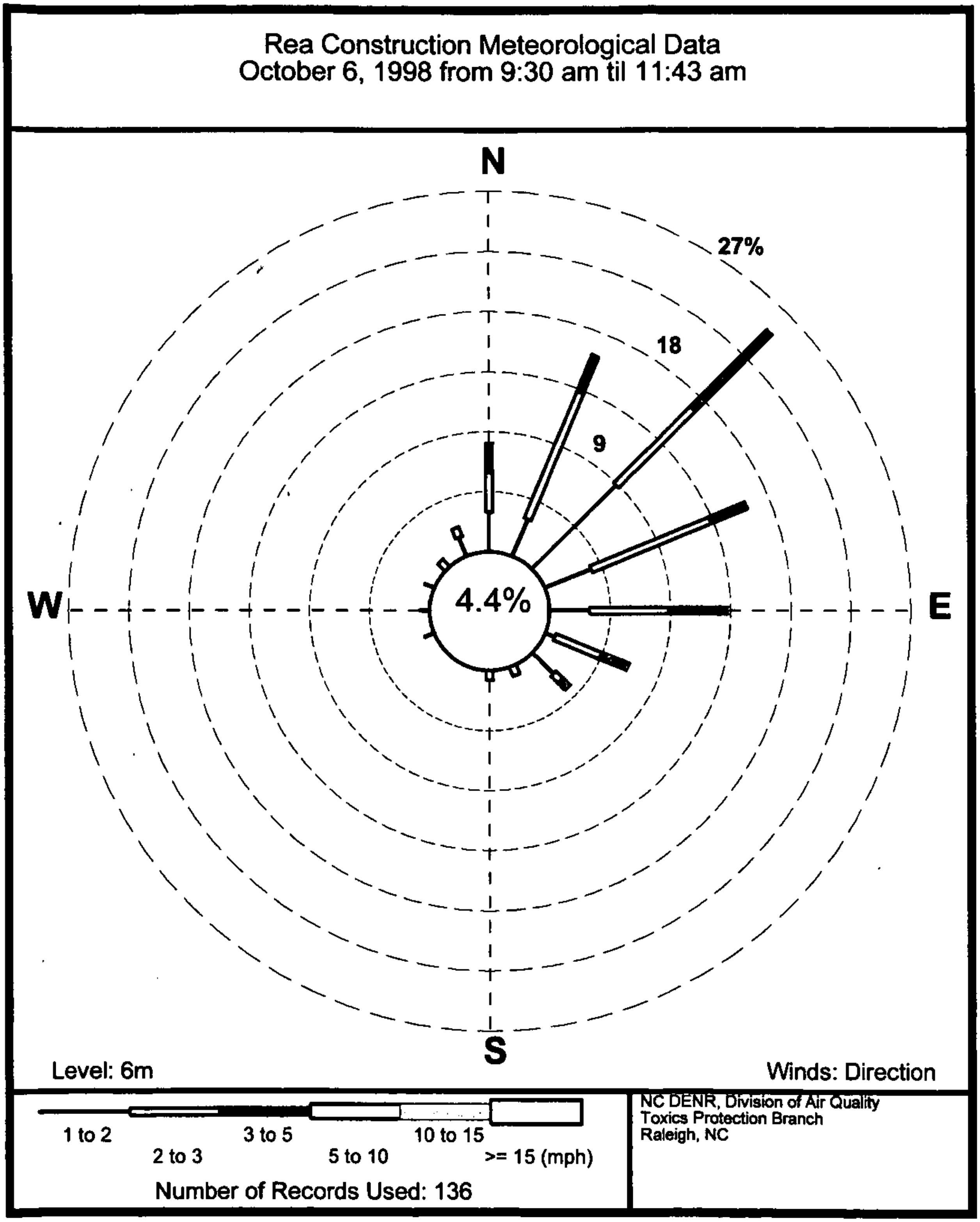

Rea Construction Meteorological Data
October 6, 1998 from 9:30 am til 11:43 am
N
27%
18
9
W
4.4%
E
S
Level: 6m
Winds: Direction
1 to 2
2 to 3
3 to 5
5 to 10
10 to 15
>= 15 (mph)
Number of Records Used: 136
NC DENR, Division of Air Quality
Toxics Protection Branch
Raleigh, NC

Figure C.1

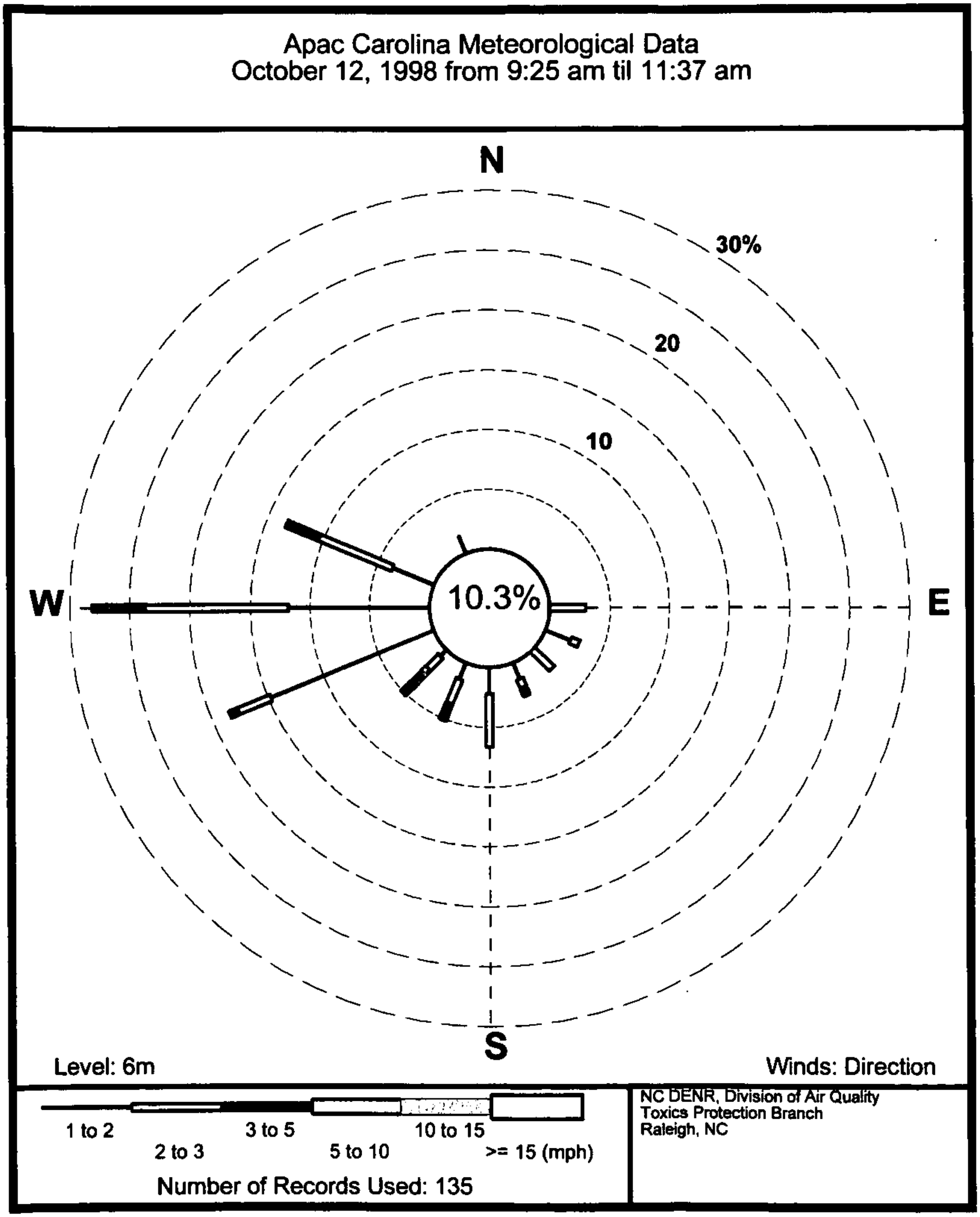

Apac Carolina Meteorological Data
October 12, 1998 from 9:25 am til 11:37 am
N
30%
20
10
W
10.3%
E
S
Level: 6m
Winds: Direction
1 to 2
2 to 3
3 to 5
5 to 10
10 to 15
>= 15 (mph)
Number of Records Used: 135
NC DENR, Division of Air Quality
Toxics Protection Branch
Raleigh, NC

Figure C.2

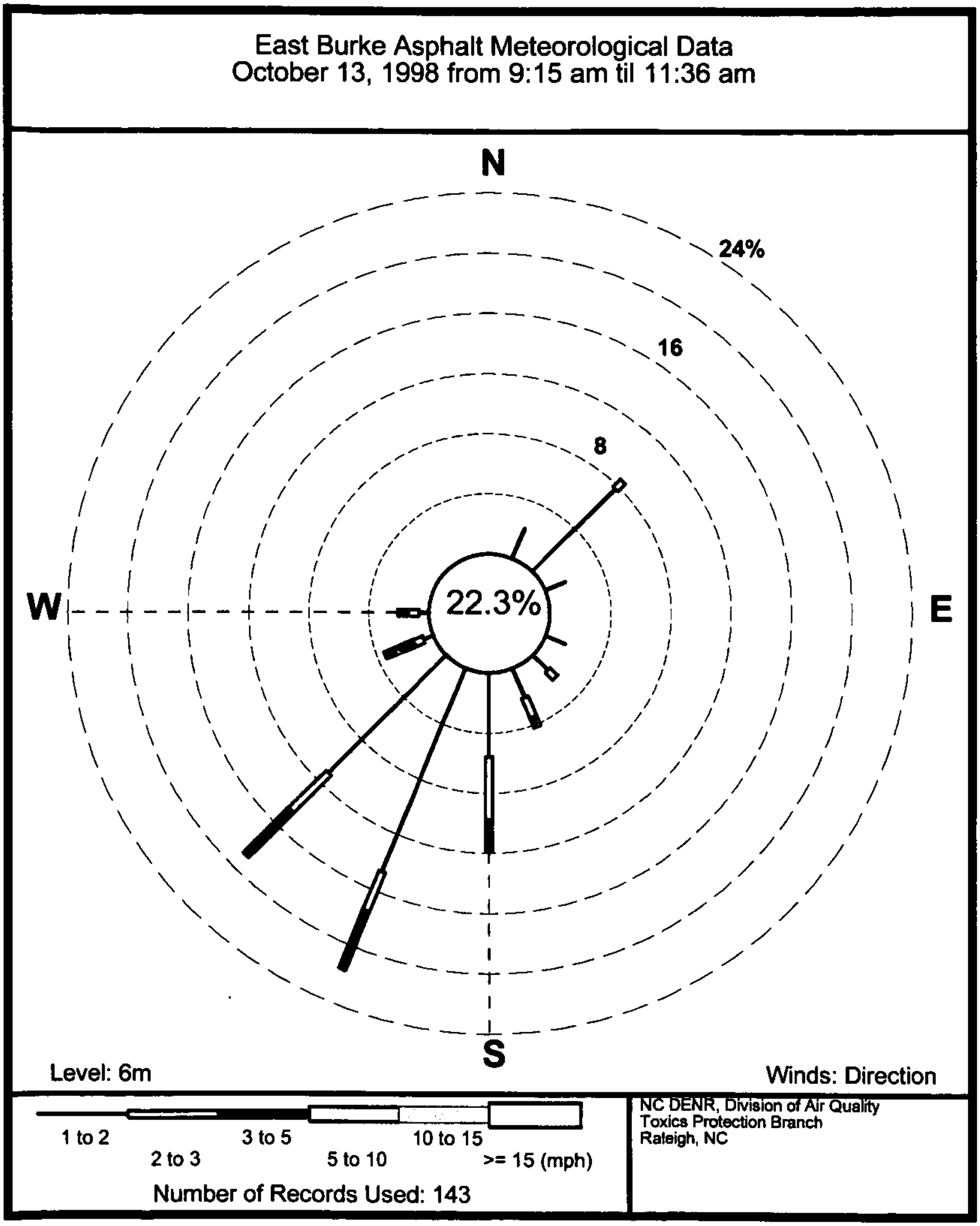

East Burke Asphalt Meteorological Data
October 13, 1998 from 9:15 am til 11:36 am
N
24%
16
8
W
22.3%
E
S
Level: 6m
Winds: Direction
1 to 2
2 to 3
3 to 5
5 to 10
10 to 15
>= 15 (mph)
Number of Records Used: 143
NC DENR, Division of Air Quality
Toxics Protection Branch
Raleigh, NC

Figure C.3

S.T. Wooten, Sims Meteorological Data
October 14, 1998 from 9:15 am til 10:18 am

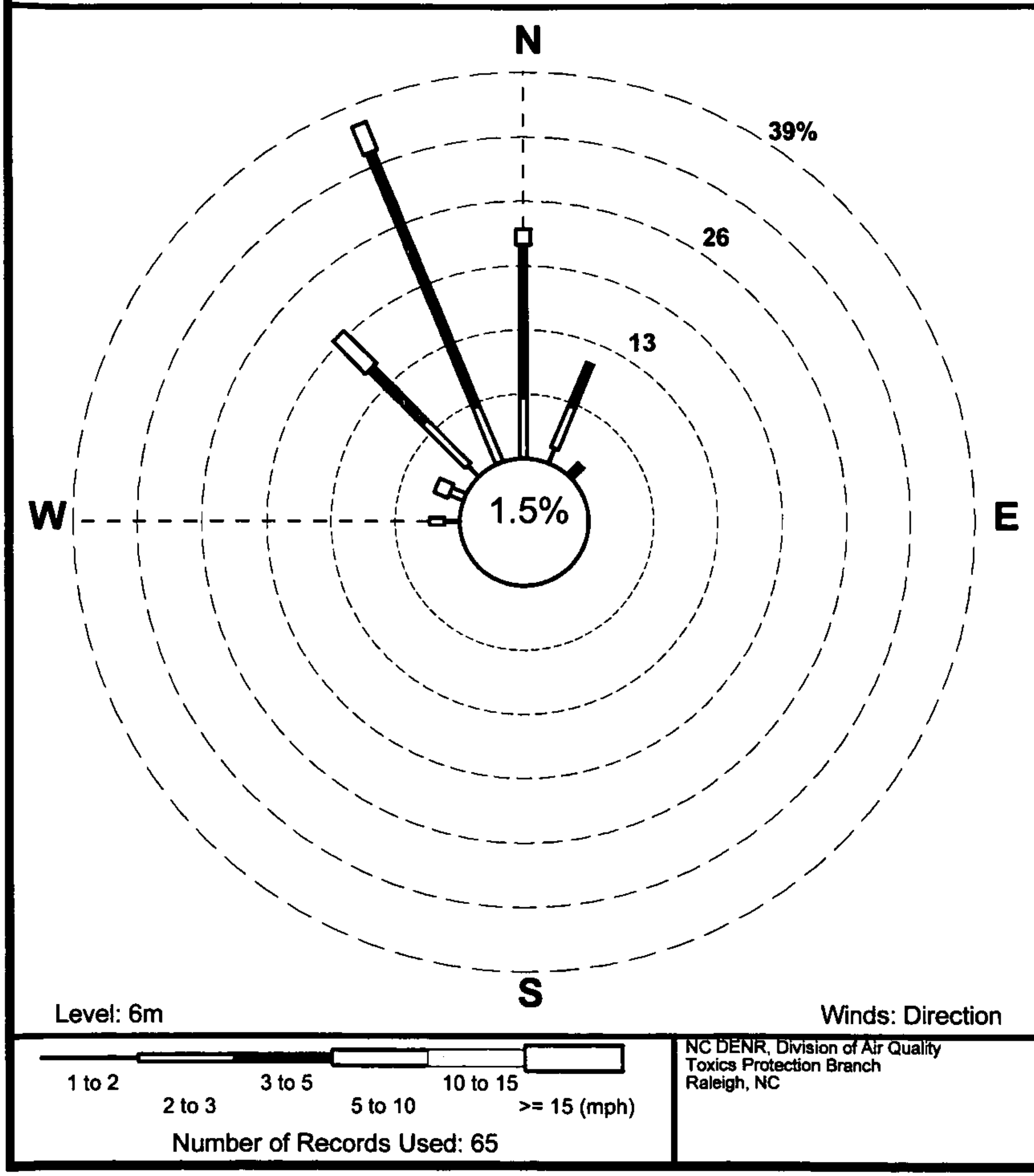
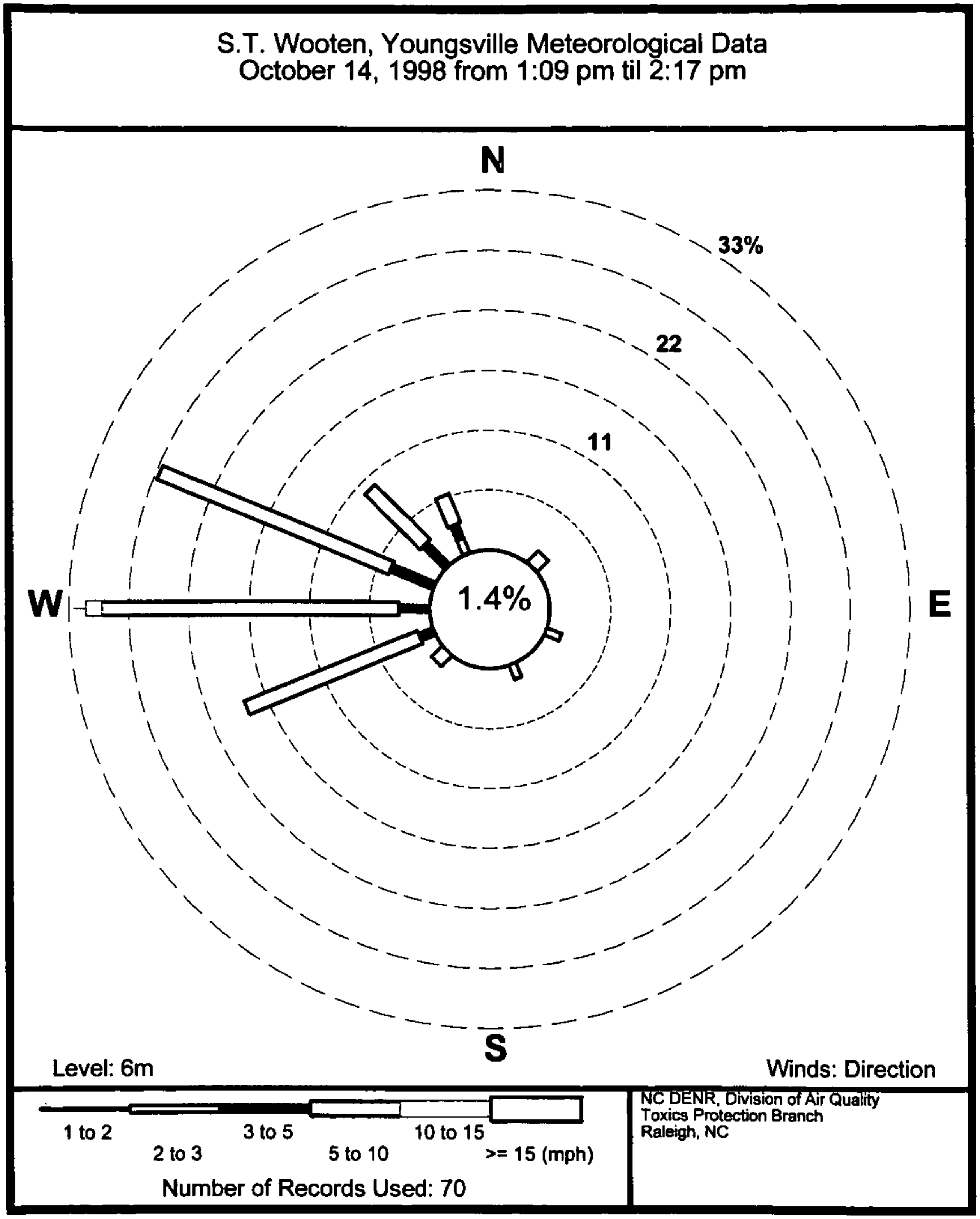
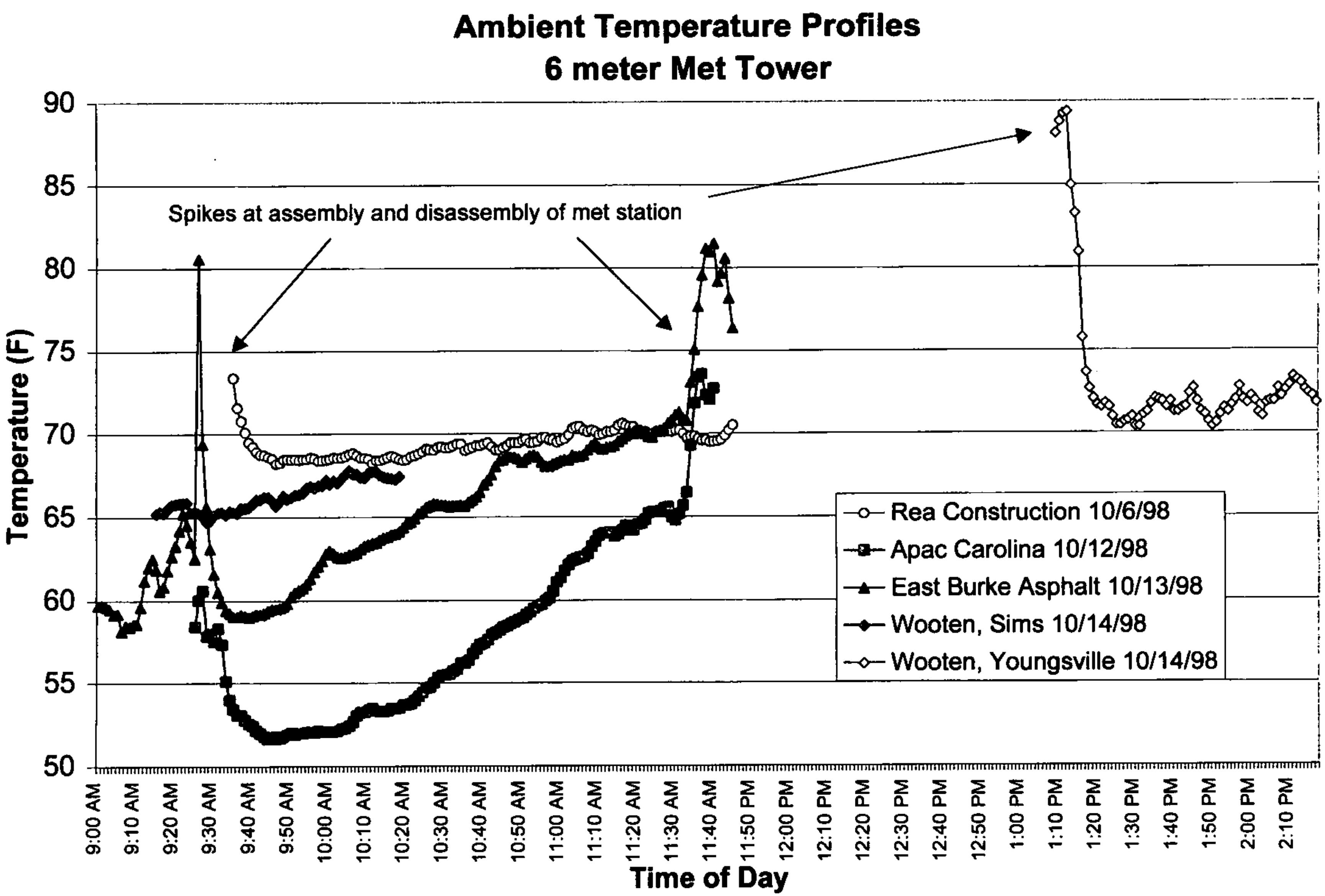



Figure C.4



S.T. Wooten, Youngsville Meteorological Data
October 14, 1998 from 1:09 pm til 2:17 pm
N
33%
22
11
W
1.4%
E
S
Level: 6m
Winds: Direction
1 to 2
2 to 3
3 to 5
5 to 10
10 to 15
>= 15 (mph)
Number of Records Used: 70
NC DENR, Division of Air Quality
Toxics Protection Branch
Raleigh, NC


Figure C.5



Ambient Temperature Profiles
6 meter Met Tower
Spikes at assembly and disassembly of met station
Temperature (F)
90
85
80
75
70
65
60
55
50
9:00 AM
9:10 AM
9:20 AM
9:30 AM
9:40 AM
9:50 AM
10:00 AM
10:10 AM
10:20 AM
10:30 AM
10:40 AM
10:50 AM
11:00 AM
11:10 AM
11:20 AM
11:30 AM
11:40 AM
11:50 PM
12:00 PM
12:10 PM
12:20 PM
12:30 PM
12:40 PM
12:50 PM
1:00 PM
1:10 PM
1:20 PM
1:30 PM
1:40 PM
1:50 PM
2:00 PM
2:10 PM
Time of Day
Rea Construction 10/6/98
Apac Carolina 10/12/98
East Burke Asphalt 10/13/98
Wooten, Sims 10/14/98
Wooten, Youngsville 10/14/98


Figure C.6

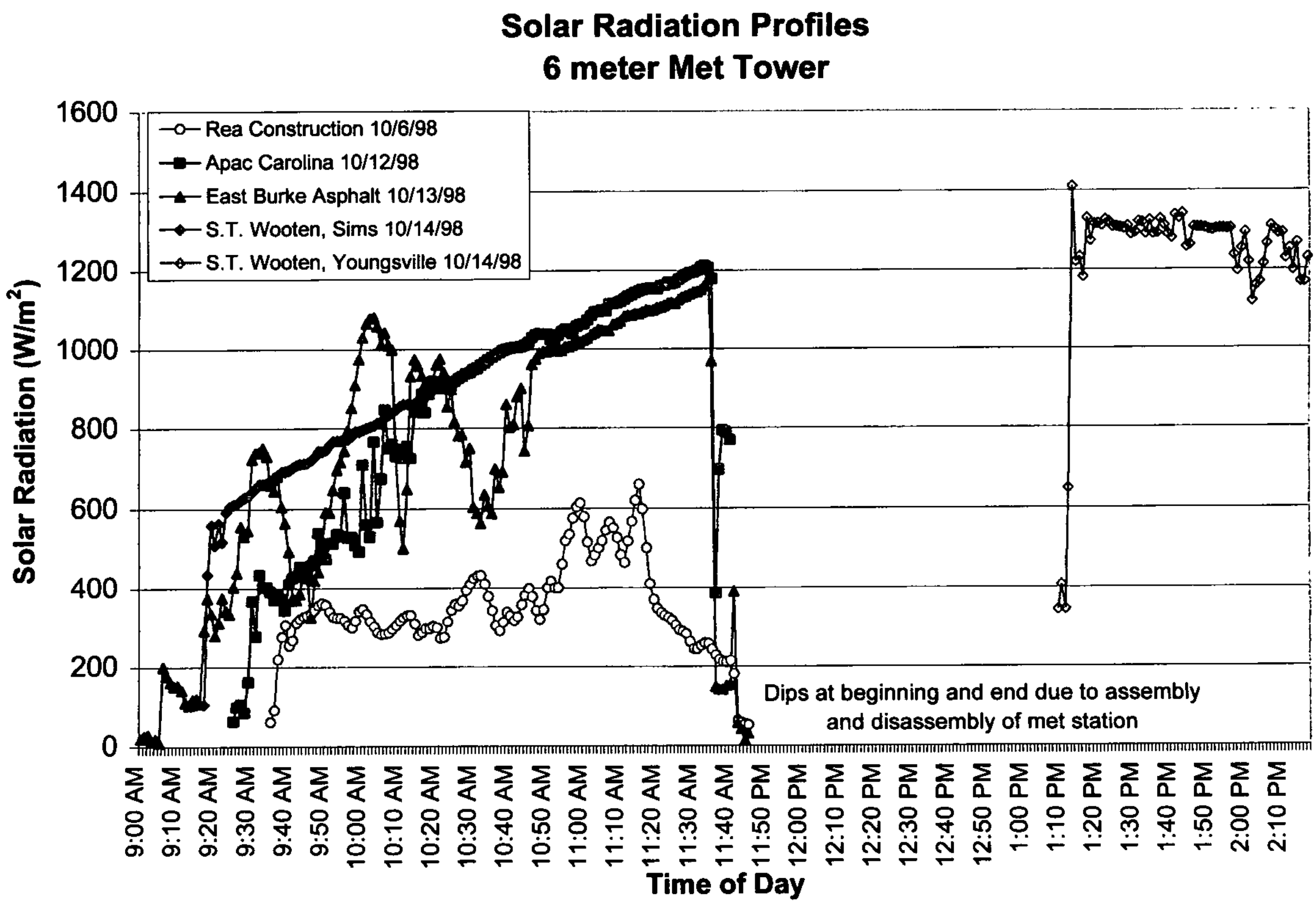
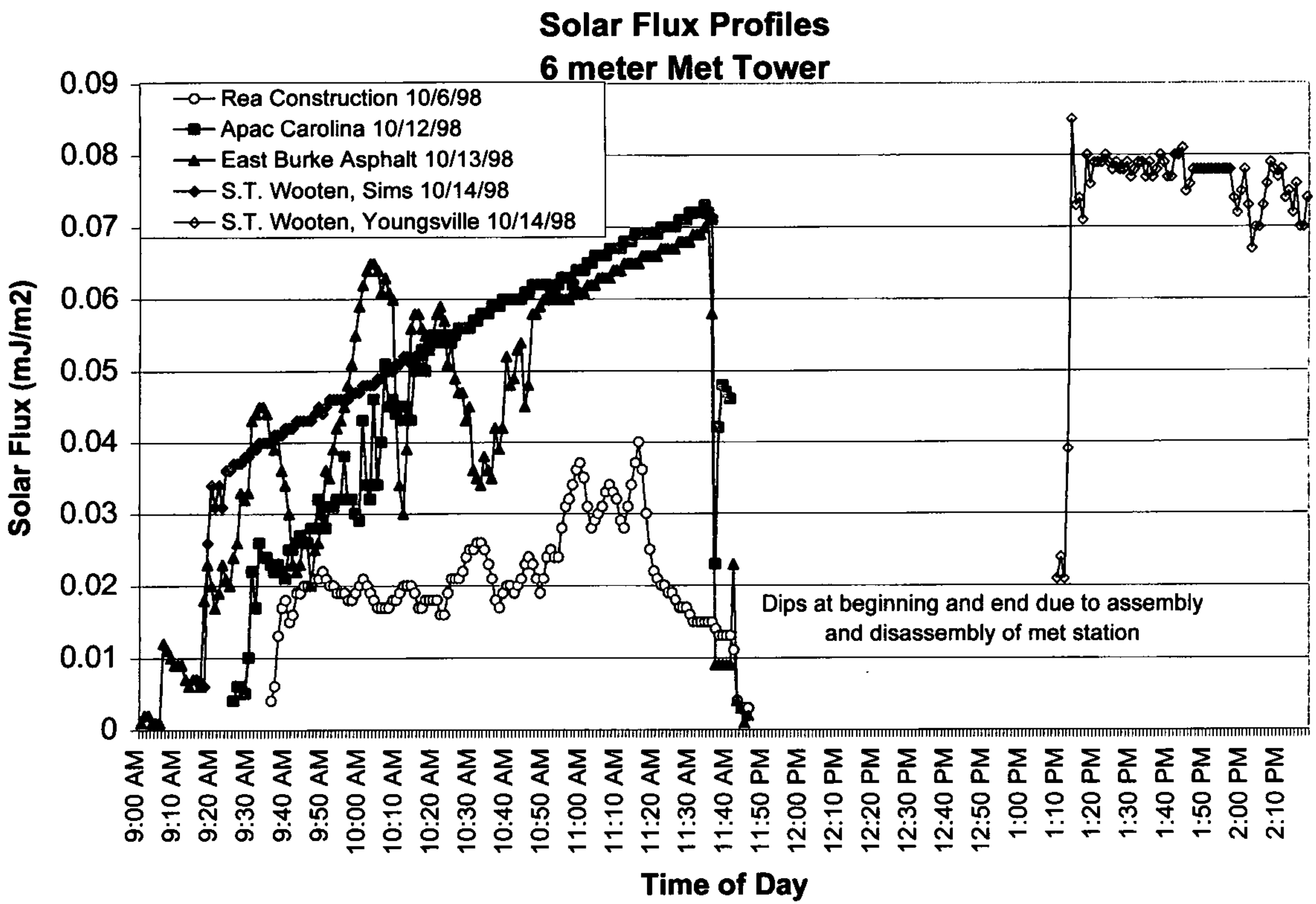

Solar Radiation Profiles
6 meter Met Tower
Solar Radiation (W/m²)
1600
1400
1200
1000
800
600
400
200
0
Rea Construction 10/6/98
Apac Carolina 10/12/98
East Burke Asphalt 10/13/98
S.T. Wooten, Sims 10/14/98
S.T. Wooten, Youngsville 10/14/98
Dips at beginning and end due to assembly
and disassembly of met station
9:00 AM
9:10 AM
9:20 AM
9:30 AM
9:40 AM
9:50 AM
10:00 AM
10:10 AM
10:20 AM
10:30 AM
10:40 AM
10:50 AM
11:00 AM
11:10 AM
11:20 AM
11:30 AM
11:40 AM
11:50 PM
12:00 PM
12:10 PM
12:20 PM
12:30 PM
12:40 PM
12:50 PM
1:00 PM
1:10 PM
1:20 PM
1:30 PM
1:40 PM
1:50 PM
2:00 PM
2:10 PM
Time of Day

Figure C.7

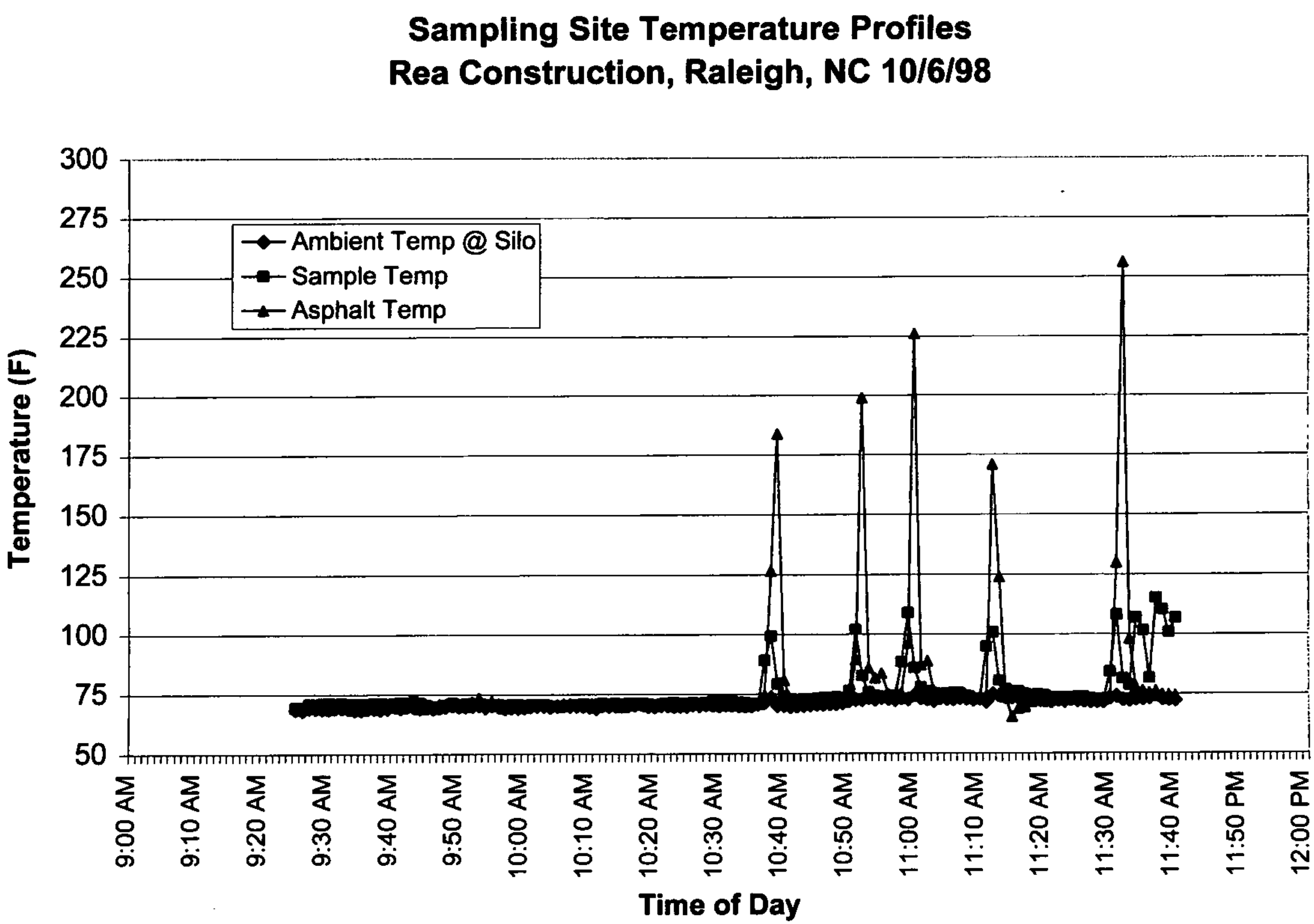


Solar Flux Profiles
6 meter Met Tower
Rea Construction 10/6/98
Apac Carolina 10/12/98
East Burke Asphalt 10/13/98
S.T. Wooten, Sims 10/14/98
S.T. Wooten, Youngsville 10/14/98
Solar Flux (mJ/m2)
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
9:00 AM
9:10 AM
9:20 AM
9:30 AM
9:40 AM
9:50 AM
10:00 AM
10:10 AM
10:20 AM
10:30 AM
10:40 AM
10:50 AM
11:00 AM
11:10 AM
11:20 AM
11:30 AM
11:40 AM
11:50 PM
12:00 PM
12:10 PM
12:20 PM
12:30 PM
12:40 PM
12:50 PM
1:00 PM
1:10 PM
1:20 PM
1:30 PM
1:40 PM
1:50 PM
2:00 PM
2:10 PM
Time of Day
Dips at beginning and end due to assembly
and disassembly of met station


Figure C.8

## Appendix D - Temperature Profiles at Sampling Site (Silo)

The following are the temperature profiles for each site during the times sampling was occurring. The temperature spikes on the asphalt profiles are due to placing the probe into the asphalt and removing it.



Sampling Site Temperature Profiles
Rea Construction, Raleigh, NC 10/6/98
Ambient Temp @ Silo
Sample Temp
Asphalt Temp
Temperature (F)
300
275
250
225
200
175
150
125
100
75
50
9:00 AM
9:10 AM
9:20 AM
9:30 AM
9:40 AM
9:50 AM
10:00 AM
10:10 AM
10:20 AM
10:30 AM
10:40 AM
10:50 AM
11:00 AM
11:10 AM
11:20 AM
11:30 AM
11:40 AM
11:50 PM
12:00 PM
Time of Day


Figure D.1

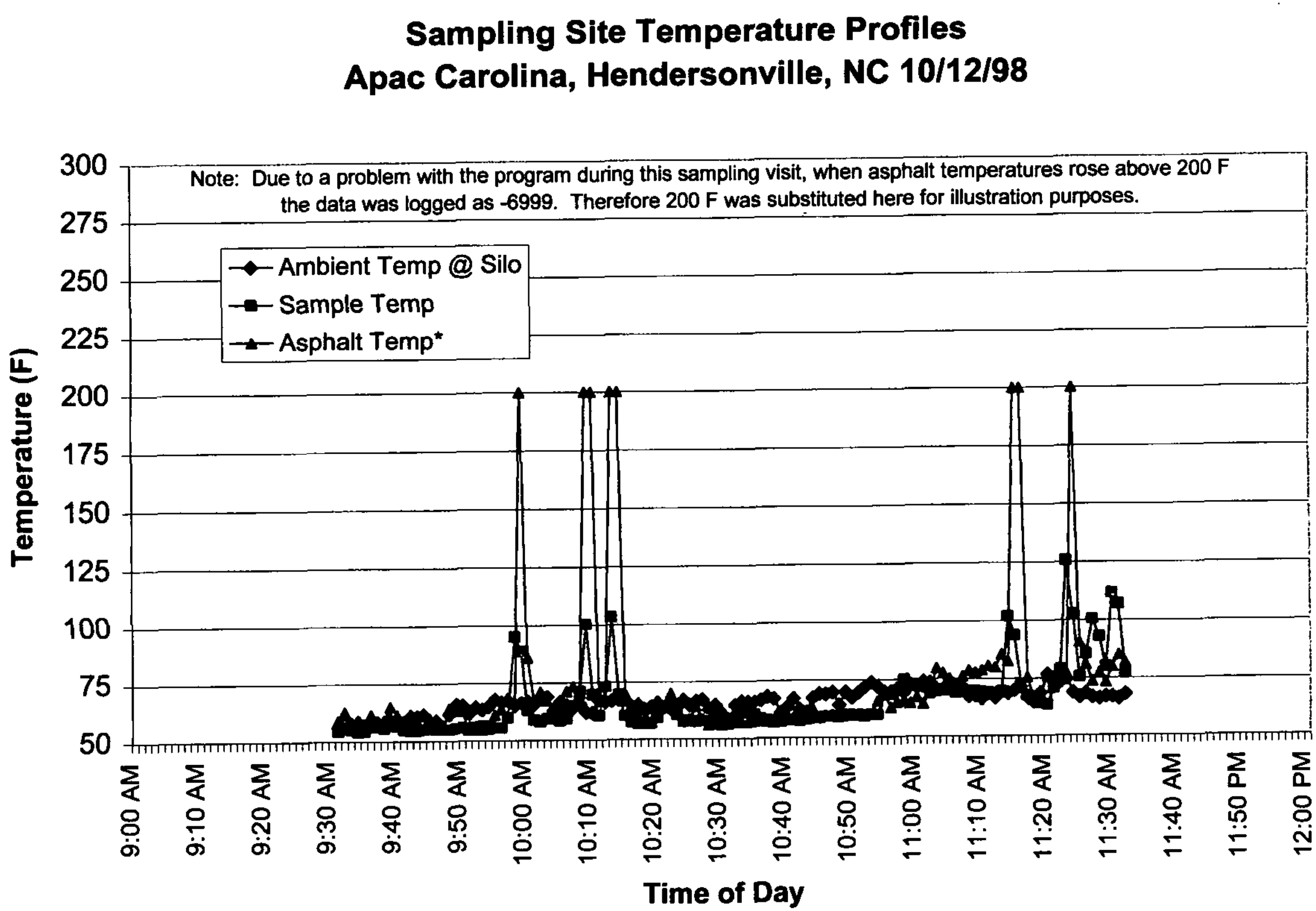
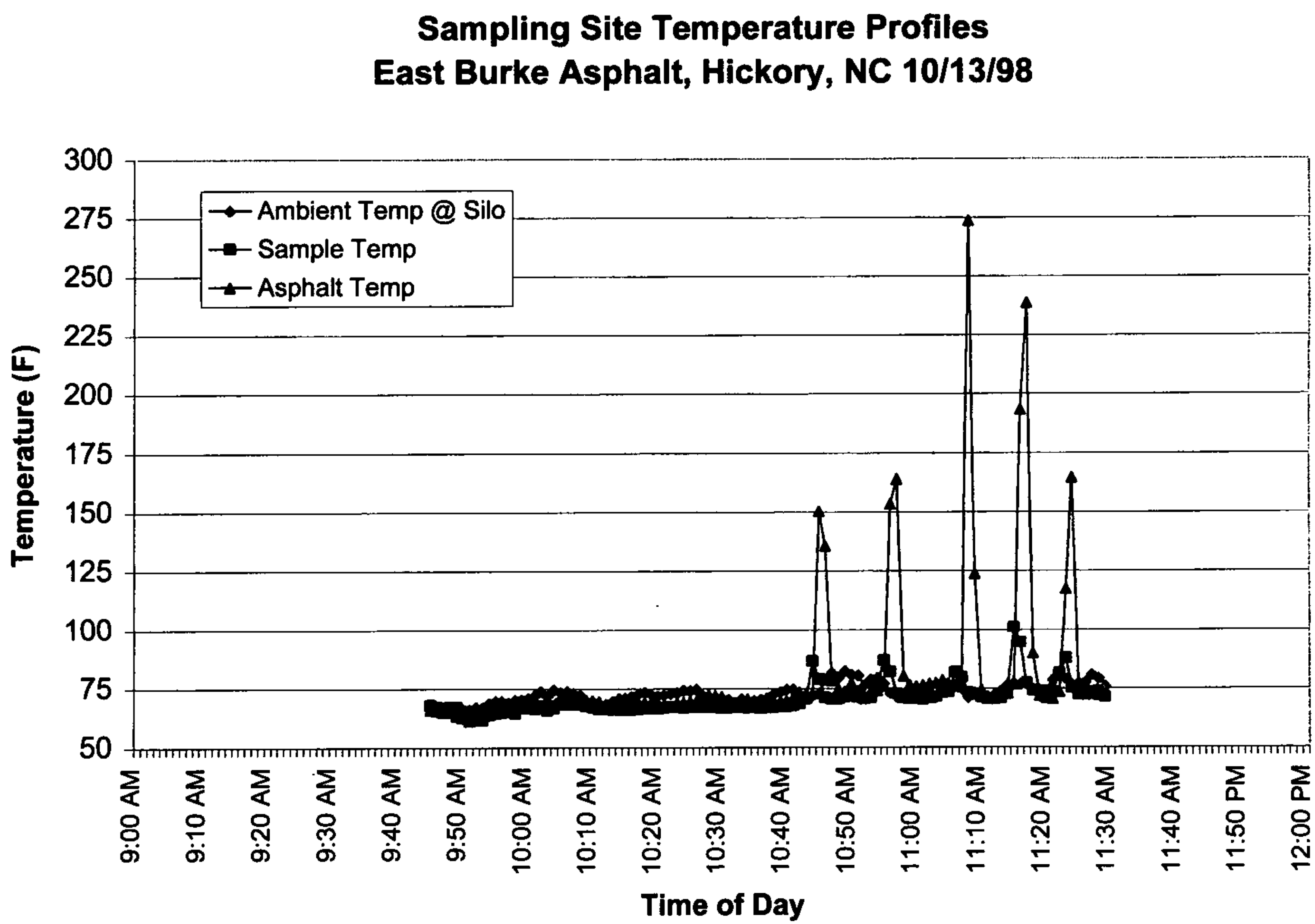

Sampling Site Temperature Profiles
Apac Carolina, Hendersonville, NC 10/12/98
Note: Due to a problem with the program during this sampling visit, when asphalt temperatures rose above 200 F the data was logged as -6999. Therefore 200 F was substituted here for illustration purposes.
Ambient Temp @ Silo
Sample Temp
Asphalt Temp*
Temperature (F)
300
275
250
225
200
175
150
125
100
75
50
9:00 AM
9:10 AM
9:20 AM
9:30 AM
9:40 AM
9:50 AM
10:00 AM
10:10 AM
10:20 AM
10:30 AM
10:40 AM
10:50 AM
11:00 AM
11:10 AM
11:20 AM
11:30 AM
11:40 AM
11:50 PM
12:00 PM
Time of Day

Figure D.2



Sampling Site Temperature Profiles
East Burke Asphalt, Hickory, NC 10/13/98
Ambient Temp @ Silo
Sample Temp
Asphalt Temp
Temperature (F)
300
275
250
225
200
175
150
125
100
75
50
9:00 AM
9:10 AM
9:20 AM
9:30 AM
9:40 AM
9:50 AM
10:00 AM
10:10 AM
10:20 AM
10:30 AM
10:40 AM
10:50 AM
11:00 AM
11:10 AM
11:20 AM
11:30 AM
11:40 AM
11:50 PM
12:00 PM
Time of Day


Figure D.3

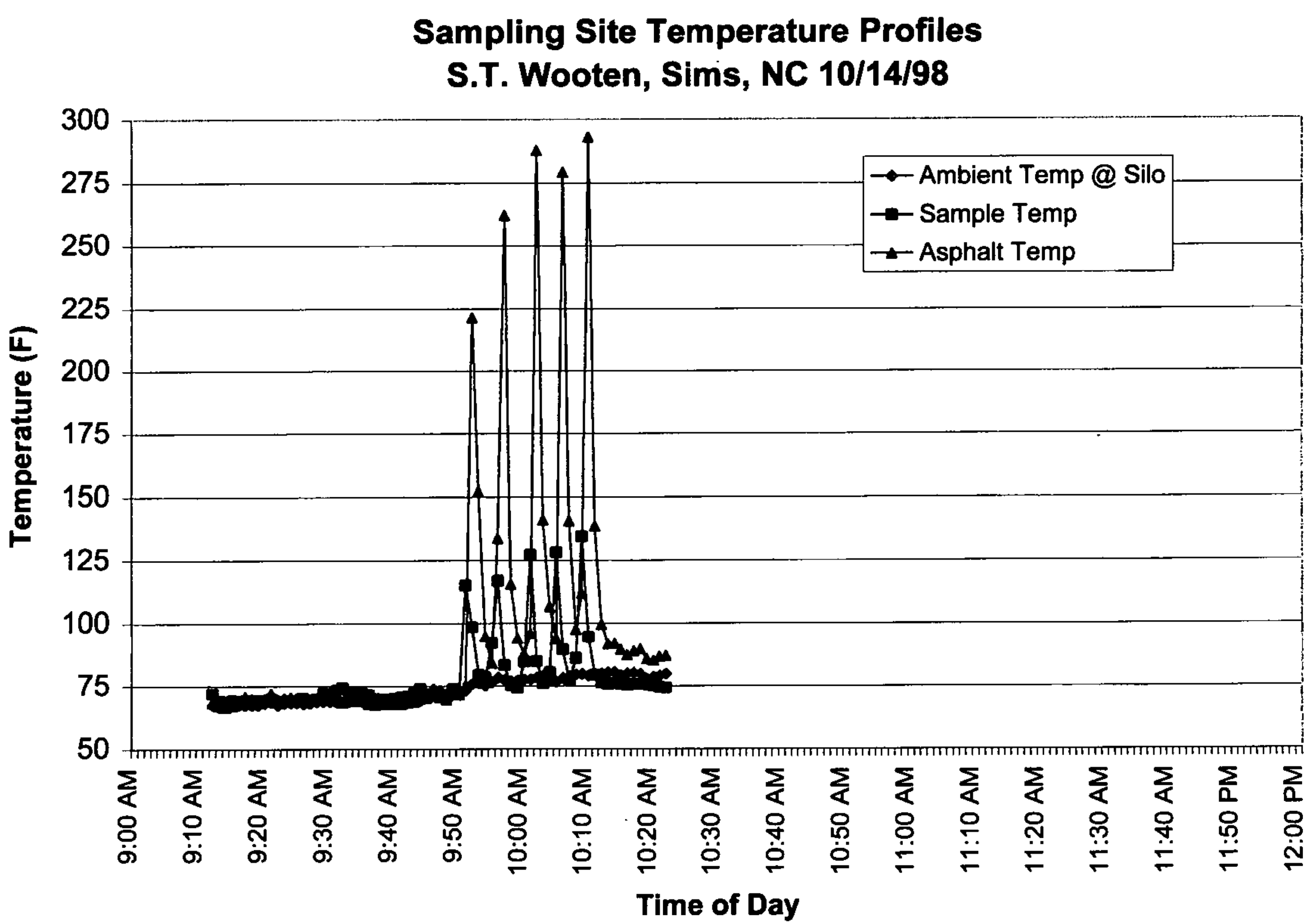
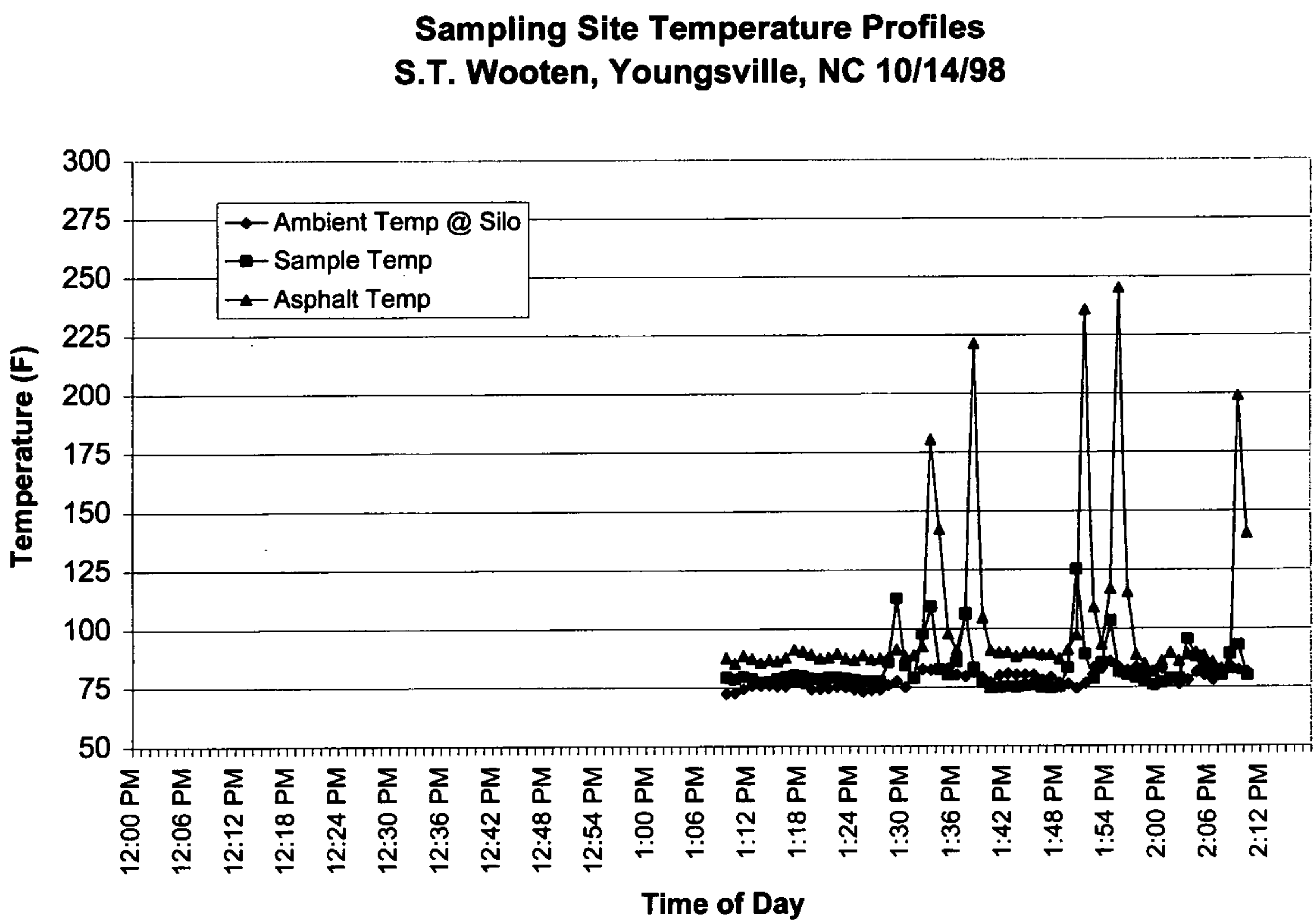

Sampling Site Temperature Profiles
S.T. Wooten, Sims, NC 10/14/98
Temperature (F)
300
275
250
225
200
175
150
125
100
75
50
Ambient Temp @ Silo
Sample Temp
Asphalt Temp
9:00 AM
9:10 AM
9:20 AM
9:30 AM
9:40 AM
9:50 AM
10:00 AM
10:10 AM
10:20 AM
10:30 AM
10:40 AM
10:50 AM
11:00 AM
11:10 AM
11:20 AM
11:30 AM
11:40 AM
11:50 PM
12:00 PM
Time of Day

Figure D.4



Sampling Site Temperature Profiles
S.T. Wooten, Youngsville, NC 10/14/98
Ambient Temp @ Silo
Sample Temp
Asphalt Temp
Temperature (F)
300
275
250
225
200
175
150
125
100
75
50
12:00 PM
12:06 PM
12:12 PM
12:18 PM
12:24 PM
12:30 PM
12:36 PM
12:42 PM
12:48 PM
12:54 PM
1:00 PM
1:06 PM
1:12 PM
1:18 PM
1:24 PM
1:30 PM
1:36 PM
1:42 PM
1:48 PM
1:54 PM
2:00 PM
2:06 PM
2:12 PM
Time of Day


Figure D.5

# Appendix E – Calculations

The following calculations are for the two methods of statistically determining outliers of data sets. The Dixon Test and Grubbs Test are fully described in the reference section of this study report. Below are the calculations involved in these tests with brief explanations of what the values mean.

Initially for each test the data points must be arranged in ascending order (see below) and a confidence level chosen. In the Dixon Test, the confidence level is chosen at 99.5% which means that there is a 0.5% risk of false rejection of a data point as an outlier. This means that there is a 99.5% confidence that the data point was correctly rejected and only a 0.5% chance that the decision to drop the data point was wrong. For most statistical data, a 95% confidence level is chosen as a scientifically valid level. The Grubb Test was performed at 99.5% and 99.9 % confidence intervals.

0.195, 0.515, 0.678, 1.252, 1.252, 1.734, 2.222, 2.625, 3.328, 4.190, 5.005, 6.657,67.261, 508.83 (n = 14) represent $X_1$ to$X_{14}$

**Dixon Test**
1. *Calculation for data point = 508.83 (n = 14):*

From equations and data taken from References 6-7, when n=14, one must calculate the value of the critical Dixon ratio of $r_{22}$.
If $X_n$ is the suspect point ($X_n = 508.83$) then $r_{22} = (X_n-X_{n-2})/(X_n-X_3)$ therefore:

$r_{22} = (508.83 - 6.657)/(508.83 - 0.678) = 0.988$

The critical value from the table A.7 in Ref. 7 for n = 14 is $r_{22crit} = 0.674$.

The critical value is **less than** the calculated ratio, therefore the data point is an outlier and can be omitted from the data set.

2. *Calculation for data point = 67.261 (n = 13):*
This same calculation is performed again for the value of $X_n = 67.261$.
n = 13, Dixon ratio is $r_{21}$.

If $X_n$ is the suspect point ($X_n = 67.261$) then $r_{21} = (X_n-X_{n-2})/(X_n-X_2)$ therefore:

$r_{21} = (67.261 - 5.005)/(67.261 - 0.515) = 0.933$

The critical value from the table A.7 in Ref. 7 for n = 13 is $r_{21crit} = 0.649$.

The critical value is **less than** the calculated ratio, therefore the data point is an outlier and can be omitted from the data set.

**Grubbs Test**

The Grubbs Test is performed at the 99.5% and 99.9% confidence level for both of the last two data points in the list above.

Sample set average ($X_{avg}$) including all points (n = 14) is 43.267.
Sample set standard deviation (s) including all points is 135.118.

If $X_n$ is suspect, then $T_{calc} = (X_n - X_{avg})/s$.

1. *Calculation for data point = 508.83 (n = 14):*

$T_{calc} = (508.83 - 43.267)/135.118 = 3.45$

$T_{crit}$ from Table A.8 in reference 7 = 2.482 (n=10) and 2.806 (n=15) at 99.5% confidence level. These two values were used because a value for n=14 was not available in this text.

$T_{crit}$ from Table A.8 in reference 7 = 2.606 (n=10) and 2.997 (n=15) at 99.9% confidence level. These two values were used because a value for n=14 was not available in this text.

In all cases the values of $T_{crit}$ are less than the value of $T_{calc}$, therefore the data point is an outlier and can be omitted from the data set.

2. *Calculation for data point 67.261(n = 13):*

Sample set average ($X_{avg}$) including all points (n = 3) is 7.455.
Sample set standard deviation (s) including all points is 18.070.

$T_{calc} = (67.261 - 7.455)/18.070 = 3.310$

$T_{crit}$ from Table A.8 in reference 7 = 2.482 (n=10) and 2.806 (n=15) at 99.5% confidence level. These two values were used because a value for n=14 was not available in this text.

$T_{crit}$ from Table A.8 in reference 7 = 2.606 (n=10) and 2.997 (n=15) at 99.9% confidence level. These two values were used because a value for n=14 was not available in this text.

In all cases the values of $T_{crit}$ are less than the value of $T_{calc}$, therefore the data point is an outlier and can be omitted from the data set.

**Confidence Interval**

Confidence intervals were calculated from the following equation.[12] The example calculation is for velocity measurements. Other confidence intervals were also calculated for the benzene concentrations ($n = 12$, $s = 1.988$, $t = 3.106$, $X_{avg} = 2.471$)

Confidence Interval = $X_{avg} \pm ts/\sqrt{n}$

$X_{avg} = 0.51$

t = "Student's t", the value for the probability value chosen for the interval that is being calculated (in this case the value was 99.5%) and the degrees of freedom (df = n-1).
= 2.750

s = standard deviation = 0.20

n = 34

Therefore, velocity measurements are $0.51 \pm 0.9$ m/s.

# P - Plates

The following pages are the photographs taken during sampling visits to the various asphalt plants in North Carolina. Each is captioned to briefly describe the equipment or action illustrated.

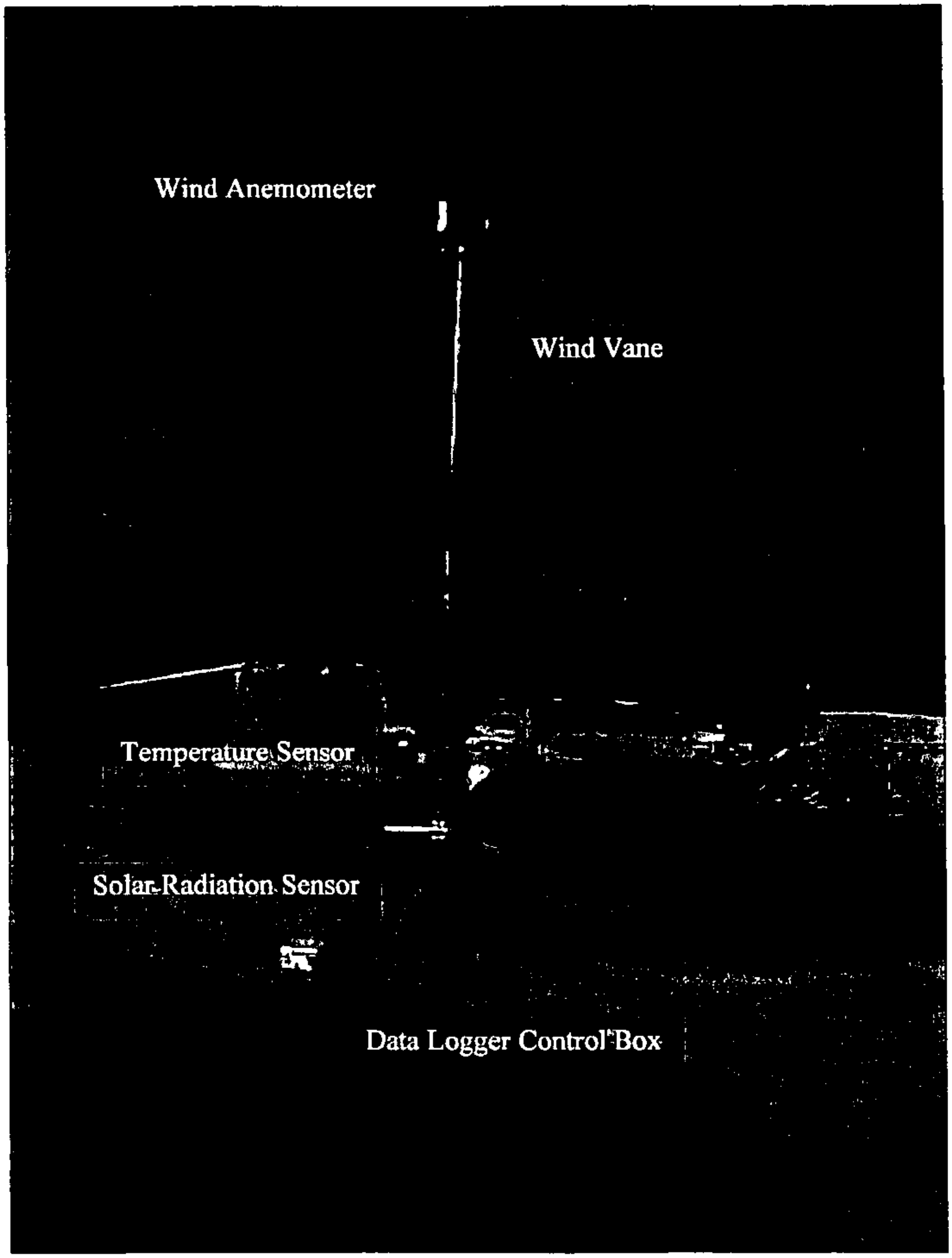



Plate 1 Typical meteorological station assembly and positioning (S.T. Wooten site, Sims, NC)

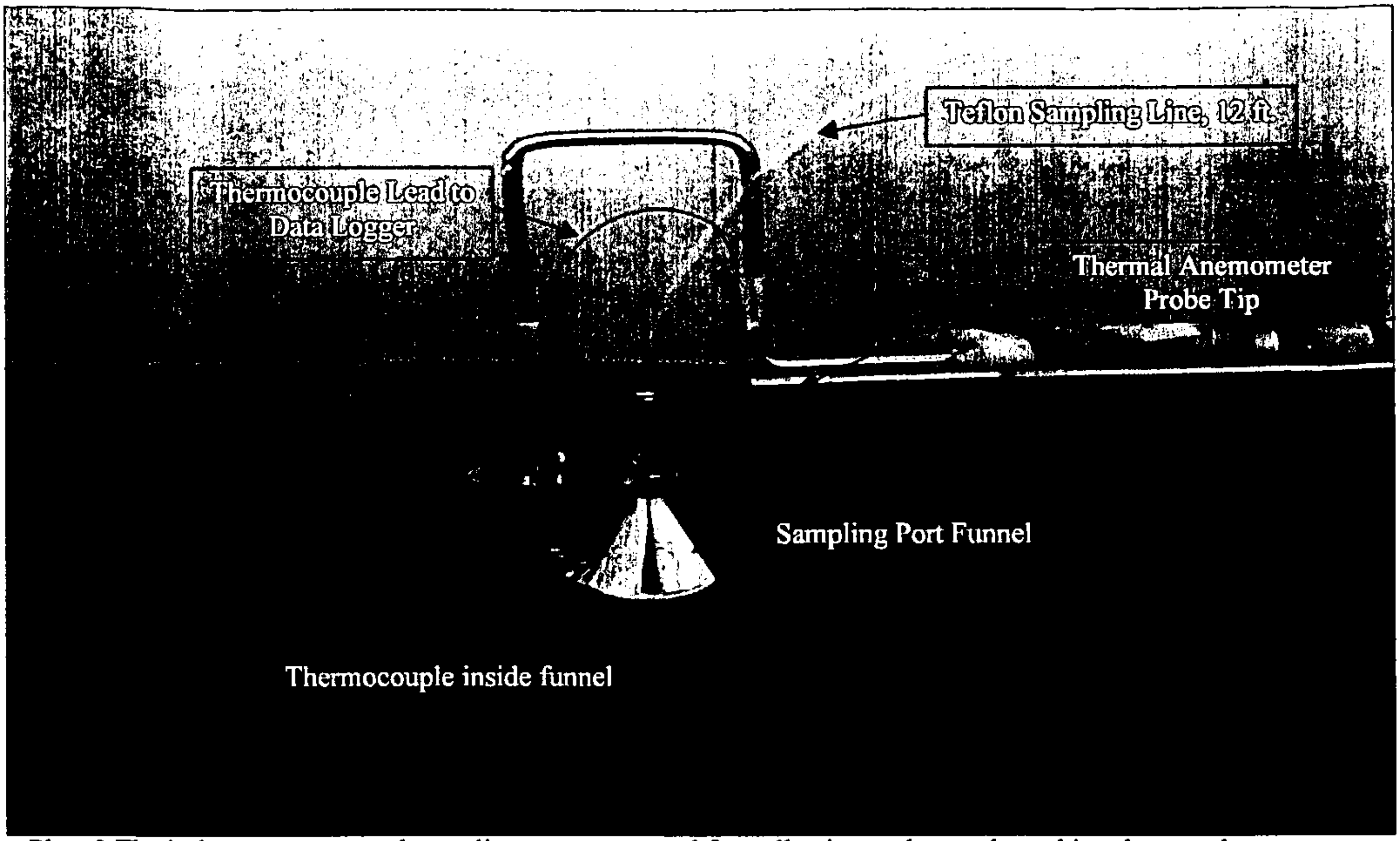
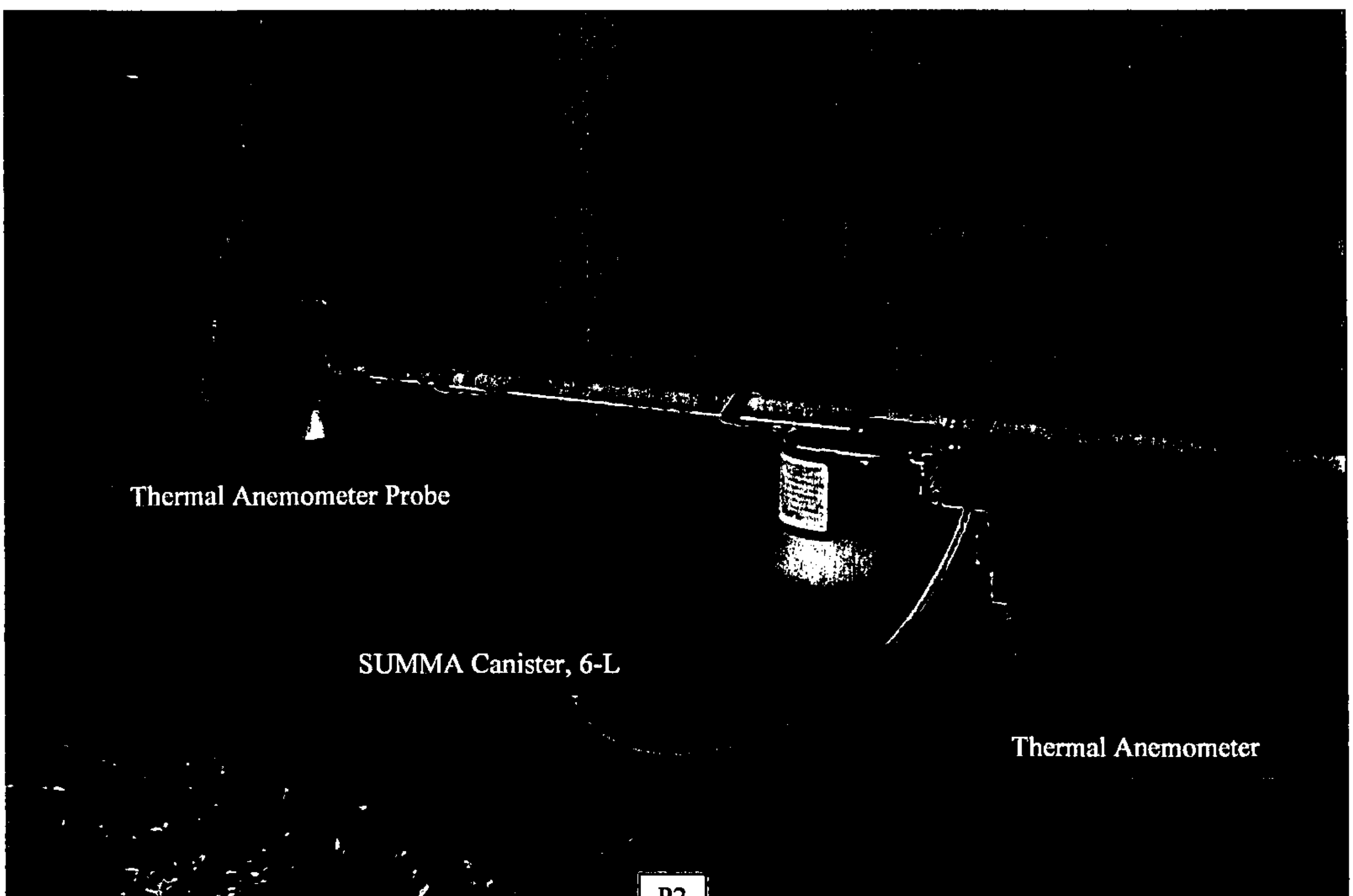



Plate 2 The in-house constructed sampling apparatus used for collecting grab samples, taking the sample temperature and making velocity measurements. Below is a full view of the sampling apparatus.



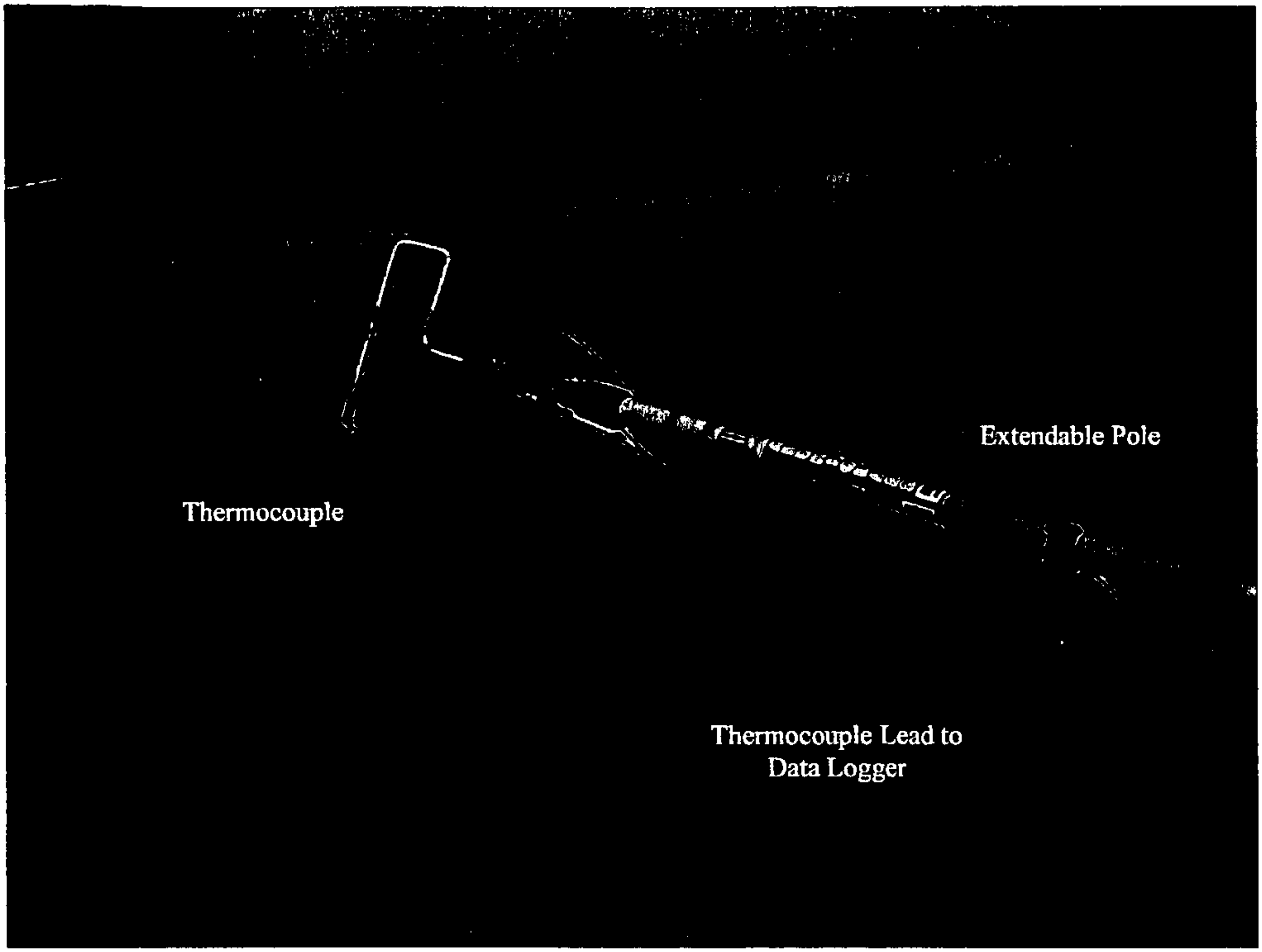



Plate 3 Asphalt probe apparatus

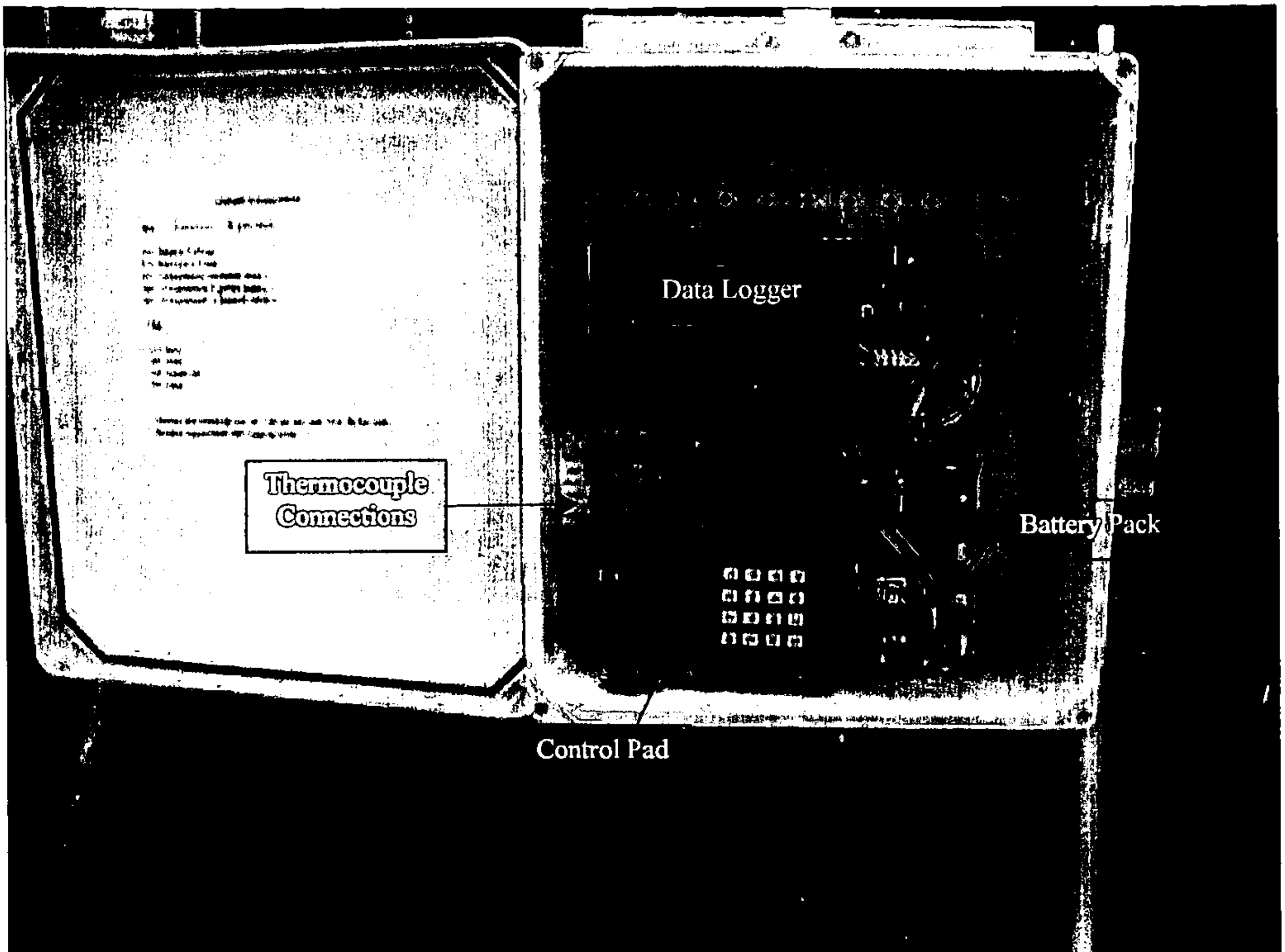


Plate 4  Temperature Data Logger with connections to the three temperature sensors (thermocouples)

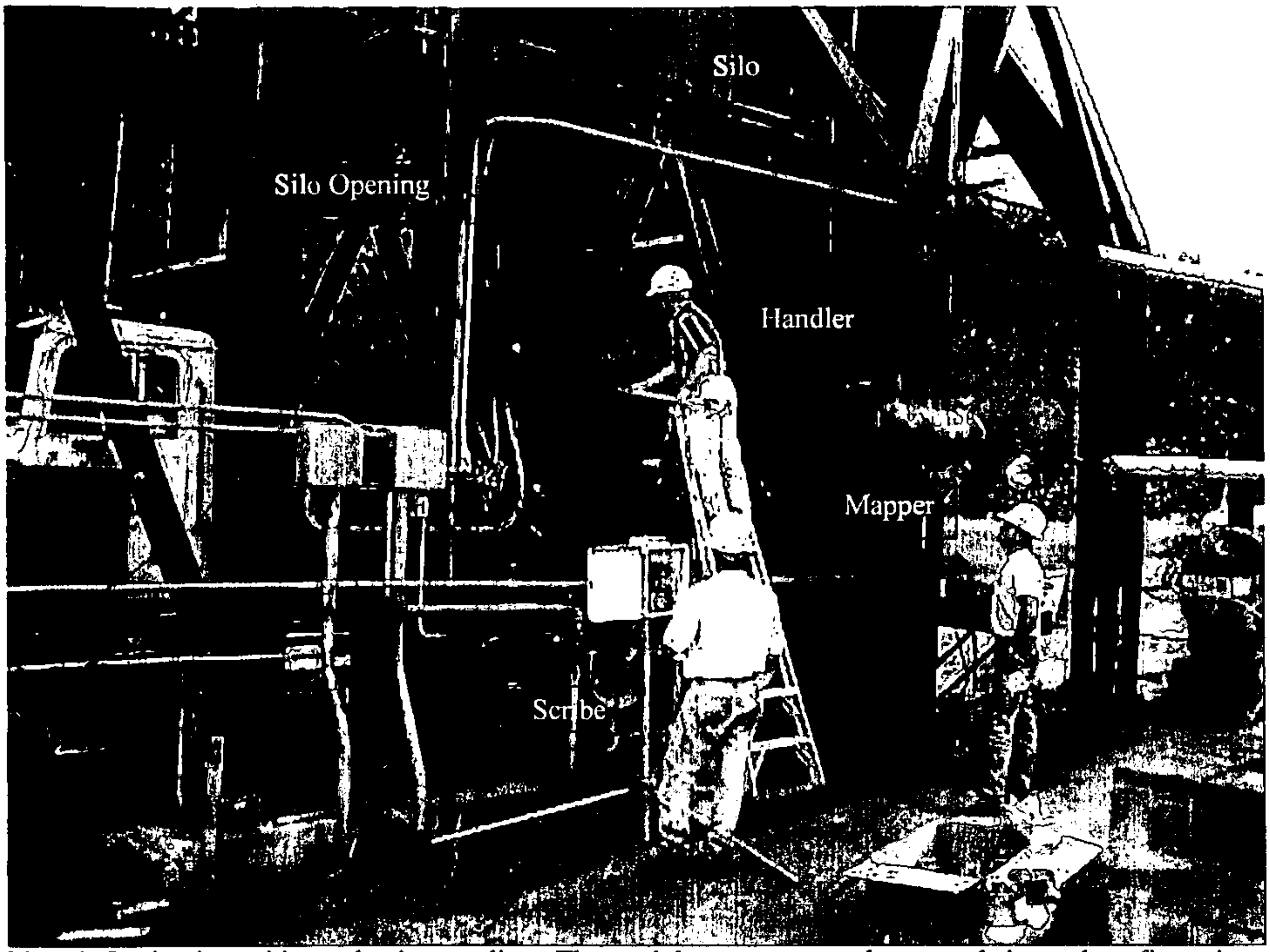


Plate 5 Getting in position to begin sampling. The truck here represents the general size and configuration of the trucks used for asphalt load-out.

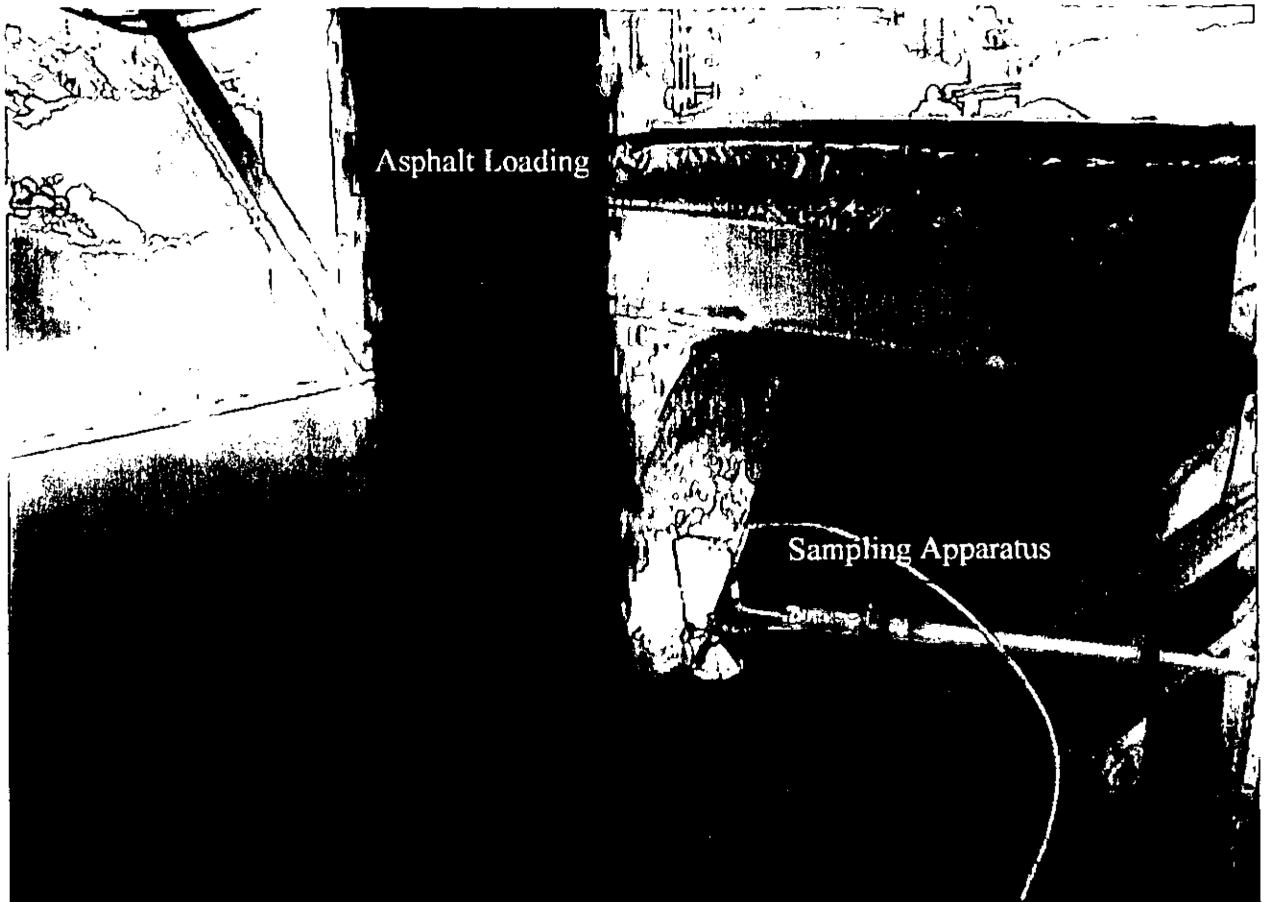



Plate 6 The loading process begins with a signal from the Handler or the Scribe to the silo operator.

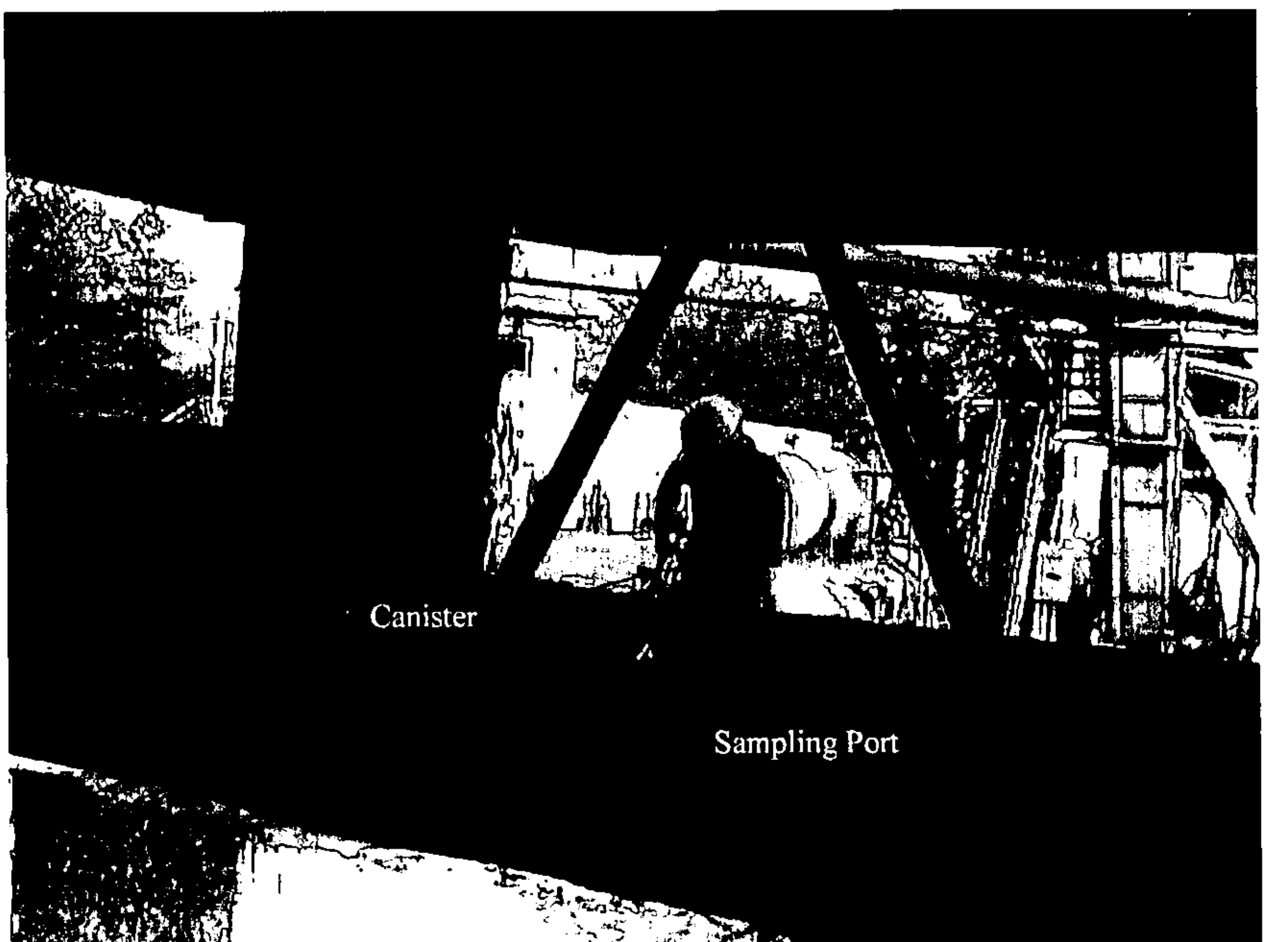



Plate 7 A few seconds later (3-4 sec) the valve is opened and the sample is taken over 1 minute. Note the sampling port is 6-8 inches over and inside the truck bed (Plates 8 & 9) during sampling.

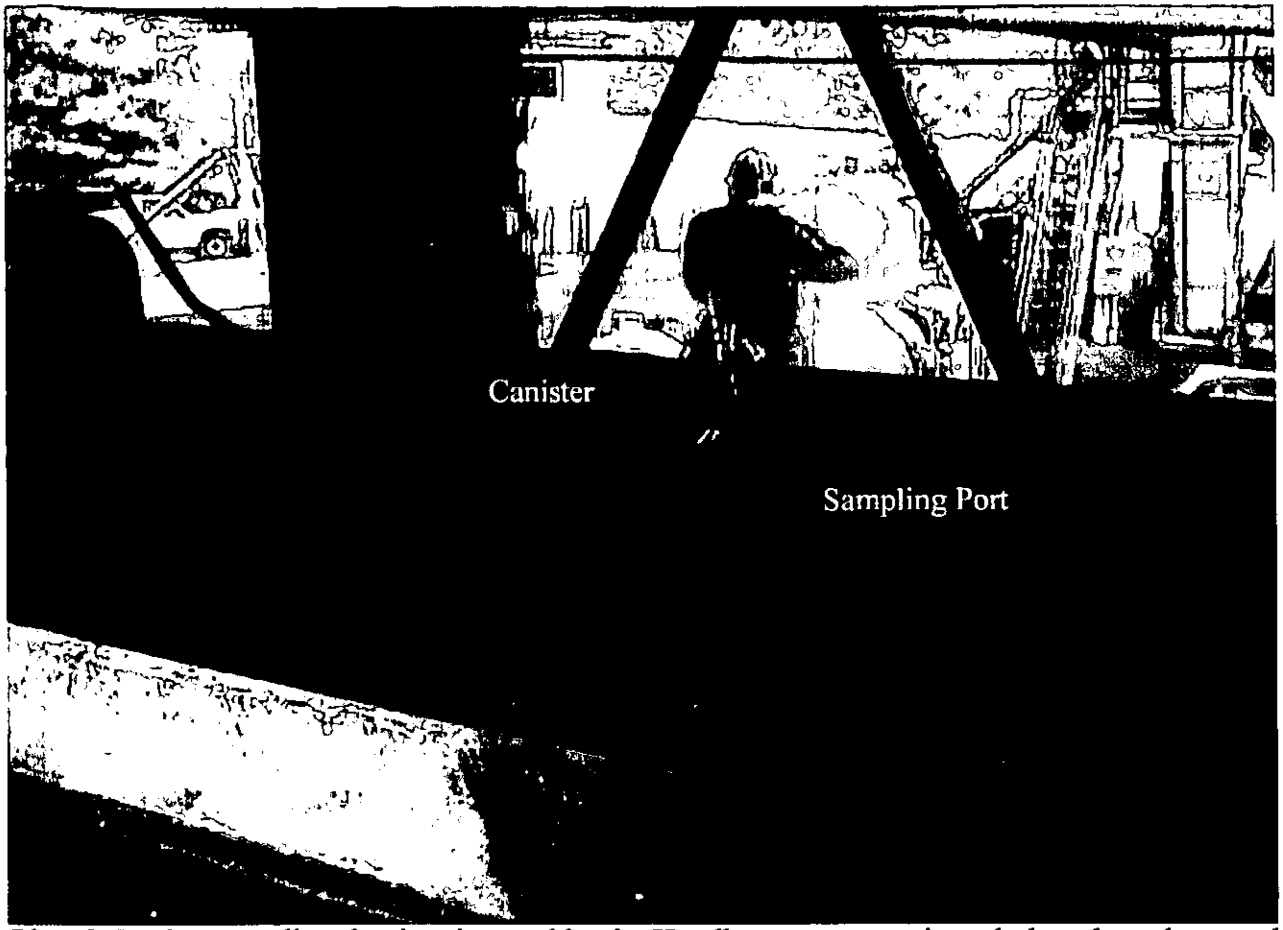



Plate 8 During sampling the time is noted by the Handler as to approximately how long the sample canister has been open. The Scribe signals for the closing of the canister at the end of 1 minute.

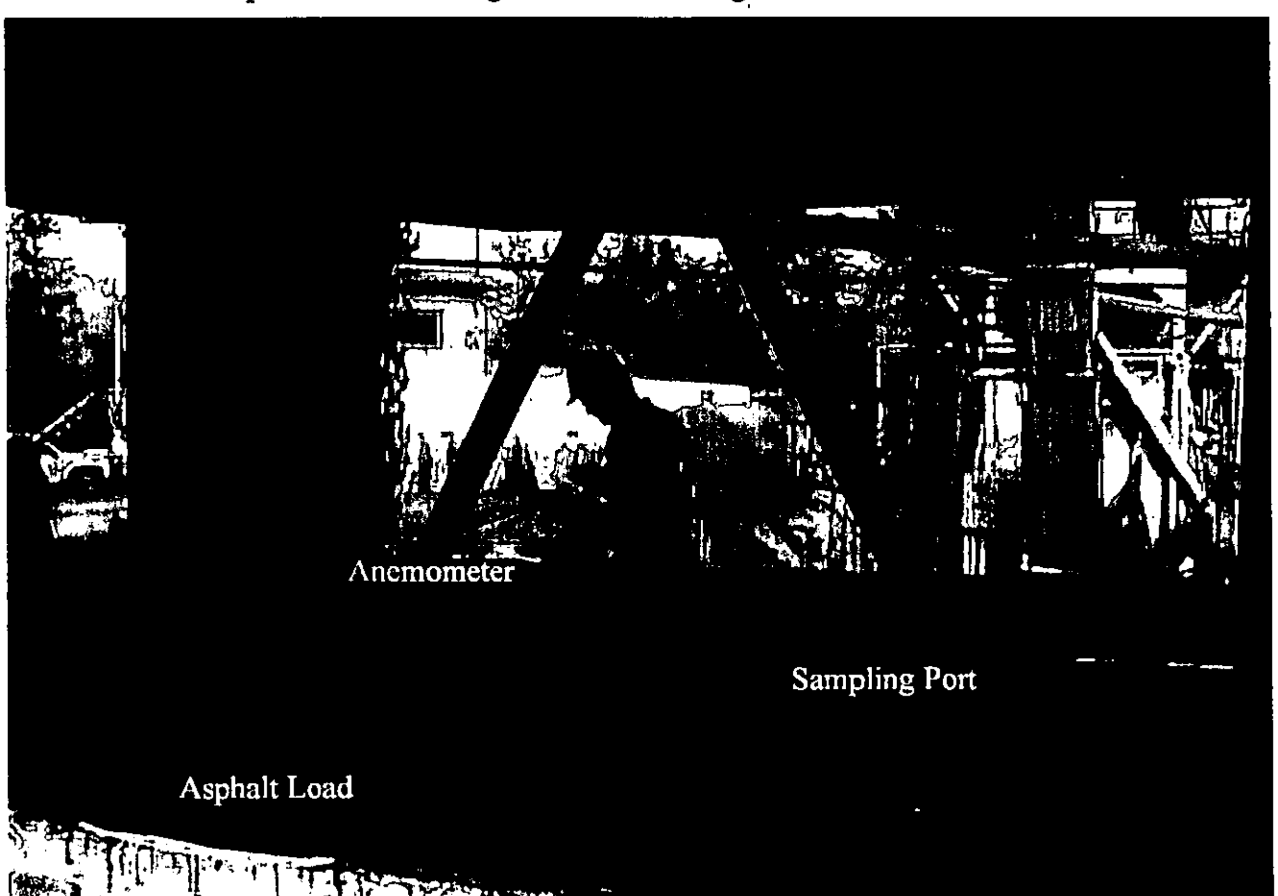



Plate 9 During the sampling, the Handler reads the maximum velocity measured by the anemometer. Truck nearly full within the one minute of the sampling.

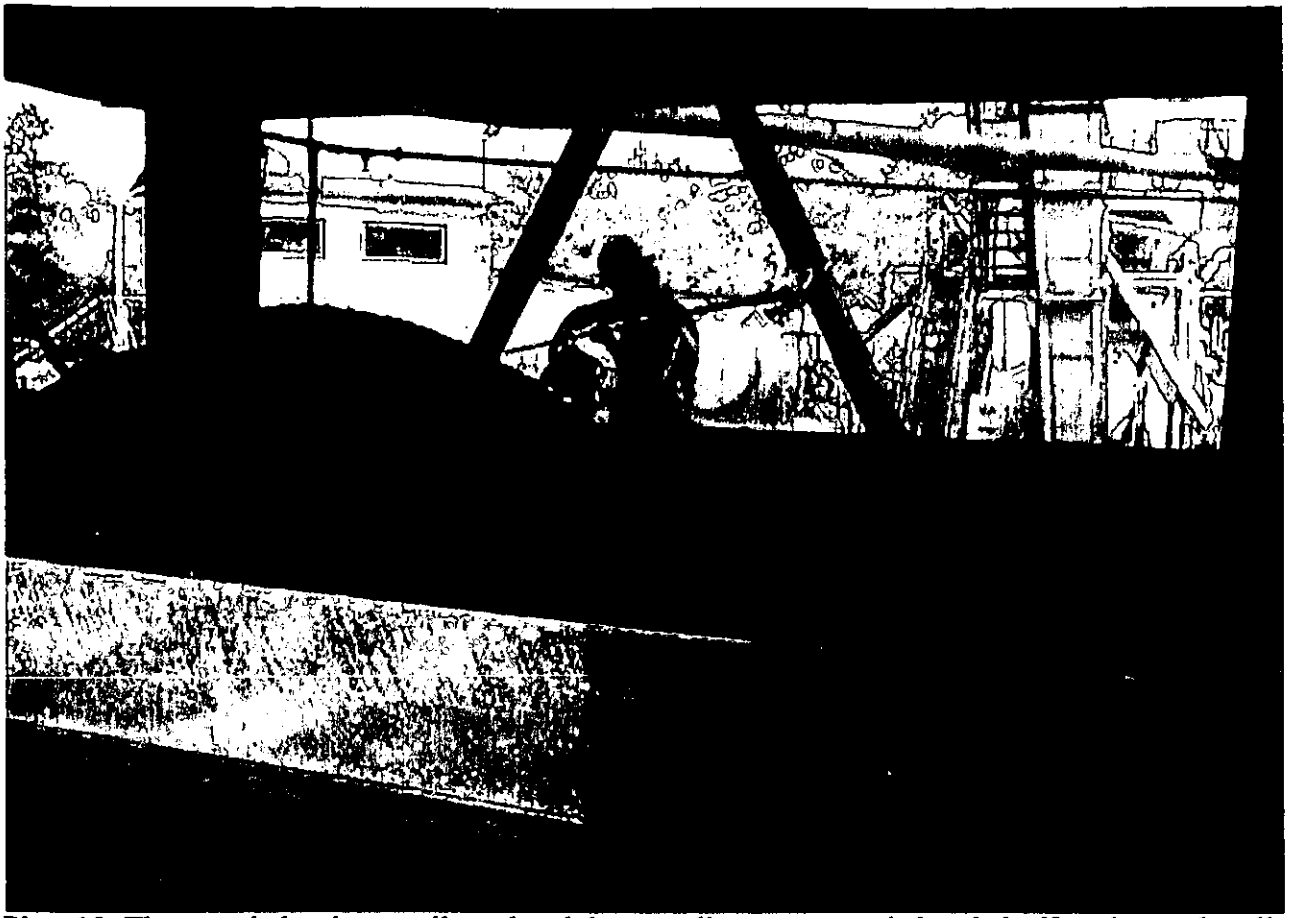


Plate 10 The sample has been collected and the sampling apparatus is handed off as the truck pulls forward and completes loading. The Handler then retrieves the asphalt temperature apparatus.

Plate 11 The Handler takes the temperature of the asphalt in the truck bed by sticking the thermocouple into the asphalt pile approximately 1-2 inches.