DIVISION OF AIR QUALITY
TOXICS PROTECTION BRANCH
AIR TOXICS ANALTICAL SUPPORT TEAM (ATAST)

ATAST Investigation Numbers 01007 and 01008

FINAL STUDY REPORT

SALISBURY AIR QUALITY MONITORING STUDY

August 29, 2003

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ACRONYMS

AFVR	Aggressive Fluid Vacuum Recovery
AAL	Acceptable Ambient Level
APAC	APAC-CAROLINA, Inc. Hot Mix Asphalt Plant
AQL	Air Quality Laboratory of the Toxics Protection Branch
AS	Air Sparging
Associated	Associated Asphalt, Inc. Asphalt Terminal
ATAST	Air Toxics Analytical Support Team
ATSDR	Agency for Toxic Substances and Disease Registry
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
cfm	cubic feet per minute
COC	Chain of Custody
DAQ	Division of Air Quality
DHHS	NC Department of Health and Human Services
DOT	NC Department of Transportation
EPA	U.S. Environmental Protection Agency
HAP	Hazardous Air Pollutants
HMA	Hot Mix Asphalt
H_2S	Hydrogen Sulfide
LA	Liquid Asphalt
MRO	Mooresville Regional Office
NAAQS	National Ambient Air Quality Standard
NC	North Carolina
NCAC	North Carolina Administrative Code
NIST	National Institute of Standards and Technology
PM	Particulate Matter
PM-10	Particulate Matter with aerodynamic diameter less than 10 microns
ppb	Parts per billion
ppm	Parts per million
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedures
SVE	Soil Vapor Extraction
SVOC	Semivolatile Organic Compounds
TAP	Toxic Air Pollutant
TPER	Toxic Pollutant Exemption Rate
VOC	Volatile Organic Compound

NOTICE

This report on the Salisbury Air Quality Monitoring Study was an effort to characterize air quality in the Milford Hills area in Salisbury, NC. The effort represents two separate but related investigations: ATAST Investigation 01007 to study volatile organic compound (VOC) issues and ATAST Investigation 01008 to study hydrogen sulfide (H_2S) issues. Accordingly, the report is organized to present and discuss VOC and H_2S topics separately to the extent possible. A variety of instruments, equipment, and other commercial products were used during this study. Mention of trade names or company names, or use of commercial products in this report, does not constitute an endorsement by either NCDAQ or ATSDR.

The draft report was completed April 30, 2002. Since only two sets of comments on the draft report were submitted (see Appendix I), the final report is essentially the same as the draft report. Following are the only changes worth mentioning in finalizing the initial draft report:

- In Section 3.2.2, three paragraphs were added qualifying the data produced by the RAE Systems monitor in the subsection “APAC HMA Preliminary Emission Data.”

- In Section 4.4.2, five paragraphs and 2 tables (Tables 15 & 16) were added describing the additional dispersion modeling DAQ performed on the current emission control configuration for the Associated Asphalt terminal.

- In Section 4.5.3, one paragraph and Table 20 were added to describe the situation with the highest H_2S monitoring data. Also, four paragraphs were edited to better clarify how the data were organized and managed to produce Table 21 and Figure 10 in the subsection “Relationship of Asphalt Facilities’ Process Data, Wind Directional Data, and H_2S Data.”

- Section 4.5.5 was created to summarize the nine sets of information that corroborate which asphalt facility was largely responsible for the local odor problem.

- In Section 5.2, three paragraphs were added to more completely represent the events and provisions involved in changing the DAQ permit issued to Associated Asphalt in November 2002.

- In Section 6 at the end of the first paragraph, the paper presented on this study at the National AWMA Conference in Baltimore in June 2002 is added.

PREFACE

This project, entitled the “The Salisbury Air Quality Monitoring Study,” was a collaborative effort. Collaborators were the NC Division of Air Quality (NCDAQ) Air Toxics Analytical Support Team (ATAST), the Agency for Toxics Substances and Disease Registry (ATSDR) in Atlanta, GA, the NCDAQ Mooresville Regional Office, and the City of Salisbury. In addition, the following companies cooperated in the study by providing data on their facility operations and/or emissions: Associated Asphalt, Inc.; APAC-CAROLINA, Inc.; Exxon/Mobil Co.; and Southern States, Inc.

The NCDAQ took the lead role for the study. This included project design and planning; field installation and data collection from the monitoring equipment; request, review, and approval of the H_2S emission test plan and test report for the Associated Asphalt terminal; collection of the preliminary H_2S emission data for the APAC-CAROLINA hot mix asphalt plant; and the data analysis and presentation of the results in this report.

The NCDAQ appreciates the assistance from those that contributed and cooperated in this effort. The following personnel with their affiliation were involved in the study:

• Lori Cherry	DAQ-ATAST
• Steve Schliesser	DAQ-ATAST
• Bryan Lange	DAQ-ATAST
• Jim Bowyer	DAQ-ATAST
• Jeff Hayward	DAQ-ATAST
• Mike Benson	DAQ-ATAST
• Julie Kinlaw	DAQ-ATAST
• Don Johnson	DAQ-ATAST
• George Kangkolo	DAQ-ATAST
• J. Thomas Anderson	DAQ-Air Quality Analysis
• Connie Washburn	DAQ-Air Quality Analysis
• Michael Landis	DAQ-MRO
• Jim Westmoreland	DAQ-MRO
• Carl Blair	ATSDR
• Greg Zarus	ATSDR
• Kim Chapman	ATSDR
• Richard Kelly	City of Salisbury
• Andy Jones	APAC-CAROLINA, Inc.
• John Kirk	Associated Asphalt, Inc.
• Larry Ettel	Associated Asphalt, Inc.
• William Medford	NC Dept of Transportation
• Ron Myers	U.S. EPA
• Ray Pierson	Lockheed Martin/REAC
• Jeffrey Burdette	TRC Environmental Corp.
• Andrew Pittner	NC Division of Groundwater

EXECUTIVE SUMMARY

SYNOPSIS

An ambient air monitoring study along with emission tests were conducted to estimate concentrations of several toxic pollutants in a residential suburban area adjacent to a liquid asphalt distribution terminal (Associated Asphalt, Inc.) and a hot mix asphalt plant (APAC-CAROLINA, Inc.). Data were collected at three monitoring sites from May through September 2001 for hydrogen sulfide (H_2S), volatile organic compounds (VOCs), and meteorological conditions. In addition, data were collected to characterize key parameters for process operations from both paving asphalt facilities, nearby road traffic, and odor complaints. These data were analyzed to evaluate relationships between H_2S and VOC concentrations, each asphalt facility's process operations, remediation activities, wind direction, and odor complaints. Integral to the monitoring study was a source test measuring emissions of H_2S and related odorous sulfur compounds conducted on the liquid asphalt terminal. Finally, dispersion modeling using emission data and emission factors was performed to determine compliance with NC regulatory acceptable ambient levels (AALs). Notable outcomes from this and related efforts include the following:

- Discovery that H_2S is the most emissive toxic compound identified to be emitted from the Associated Asphalt liquid asphalt terminal and appears to be emitted at significant levels from hot mix asphalt plants.
- H_2S emission control practice at many liquid asphalt terminals in NC is non-existent.
- Monitoring data, process data, citizen complaints, and dispersion modeling argue strongly that the liquid asphalt terminal is the primary contributor to H_2S levels above the odor threshold in the nearby area.
- Monitoring data and dispersion modeling show that ambient concentrations of benzene and other VOCs in Salisbury are typical of air in similar areas and communities.
- In March 2003 additional carbon beds were installed at the Associated Asphalt liquid asphalt terminal to control all the storage tank vents streams.

INTRODUCTION

This study was conducted in response to air quality issues arising from odor complaints and potential health concerns from residents of the Milford Hills area in Salisbury, NC. To address these concerns, the NC Division of Air Quality (DAQ) performed ambient air monitoring and dispersion modeling of the relevant air pollutants of interest such as volatile organic compounds (VOCs, namely BTEX (benzene, toluene, ethyl benzene, xylenes) and hydrogen sulfide (H_2S). The federal Agency for Toxic Substances and Disease Registry (ATSDR) provided H_2S monitors and technical assistance to support the quality control of the data produced by the monitors.

Additionally, ATSDR conducted sampling and analysis of several other compounds such as benzene-soluble particulate matter (PM), total organic compounds, polycyclic aromatic hydrocarbons (PAHs), and crystalline silica. This document does not address the ATSDR effort.

EXPERIMENTAL METHODOLOGY

Process data from each asphalt facility were collected throughout the 117-day study period. Process operations – and the corresponding emissions – for each asphalt facility varied in time depending on several factors. Asphalt facility process records were collected and formed an integral part of the project's data collection in order to evaluate any relationship with monitored data. Process data, accounting for 90% of asphalt facility emissions, were collected weekly and organized into a computerized database.

Source testing was performed at the Associated Asphalt distribution terminal under normal operating conditions using EPA Method 15 for H_2S. In addition, DAQ staff collected preliminary H_2S data at the APAC hot mix asphalt plant and the two companies with remediation (ExxonMobil and Southern States) performed VOC emission tests during the study.

Three monitoring sites were selected to characterize ambient air pollutant concentrations and meteorological data. Each monitoring site was configured with one meteorology station, one volatile organic compounds sampling system, and one hydrogen sulfide tape meter housed in a climate-controlled enclosure. Meteorological parameters measured were wind speed, wind direction, temperature, relative humidity, and barometric pressure.

Each VOC sampling system consisted of instrumentation to collect 24-hour ambient air samples in SUMMA™ canisters via XonTech™ 911A/912 equipment. The VOC sampling consisted of 24-hour periods from midnight to midnight. A total of 34 VOC samples covering 24-hour periods were collected on a random schedule and analyzed within the holding time. DAQ ATAST staff analyzed the ambient air samples for VOCs following EPA Method TO-14A. This method can identify and quantitate up to 40 organic compounds.

H_2S data for ambient air levels were collected using Zellweger Analytics Tapemeters™ obtained from ATSDR. This instrument uses a lead acetate-treated cloth tape reel to analyze for H_2S across 2-90 parts per billion (ppb) range. After each 15-minute sample period the concentration data were stored on an attached data logger.

STUDY RESULTS AND DISCUSSION

The analysis in this report provides several important insights into the origin and extent of perceived air quality issues in the study area. This was accomplished by evaluating the relationships among VOC concentrations, H_2S concentrations, emissive source profiles, meteorological conditions, and odor complaints. The significant findings from analyzing this large body of data included:

VOC Emissions. Two of the six emission sources were found to release benzene emissions above the NC DAQ permitting threshold, or toxic pollutant emission rate (TPER) value, of 8.1 lb/yr. These sources of benzene included the APAC hot mix asphalt plant (29 lb/yr) and the Southern States remediation site (58 lb/yr). The remaining four emission sources (Associated, Concrete Supply, Exxon/Mobil, and traffic from a one-mile stretch of Jake Alexander Blvd.) combined only emit 2.5-lb/yr benzene.

VOC Dispersion Modeling. Dispersion modeling prediction results show that benzene from Southern States is the only TAP in this study predicted to exceed its respective annual AAL guideline (1.2 x10^{-4} mg/m^3, 0.12 ug/m^3, or 0.038 ppb). Its predicted ground level maximum impact was 1.02 x10^{-3} ug/m^3 (0.32 ppb), a level 850% of the AAL. However, the predicted maximum impacts are centered in the immediate vicinity (within 50 m) of the emission source rapidly drop below AAL concentrations, and pose little/no long-term exposure potential to any individual. Furthermore, Southern States decided in March 2002 to discontinue operation of the air sparging system and is in the process of evaluating alternative technologies that will minimize or eliminate benzene emissions.

VOC Ambient Concentrations. Benzene, toluene, xylene and other VOC concentrations measured in the study were compared to 24-hour data from other sites similar to Salisbury and found to be in the same range. For example, the average 24-hour benzene concentration for Salisbury was 0.16 ppb, within the range of 0.13 - 0.24 ppb measured in other suburban and rural sites during 24-hour periods. DAQ concludes that in terms of ambient air quality, the concentrations measured in the Salisbury study indicate that the air in this area is typical of air in other similar areas. However, the concentration data from the Salisbury sites will be assessed in terms of health effects and risk assessment in a separate report through the NC Department of Health and Human Services (DHHS) and ATSDR.

H_2S Emissions. The results from this study provide new insight into the emissive profile of toxic compounds released from liquid asphalt and from hot mix asphalt operations. Comparison with VOC data shows that H_2S was by far the most emissive toxic compound from this particular liquid asphalt operation. New emission test data from Associated Asphalt showing 2,400 parts per million (ppm) H_2S from filling storage tanks with paving-grade liquid asphalt is in relative agreement with roofing asphalt data for levels up to 1,700 ppm. The derived emission factor for liquid asphalt railcar pumping operations is 0.0049 lb H_2S/ton of liquid asphalt. Facility wide emission rates for Associated were determined to be 0.41 lb/hr H_2S for normal operating conditions.

Preliminary data collected using hand-held instruments at the APAC hot mix asphalt (HMA) plant suggest H_2S emission concentrations on the order of 90 ppm and 6 ppm emitted from liquid asphalt storage tank filling and the dryer/mixer, respectively. Similarly, comparison with VOC data shows that H_2S is by far the most emissive toxic compound from this particular hot mix asphalt operation. Facility wide emission rates are estimated to be 0.76 lb/hr, a level above the TPER guideline of 0.52 lb/hr.

(Subsequent dispersion modeling shows a permissible AAL; see discussion below). The derived emission factor for the dryer/mixer operations is estimated to be 0.005 lb H_2S/ton of HMA produced.

H_2S Dispersion Modeling. Dispersion modeling results shows that the ground level maximum impact for H_2S was predicted to be below its respective hourly AAL of 2.1 mg/m^3 (~ 1500 ppb) for APAC (0.006 mg/m^3 or 4.3 ppb) and for Associated (0.404 mg/m^3 or 290 ppb), individually. The isopleth analyses for H_2S show that maximum impacts are distributed close to Associated's northern property boundary near the Access Road sampling site (within 30 m) and then rapidly diminish. In addition, ground level maximum impact concentrations above the odor threshold (0.011 mg/m^3, 8 ppb) were predicted for much of the area inside the Milford Hills subdivision. More favorable source characteristics accounted for a lower and more distant (100 m from its property line) predicted maximum impact point for APAC as compared to Associated.

H_2S Ambient Monitoring.
Measured 1-hour average H_2S data at the Access Road site located within 30 meters of the asphalt terminal exceeded odor threshold levels 28 times and approached or exceeded odor nuisance levels (40 ppb) only 3 times in 4 months. Measured 1-hour average H_2S data at the Cul-de-sac site located 200 meters from the asphalt terminal were above odor threshold levels only 4 times in 4 months, but did not approach odor nuisance levels. Measured 1-hour average H_2S data at the remediation site located 400 meters from the terminal neither exceeded odor threshold levels nor approached odor nuisance levels. Evaluation of the H_2S monitoring data relative to process and wind directional data revealed the following:

- H_2S ambient levels at the Access Road site were highest and occurred most frequently in the late evening hours when only the Associated Asphalt terminal was unloading railcars, its most H_2S emissive operation. The observation of peak H_2S ambient levels in the late evening is consistent with two other similar investigations performed by ATSDR. These peak H_2S levels can be explained by reduced conversion of H_2S to sulfur dioxide due to lower ozone levels and by reduced dispersion conditions, each of which is allied with late evening circumstances.

- H_2S ambient levels at the Access Road site were highest and occurred most frequently when only Associated was unloading railcars and the wind direction was from Associated.

Odor Complaints.
During the study the City of Salisbury documented 38 citizen complaints. Most of the complaints occurred when only Associated was operating.

Collective Data Base. Collectively, this body of results (H_2S source emission data, dispersion modeling, H_2S ambient monitoring data, process data, wind directional data, and odor complaints) point to the liquid asphalt terminal as the primary contributor largely responsible for the odor complaints and odor problem in Milford Hills.

SECTION 1

INTRODUCTION

This document serves as the Final Report for the Salisbury Ambient Air Quality Monitoring Study. The objective of the effort performed by the NC Division of Air Quality was to characterize the ambient air near the emission sources. It was done by monitoring ambient concentrations of hydrogen sulfide and volatile organic compounds released from nearby emission sources. The central issue behind this study was to determine whether the ambient air in the Milford Hill area contained air pollutant concentrations imposing a health concern or a nuisance from their odor. All data and results of the study, including this report, will be forwarded to the NC DHHS and the Agency for Toxic Substances and Disease Registry (ATSDR) for a human exposure assessment as well as for a subsequent report through DHHS.

The following report describes each part of the study, how the parts were integrated into the overall project, and the project results. The document describes the:

- Emission sources under investigation,
- Ambient monitoring methods at three sampling stations,
- Quality assurance and quality control activities, and
- Related project data collection, management, modeling, and analysis results.

1.1 BACKGROUND

Two distinct forces converged to establish the basis for this environmental study. One was a grass roots effort driven by the local community warranting the attention of local, state, and federal government agencies to evaluate odor nuisance and potential human health concerns posed by a nearby cluster of industries. The second was a growing body of technical data supporting the feasibility that H_2S emissions from the asphalt facilities could be high enough to exceed the H_2S odor threshold and, in combination with VOCs, potentially approach or exceed levels deemed acceptable to human health.

1.1.1 Historical Background

Milford Hills is a long-established sub-division within the City of Salisbury, North Carolina located on its northwest side off Jake Alexander Boulevard. Also located nearby on Jake Alexander Boulevard are a cluster of industrial properties with current and previous commercial operations, most of which do or did involve petroleum products. Current operations include two asphalt-related businesses and one concrete batching plant, while past operations also included a large gasoline terminal and an above ground storage tank with a retail fuel dispenser island where there are now two sites undergoing soil and water remediation.

The City's recent land use study showed the following suburban character of the area near the asphalt facilities:

- Within a ½ mile radius there are approximately 950 residents, five churches, five restaurants, and twelve other public gathering and business locations; and
- Within a one-mile radius there are an additional 2900 residents, one church, nine restaurants, and five other public gathering and business locations.

Between 1997 and September 2001 the residents in this area registered on the order of 400 asphalt-related odor complaints to either the City of Salisbury or the Mooresville Regional Office of the Division of Air Quality (DAQ). Notice of Violations for odor nuisance have been issued several times by the City of Salisbury and once by DAQ.

The federal Agency for Toxic Substances and Disease Registry (ATSDR) received three petitions in the year 2000 for a public health assessment of these asphalt facilities. The local environmental group, the Rowan County Health Director, and the NC State Health Director submitted the petitions, citing an allegedly high incidence of serious health problems in nearby residents and workers. A concerned citizen reported to ATSDR that over 60 residents and workers have developed cancer-induced fatalities, debilitating cancers, diabetes, strokes, severe respiratory illnesses, miscarriages and behavioral/learning problems believed to be related to contamination in the air and other media in the local environment.

Upon completing their review of the petitions and alleged evidence of contamination, ATSDR determined that the petitions met their criteria for conducting public health assessment activities. Under authority of the Comprehensive Environmental Response, Compensation, and Liability Act, ATSDR is conducting a public health assessment of Associated Asphalt and APAC-Carolina, both located on Jake Alexander Boulevard in Salisbury, NC.

As is customary, ATSDR requested the assistance of the responsible state agencies, NC DAQ and the NC Department of Health and Human Services, to participate in this assessment. Towards this end, the NC DAQ agreed to conduct the majority of the ambient monitoring study, the scope and results of which are described in this report.

1.1.2 Technical Background

Liquid asphalt is defined by the American Society for Testing and Materials as a brown to black colored cementitious material in which the predominant constituents are bitumens occurring in nature or produced in petroleum processing.[1] Liquid asphalt is produced at many oil refineries, where crude oil is distilled into various low molecular weight fuels and, from what is left after distillation, is made into high molecular weight asphalt for paving, roofing and sealing. Asphalt is a complex mixture with hundreds of organic compounds varying so widely in concentration that its exact molecular composition is seldom attempted and defies definition. Accordingly, it is a commercial material specified and sold in terms of its physical and engineering properties (flash point, viscosity, penetration, ductility, etc.) rather that its composition and purity. The generally accepted composition of most asphalt is 79-88% carbon, 7-13% hydrogen, 0.1-6% sulfur, 0.1-2% nitrogen, and 0.1-1.5% oxygen.[1, 2] Liquid asphalt is classified in terms of its engineering performance; most asphalt is produced as Performance Grade (PG) 64-22, PG 70-22, and PG 76-22. The numerical values in the PG rating indicate the working temperature range of the asphalt in degrees Centigrade (°C); e.g., PG 64-22 can be applied between 64°C and minus 22°C.

The oil industry began studying the distribution of sulfur in crude oil in 1891.[2] Many crude oils contain sulfur compounds and those crudes with greater than 1% sulfur are accompanied by a gas with H_2S properties. During oil refining, much of the original sulfur is converted to H_2S and organosulfur compounds. Sulfur compounds are important constituents in asphalt, as sulfur is beneficial in strengthening and hardening asphalt.[2] High levels of sulfur in liquid asphalt can lead to the release of sulfur gases such as H_2S during its processing and commercial distribution.

H_2S is a malodorous compound with known irritant, neurotoxic and asphyxiant properties. It is highly volatile, with a vapor pressure of 15,200 mm Hg at 78°F, and has an atmospheric half-life of approximately 2 days.[3] H_2S is a leading cause of occupational mortality and exposures above 500 ppm can lead to serious adverse effects including pulmonary edema, unconsciousness, coma and death.[4] Ironically, olfactory paralysis, a neurological phenomenon that results in an impaired ability to detect odors, may be experienced following H_2S exposures above 50 ppm. There is unambiguous evidence of toxicity following short- and long-term exposure to H_2S at levels above 10 ppm; adverse effects include irritation of the eyes, nose and throat, ocular toxicity, and headache and nausea. [4-6] Human health effects associated with single digit (less than 10) ppm and ppb-level exposures include altered metabolism, asthmatic responses, and physiological or psychological responses to the detection of foul odors, including headache, nausea, loss of appetite and emotional disturbances. [7-12]

Despite the clear evidence for adverse health effects, H_2S is not currently listed by the US EPA as a hazardous air pollutant (HAP). This in part explains why H_2S emissions from asphalt operations are normally overlooked in air quality activities.[13] Following a study on the petroleum industry, EPA concluded in 1993 that there was “no evidence of significant threat” posed by H_2S emissions.[14, 15] Besides oil, there are other major industries with considerable H_2S emissions, including paper, coke, refuse, food, fertilizer, agriculture, and animal production. Currently, at least ten States have or are pursuing development of new emission control rules and/or health protection programs relative to H_2S.[16] And because several agencies have petitioned EPA to relist H_2S as a HAP, EPA is currently reevaluating this issue.[14]

Given its emissive, toxic, and odorant properties and widespread industrial profile, it is little wonder that there is an emerging push to investigate issues concerning emissions, emission control, and odor from asphalt and its anti-strip additives. There is ample evidence supporting the supposition that H_2S emissions from asphalt facilities could be of concern, including:

- Numerous citizen complaints statewide in NC relating to foul odors believed to be associated with liquid asphalt and/or anti-strip additives used at asphalt facilities.

- Material Safety Data Sheets from asphalt suppliers noting H_2S content in asphalt up to 1% with strong precautionary statements about H_2S exposure dangers to workers.[17]
- Recent experience with a serious odor problem caused by H_2S emissions up to 1,000 ppm and 7 lb/hr from emulsified liquid asphalt storage, resolved by a mist eliminator, regenerative catalytic oxidizer, and wet scrubber.[18]
- Data in Owens Corning report showing H_2S concentrations up to 1,700 ppm from roofing asphalt storage tanks.[13]
- Patent statements by Owens Corning that "The trend in worldwide sources of asphalt is that … the sulfur content is steadily increasing… One of the problems with asphalt processing is… unpleasant gaseous byproducts. Sulfur …compounds are a significant component of these gaseous emissions, … including…H_2S."[19]
- At least four other patents from the 1970s-1990s, including three by major oil companies, dealing with emissive behavior or other technical issues inherent with the fact that liquid asphalt contains H_2S in appreciable quantities.[20-23]

1.2 OBJECTIVES

The objectives of this multi-dimensional project were to:

- Measure and characterize the airborne concentrations of several toxic air pollutants (TAPs), including hydrogen sulfide (H_2S) and volatile organic compounds (VOCs).

- Collect signature process and emission data on the TAP sources.

- Perform dispersion modeling using source emission data to compare with the acceptable ambient level guideline levels for NC TAPs.

- Analyze the body of data and correlate any relationships among VOC concentrations, H_2S concentrations, emissive source profiles, meteorological conditions, and odor complaints.

1.3 SCOPE OF THE PROGRAM

The scope of the project activities included:

- Selection of three sample collection sites based on regional meteorology, micrometeorology and topography.
- Collection of meteorological data for wind direction, wind speed, temperature, relative humidity, and barometric pressure.
- Installation and operation of H_2S tape meters at three sites for continuous measurement of this pollutant.
- Installation and operation of VOC sampling systems at each of the three monitoring sites.

- Analysis of the VOC sample extracts for the identification and quantification of up to 40 organic compounds using the U.S. EPA Method TO-14A procedure.
- Collection of data depicting process operating levels and schedules for the nearby asphalt facilities.
- Collection of emission data for the asphalt facilities and the remediation sites.
- Inclusion of local citizens complaints to document and report objectionable odor events.
- Analysis and interpretation of the process, emissions, meteorological, VOC monitoring, H_2S monitoring, dispersion modeling, and complaint data.
- Preparation of a detailed report for peer review and subsequent public release.

1.4 REPORT ORGANIZATION

Following the executive summary, the synopsis, background, objectives, and scope of the air quality monitoring study are given in **Section 1**. **Section 1** also provides the overall picture, including the potential human health effect concerns and the technical feasibility that served as the basis for the study. **Section 2** describes the facility processes and pollutants for the nearby emission sources. Included is a discussion of the collected data depicting process operating levels and corresponding time periods for the nearby asphalt facilities.

Section 3 covers the methodologies and instrumentation used in collecting the project data. Included is a discussion of the how the process data was collected and the source emission measurements were performed. Three types of air quality and meteorological monitoring systems/instruments were used to characterize the air quality of the Milford Hills neighborhood. The purpose, scope and applicability of using each of these systems are discussed in detail in **Section 3** of this report. A large volume of data was generated during the study period using a variety of instrumentation and equipment. **Section 4** presents and summarizes the results and provides a detailed discussion of the implications of these results to the Milford Hills air quality. Also included in this section are the details of the evaluation of the correlations among asphalt facilities' process operations, monitored pollutant levels, and wind directional data during the study period. The concluding remarks of the study and recommendations for further work are given in **Sections 5** and **6** respectively. References cited in the text of report are in **Section 7**.

An electronic appendix containing data storage folders for raw and tabulated meteorology, VOC chemistry, process, and H_2S data is included with this report. Meteorology data are broken down into data tables and stored for each month and site. VOC data are filed for each site. H_2S data are filed for each site for each monthly averaging period. And citizen complaint data are included as well as dispersion modeling results and the Quality Assurance Project Plan.

SECTION 2

EMISSION SOURCE PROCESS DESCRIPTIONS

Located near the Milford Hills community is a cluster of industrial properties on Jake Alexander Boulevard with current and previous commercial operations. Four of the five industries involve petroleum products in current or past businesses. The current operations include two asphalt-related businesses and one concrete batching plant, while the past operations involved two bulk petroleum storage facilities where there are now located two sites undergoing soil and water remediation. **Figure 1** is an aerial photograph taken of the study area prior to the modification of the asphalt terminal facility made by Associated Asphalt, Inc. in 1997. The photograph is useful in that it illustrates the orientation of the monitoring stations relative to the asphalt facilities and remediation sites. The roadway leading from the bottom to the top of the photo is Jake Alexander Boulevard, and the diagonal line running from left to right in the photo is the rail line crossing Jake Alexander Blvd. The monitoring sites and industrial sites in **Figure 1** are numbered according to the following legend:

A	Cul-de-sac DAQ Monitoring Site [Neighborhood Exposure Site]
B	Access Road DAQ Monitoring Site [Source Dominated Site]
C	Remediation DAQ Monitoring Site [Upwind and Off-axis Site]
1	Concrete Supply Batch Concrete Plan
2	APAC-CAROLINA Hot Mix Asphalt Plant
3	Associated Asphalt, Inc. Distribution Terminal
4	Exxon/Mobil Remediation Site
5	Southern States Remediation Site
6	Southern Railway
7	Jake Alexander Boulevard

2.1 ASSOCIATED ASPHALT, INC. LIQUID ASPHALT TERMINAL

The Associated Asphalt, Inc. (Associated) facility is a liquid asphalt distribution terminal handling 120,000-tons/yr of liquid asphalt on a year round 24-hours a day schedule. Associated is located at 1825 Jake Alexander Blvd. in Salisbury, NC. Between 1997 and 2001 Associated expanded its processing capacity 6-fold (from 630,000 to 4,000,000 gallon storage tank capacity) and its boiler capacity 7-fold to heat asphalt in the storage tanks. This expansion has lead to an 85% relative rise in sales of liquid asphalt from 65,000-tons in 1997 to 120,000-tons in 2001. Liquid asphalt handling operations include rail car unloading, tank storage, and truck offloading all within a temperature range of 280-310°F. Roughly 90% of the liquid asphalt sold at Associated is PG 64-22, with the balance PG 70-22. **Table 1** identifies the specific emission sources at the Associated Asphalt terminal and the APAC Hot Mix Asphalt plant that are enumerated in **Figure 2** **Figure 2** shows an aerial view of the two asphalt facilities; Associated is shown in the foreground and APAC is in the upper right hand corner of the picture. North in **Figure 2** is to the right.

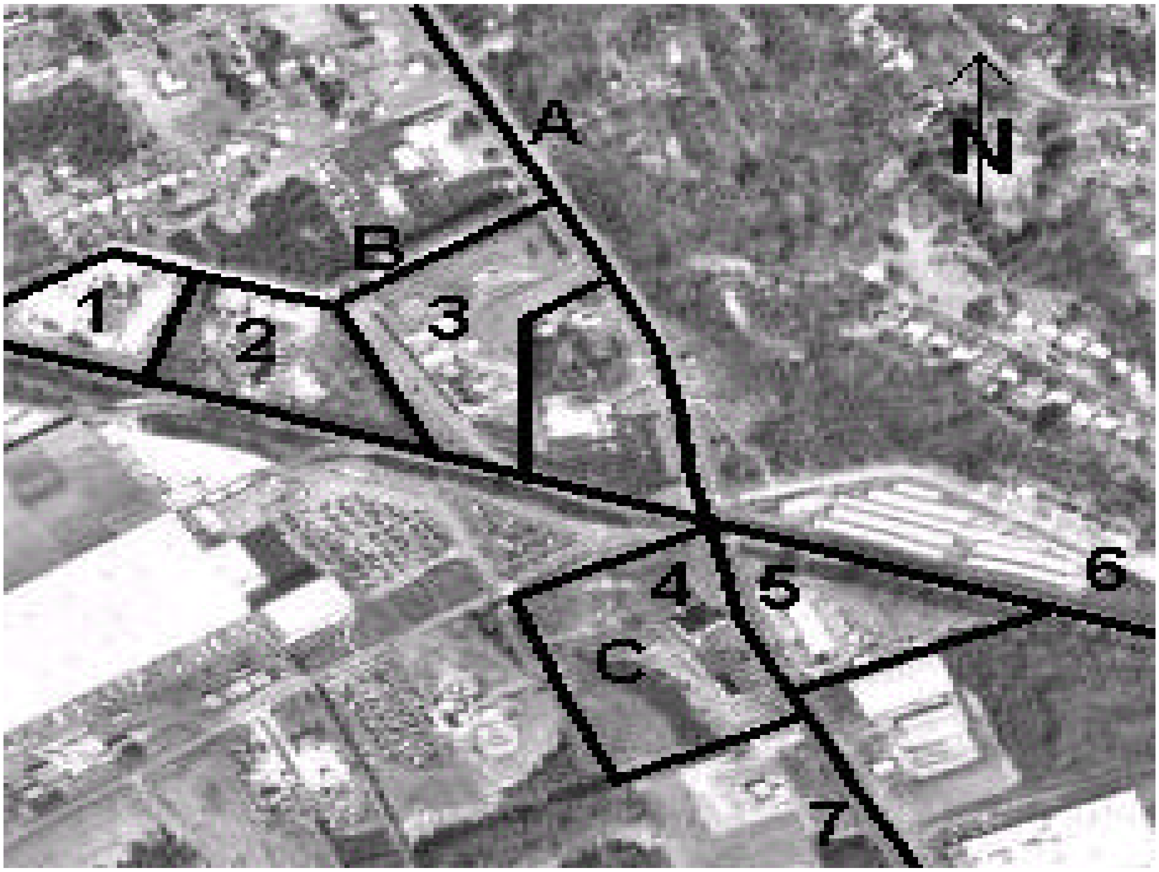


Figure 1. Salisbury Study Area. Aerial View of the Salisbury Monitoring study area showing the monitoring stations (A [Cul-de-sac], B [Access Road], C[Remediation site]), asphalt facilities (2, 3), concrete plant (1), remediation sites (4, 5), Southern Railway (6), and Jake Alexander Boulevard (7).

2.1.1 Railcar Operations

The terminal receives product from various refineries in railcar shipments delivered on average about 6 times per month. Each railcar is 21,000-gallons in capacity, 50-feet long and 10-feet in diameter containing 90-tons of liquid asphalt (density of 8.4-8.7 lbs/gal). The railcar unloading area consists of two parallel sets of rail lines, each capable of holding nine railcars (7 in **Figure 2**). Shipments range from 8 to 18-railcars and, once received, take 1-3 days to reheat and unload.

Natural gas-fired boilers produce steam to reheat the liquid asphalt in the railcars. Heating generally takes between 12 to 24-hours depending on the arrival temperature, ambient temperature, and thermal performance of the individual railcar. Heating of individual railcars continues until a target temperature of 280°F is reached, as determined by a portable thermocouple. After heating, liquid asphalt is pumped through insulated, steam-heated piping into storage tanks. The unloading pumps operate at a rate of 200-350 gallons per minute (gpm). Typically a single pump unloads 1-3 railcars simultaneously. A single railcar unloading takes approximately 1-1½ hours, and correspondingly longer time when multiple railcars are pumped simultaneously. There are no effective emission controls in place on the railcar hatches. The hatches are opened during heating and unloading as a safety measure.

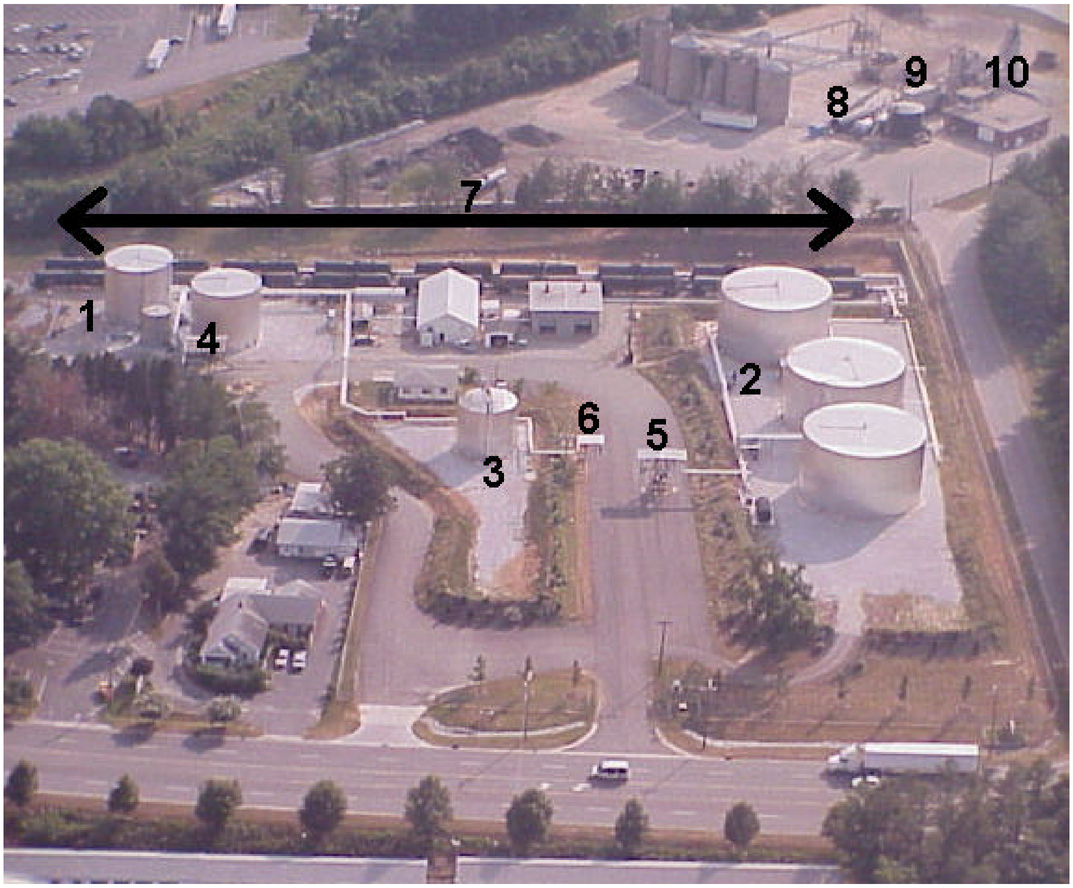


Figure 2. Aerial View of the Asphalt Facility Sites showing the emission sources at the liquid asphalt terminal (1-7) and at the hot mix asphalt (8-10).

Table 1. Emission Sources at Two Asphalt Facilities

Asphalt Facility	**Source ID in Figure 2.**	**Emissive Activity**
Associated Terminal	1	Tank System 1- Two 400,000-gallon storage tank vent
	2	Tank System 2- Three 1,000,000-gallon storage tank vent
	3	Tank System 3- One 200,000-gallon storage tank vent
	4	Tank System 1-Truck Loadout from tank system 1
	5	Tank System 2-Truck Loadout from tank system 2
	6	Tank System 3-Truck Loadout from tank system 3
	7	Rail lines for 18 Railcars
APAC Hot Mix Plant	8	Liquid Asphalt Storage Tank
	9	Dryer Exhaust
	10	Truck Loadout

2.1.2 Storage Tanks

Liquid asphalt is stored at Associated in three tank systems: two 400,000 gallon tanks (1 in **Figure 2**), three 1-million gallon tanks (2 in **Figure 2**), and one 200,000 gallon tank (3 in **Figure 2**). Each storage tank is insulated and cylindrical with a fixed-roof design and comparable height-to-diameter ratio. The tanks are splash filled from the top. While liquid asphalt is stored in the tanks, hot oil heaters maintain a temperature near 300°F for PG 64-22 and 310°F for PG 70-22. Liquid asphalt is stored in the tanks until pumped to the nearest truck loadout station.

Each tank system was separately vented with hard plastic ducting and treated by an individual scrubber spraying a dilute solution of plant oils, known as Ecosorb® solution.[24] A knockout tank to collect condensed oils precedes the scrubber. There is no induced draft fan on the scrubber system. Rather, gas flow is forced from displaced air during tank filling. The physical dimensions for each of the three sizes of storage tanks are presented in **Table 2**.

Table 2. Dimensions for Associated Asphalt Storage Tanks

Identification	Storage Capacity, gallons	Height, feet	Diameter, feet
Tanks 1, 2, and 3	1,000,000	40	66
Tanks 4 and 6	400,000	40	41
Tank 5	200,000	30	34

In January 2002 after the study was completed, DAQ withdrew Associated Asphalt's temporary permit requiring Associated to remove the Ecosorb® scrubbers and replace them with activated carbon beds to control the storage tank vents. This action was taken due to the odor complaints received by the City of Salisbury and the fact that the emission testing reported in November 2001 indicated that the Ecosorb® scrubbers were not reducing emissions of odorous compounds.

2.1.3 Truck Loadout

Liquid asphalt is distributed to tanker trucks at three loadout stations (two stations have dual loading bays). The tanker trucks are filled to 80% capacity, or 6000 gallons (nominal 25 tons), and splash filled from the top at a 500-gpm pump rate. The same type pumps are used in truck loadouts as used in railcar unloading, but the shorter distance and reduced viscosity from higher temperature account for the higher pump rate. A NC Department of Transportation (DOT) required anti-strip material primarily composed of amine compounds is normally added to the asphalt during loadout to enhance its adhesion properties in ¼, ½, or ¾ % proportions by volume. Generally about 65% of the truck loadouts (4-6 in **Figure 2**) contain anti-strip additive.

Each truck loadout station is separately vented with flexible and hard ducting and treated by a 1000 lb activated carbon bed. Gas flow through each system is induced through a 1,000 cubic feet per minute (cfm) rated fan.

2.1.4 Combustion Sources

There are two natural gas fired boilers rated at 12.6 million British thermal units (Btu) per hour to produce steam for heating the liquid asphalt in the railcars. There are also two small natural gas fired hot oil heaters using Dowtherm™ for heating liquid asphalt in the storage tanks.

2.2 APAC-CAROLINA HOT MIX ASPHALT BATCH PLANT

The APAC-Carolina Plant (APAC), located at 1831 Jake Alexander Blvd. in Salisbury, NC, produces hot mix asphalt (HMA) which is used as paving for highways and roads. HMA consists of a mixture of roughly 95% aggregate (various sizes of gravel and sand) and 5% liquid asphalt, both of which are heated and mixed in measured quantities. The APAC facility is considered a typical batch mix plant with a maximum permitted production rate of 180 ton/hour at 61.2 million Btu/hr heat input. APAC's annual production level during its 2001 fiscal year was 101,000 tons, representing a nearly 50% relative increase from its 1999 production quantity of 68,000 tons.

Raw aggregate is stockpiled at the plant with the bulk aggregate moisture content typically in a range between 3 to 5percent by weight. APAC has several storage silos to house a variety of aggregates. It also has a 15,000 gallon heated tank to store PG 64-22 liquid asphalt (8 in **Figure 2**) with a natural gas fired boiler to maintain the temperature at 300°F. APAC normally receives liquid asphalt with a 0.5% mixture of anti-strip additive. A computerized system is used to control and record process operation.

2.2.1 Dryer/Mixer

The most significant ducted emission source from batch mix HMA plants is the rotary drum dryer and mixer (9 in **Figure 2**). Natural-gas fired dryer emissions primarily consist of particulate matter (PM), products of combustion, and small amounts of inorganic metals; mixer emissions primarily consist of numerous organic HAP compounds.[25, 26]

The APAC dryer/mixer is equipped with a "scavenger" and baghouse system for PM emission control. The dryer exhaust gas is contained in ducting and drawn through the baghouse by an induced draft fan. The scavenger system merely carries PM and gaseous emissions from various aggregate transfer points and the mixer in a series of hoods and connected ductwork for transfer to the baghouse. The baghouse is a reverse-air-cleaned system with Nomex™ bags designed to operate within a pressure drop range of 3-7 inches water column with an exhaust gas temperature of 250-270°F. While such a baghouse is highly effective (typically 99% efficiency) in removal of PM and other solid-phase pollutants, it is inherently ineffective (typically < 1% efficiency) for removal of gaseous pollutants such as H_2S and VOCs.

2.2.2 Batch Truck Loadout

APAC maintains only one loadout station. All HMA batches are produced to the customer's specifications and generally sold immediately after production. Customers drive directly underneath the mixer where HMA is dumped into the truck bed (10 in **Figure 2**). The typical loadout size is 16 tons.

2.2.3 Combustion Source

There is a small natural gas fired boiler for heating liquid asphalt in the 15,000 gallon storage tank.

2.3 EXXONMOBILE REMEDIATION SITE

Petroleum contaminated soil and groundwater, resulting from historic releases at the former Exxon Terminal bulk petroleum storage facility at 1715 Jake Alexander Blvd, has been under active remediation since July 1998. The ExxonMobil remediation facility has used the following combination of remedial technologies to address the contamination: soil-vapor extraction (SVE), bioventing, monitored natural attenuation, and aggressive fluid vacuum recovery (AFVR).

SVE is an *in situ* remediation technology designed to promote the volatilization of petroleum hydrocarbons in the soil. A SVE system uses a series of extraction points that are screened in the soil above the water table and piped to vacuum that induces the movement of vapor through the soil. As the soil vapors migrate towards the extraction points, VOCs volatilize and are removed from the subsurface. These vapors are concentrated by the system and, at the ExxonMobil facility, emitted to the atmosphere through a short stack. Bioventing is an in situ remediation technology that uses native microorganisms to biodegrade organic constituents adsorbed to soils in the unsaturated zone. Soils in the capillary fringe and the saturated zone are not affected. In bioventing, the activity of the native bacteria is enhanced by inducing air (oxygen) flow into the unsaturated zone (using extraction or injection wells) and, if necessary, by adding nutrients. When extraction wells are used for bioventing, the process is similar to SVE. However, while SVE removes constituents primarily through volatilization, bioventing systems promote biodegradation of constituents and minimize volatilization (generally by using lower air flow rates than SVE). In practice, some degree of volatilization and biodegradation occurs when either SVE or bioventing is used. Monitored natural attenuation is an in situ remediation technique that results from the combination of several naturally occurring processes in the subsurface. The processes, which include biodegradation, adsorption, dilution and dispersion, remove the contamination. The effectiveness of this technique is assessed by regular sampling of monitoring wells. AFVR is an event-based *ex situ* remediation technique for treatment of soils and groundwater containing multi-phase VOCs. In a typical AFVR event, a truck-mounted vacuum system is connected to one or more monitoring wells and uses high vacuum pressures and flow rates over about several hours to remove vapor, free-product and groundwater from the subsurface. The material removed is contained in a tank on the truck and transported off-site for treatment. At the ExxonMobil facility, AFVR has been used in November 1999 and December 2000 and was planned for January 2002.

From July 1998 until December 2001, the ExxonMobil remediation system primarily consisted of a bioventing system in the northern portion of the site and a SVE system in the southern portion. In April 2001, two 200-lb vapor phase carbon vessels were added to the SVE system to reduce VOC emissions. In December 2001, the SVE system was converted to a bioventing system effectively eliminating concentrated VOC emissions at this site.

2.4 SOUTHERN STATES REMEDIATION

Petroleum contaminated soil and groundwater, resulting from historic releases from a former above ground storage tank system and retail fuel dispenser island at the former Farmers Cooperative Exchange facility (now Southern States Cooperative, Inc.) at 1710 Jake Alexander Boulevard has been under active remediation since October 1999. The Southern States remediation site has used the following combination of remedial technologies to address the contamination: air sparging (AS), soil-vapor extraction (SVE), bioventing, and monitored natural attenuation.

An AS system is an in situ groundwater remediation technique that involves injecting air into the saturated zone to volatilize VOCs and to promote biodegradation of contaminants in both the saturated and unsaturated zones by increasing the supply of oxygen. Vapors, including volatilized VOCs, migrate upwards into the unsaturated zone where an SVE system (described above in ExxonMobil remediation system) continues the removal process. AS has proven to be a very effective technique to remediate petroleum-contaminated groundwater.

At the Southern States site, the AS/SVE system became fully operational in October 1999 in the core of the contaminant plume and it has achieved reductions in groundwater VOC concentrations and soil total petroleum hydrocarbons. Monitored natural attenuation has been used outside the core of the plume. In early March 2002, Southern States voluntarily deactivated the AS/SVE system and began to evaluate possible system modifications and alternative treatment options to reduce VOC emissions.

2.5 CONCRETE SUPPLY COMPANY BATCH CONCRETE PLANT

Concrete Supply is a concrete batching plant which stores, conveys, measures, and discharges a mixture of water, cement, sand, fine and coarse aggregate into trucks for transport to a job site. The plant is at 1833 Jake Alexander Blvd., located with a common property line with APAC.

Concrete is composed essentially of water, cement, fine and coarse aggregate. Fine aggregate is made of sand and flyash, while the coarse aggregate consists of gravel and crushed stone. Raw materials are delivered to the plant by truck. The cement and flyash are transferred to elevated storage silos pneumatically, while the sand and coarse aggregate are transferred to elevated silos by a belt conveyor. From these elevated bins, the constituents are fed to weigh hoppers, which combine the proper amounts of each material. The plant is equipped with central mixing capability. Sand, flyash, aggregate, cement, and water are all gravity fed from the weigh hopper into the central mixer. The mixed concrete is then transferred to an agitator truck for transport to the job site.

All but one of the emission points is fugitive in nature. (Fugitive emissions are non-ducted emissions, such as those produced from wind blowing over a dirt road or over a storage pile of dry lightweight material.) The only point source is a small pulse-jet baghouse located above the central mixer. The baghouse collects the ducted emissions from the pneumatic transfer of cement and flyash to the silo and the emissions from the central mixer. The single-compartment baghouse is designed to treat a volumetric flowrate of 6000 cubic feet per minute (cfm) with filter surface area of 504 square feet. Material collected in the baghouse is recycled back to the flyash silo. Fugitive sources include the transfer of sand and aggregate, truck loading, mixer loading, vehicle traffic, and wind erosion from sand and aggregate storage piles.

2.6 JAKE ALEXANDER BOULEVARD

For this study, the vehicle traffic on the 5-lane Jake Alexander Boulevard is considered an area source of emissions. Milford Hills is located to the northeast of the abovementioned industrial sources and across Jake Alexander Blvd., also designated as US Route 601, a 4-lane undivided highway. Based on NC DOT portable traffic counts, 36,000 total cars, going either way, travel this road on an average day. The vehicle mix was approximated from 95 vehicle classification counts for Rowan County supplied by NC DOT and for modeling purposes was assumed to be 80% cars, 10% pickup trucks, 4% single unit trucks, 5% tractor trailers, and 1% motorcycles.

SECTION 3

EXPERIMENTAL METHODS

3.1 PROCESS DATA FROM ASPHALT

Process data from each asphalt facility were collected throughout the study period (May 14-September 7, 2001). Process operations and the corresponding emissions for each asphalt facility varied in time depending on the general weather conditions, day of week, time of day, and production level. Since both facilities operate intermittently, each was requested to provide information on their operations. Available records documenting various process operations for each asphalt facility were collected and formed an integral part of the project's database in order to evaluate any relationship with monitored data. Such process data were collected weekly and organized into a computerized database for subsequent evaluation. The goal was to collect process data accounting for 90% of the emissions from the asphalt facilities over time periods rounded to the quarter-hour. Such data were examined to evaluate:

- The representativeness of facility performance during the study period as well as emission testing, and
- Whether there was a relationship between facility emissions and monitored ambient pollutants during the study.

3.1.1 Associated Asphalt Terminal

H_2S emissions from the Associated terminal are released from railcar heating, railcar unloading (storage tank filling), and tanker truck loadout. Accordingly, records were obtained for:

<u>Railcar heating</u>: Number of asphalt-filled railcars and time periods when individual railcars were heated before unloading,
<u>Railcar unloading</u>: Amount and time periods when liquid asphalt was pumped from the railcars to the storage tanks, and
<u>Truck loadout</u>: Amount, asphalt type, and type of any additive loaded into trucks with corresponding times.

3.1.2 APAC-Carolina Hot Mix Asphalt Plant

An engineering evaluation indicated that over 90% of APAC's H_2S emissions were released from the dryer/mixer and from filling the liquid asphalt storage tank. Accordingly, records were obtained to account for:

1. The production rate of HMA dryer operations with corresponding time periods, baghouse pressure drop, and fuel consumption;
2. The amount of each tanker truck delivery with corresponding time; and
3. Liquid asphalt shipments received, including amount, source/type, and arrival date.

3.2 SOURCE EMISSION DATA

Data on the emissions from the various facilities in the study were collected using the best available sources of information. For VOC emissions from the two asphalt facilities and the concrete batch plant, the best available source of information was EPA's Compilation of Emission Factors.[27] The remaining emission data used in the study were produced in site specific emission testing. Test data were available for H_2S for the two asphalt facilities and for individual VOC species for the two remediation sites.

Emission factors are the most common method available for estimating emissions. An emission factor is considered a representative value to relate emission rates directly to production rate. For instance, individual VOC species' emissions were measured during a series of emission factor tests conducted by EPA on hot mix asphalt plants at or near the maximum production rate. On the accepted premise of a linear relationship between emission rates and production rates, emission rates can be estimated by multiplying the appropriate emission factor with the production rate. Such is standard practice – and the means in this evaluation - for estimating emissions using emission factors.[27] For example, benzene emissions from the APAC dryer are estimated by multiplying its respective emission factor (28 lb/100,000 ton) by a given production rate (such as 180 ton/hr); in this case the benzene emissions are calculated to be roughly 0.05 lb/hr.

3.2.1 Source Emission Data For Volatile Organic Compounds

VOC emissions from the two asphalt facilities and the concrete batch plant were estimated using the methodology described in EPA's Compilation of Emission Factors, commonly known as AP-42.[25]

Associated Asphalt Distribution Terminal

Railcar, Storage Tanks, and Truck Loadout

Emissions of VOC TAPs from Associated's railcar, storage tanks, and truck loadout operations were calculated in a two-step process. First, the EPA's TANKS 4 software program was used to estimate the total VOCs emitted.[28] Then the speciation profile emission factors in AP-42 Section 11.1, Table 11.1-15 were used to calculate emissions for the individual VOC species from terminal operations.[25] The data for the storage tanks and railcars emissions were initially developed and submitted by Associated and later confirmed by DAQ. Emission factors were multiplied by the appropriate process data to estimate emission rates on a hourly and annual basis. For this study, DAQ used the calculated storage tank emission rates for truck loadout, since EPA's speciation profile data applies to both loadout and asphalt storage.

The inputs and assumptions used in the TANKS4 program were:

- The tank dimensions in **Table 2** apply; the tanks are white in color, in good condition, of fixed-roof design, and normally half full.
- Tanks are heated from 315-325°F, with a 320°F average (worst case) liquid temperature.

- Short-term emission rates (daily and hourly) were based on a maximum daily throughput of 378,000 gallons (~ 1,600 ton/day) and a maximum hourly throughput of 42,000 gallons (~ 180 ton/hour).
- Long term (annual) emissions were based on a maximum theoretical annual throughput of 51,000,000 gallons (~ 216,000 ton/year). Using the TANKS 4 program, total VOC emissions are estimated to be 2342.1 lb/year for this maximum throughput level.
- EPA specified values for the liquid asphalt molecular weight of 1000, its vapor molecular weight of 100, and values for Antoine's constants A of 73,350.6 and B of 9.00346.
- A railcar is 21,000 gallon capacity, 50 ft. long and 10 ft. in diameter; treated as a heated horizontal storage tank, with the darkest color (red/primer), and the liquid asphalt is heated from 150°F to 325°F, with a 290°F average liquid temperature.
- All storage tanks have both working (filling) and breathing (standing storage) losses, whereas the railcars only experience breathing losses, since the cars are not filled at the terminal.

The total VOC emissions were then multiplied by the respective speciation values in AP-42 Section 11.1, Table 11.1-15 for each TAP. For example, the maximum 1-hour total VOC emission rate for the storage tanks is 1.68 lb/hr and the benzene speciation value is 0.032%, so when multiplied together their product is 0.00054 lb/hr benzene (1.68 times 0.00032).

Combustion Sources

Associated has 2 boilers producing steam to heat the liquid asphalt in the railcars and two hot oil heaters to maintain a suitable temperature in the storage tanks. These units are fired with natural gas. Individual TAP emissions were estimated on an hourly and annual basis using DAQ spreadsheets for Natural Gas Combustion Emissions, based on AP-42 emission factors.

APAC-CAROLINA HMA Plant

The appropriate tables in AP-42 Section 11.1 were used to calculate emissions for the individual VOC species from the hot mix asphalt plant operations.[25] In this case, the emission factors in the appropriate table in Reference 25 were multiplied by the proper process data to estimate emission rates on a hourly and annual basis. The tables in Reference 25 used for these calculations are Tables 5 (Batch mix plant dryer/mixer), Table 6 (Batch mix plant loadout), Table 7 (Batch mix plant asphalt storage tank), and Table 12 (Batch mix plant yard emissions). For the hourly and annual emission rates, the DAQ permitted maximum production rate of 180 ton/hr and the 2001 annual production level of 101,000 ton/year were applied, respectively. Since the emission factor is given for each TAP species, emission rate calculation is performed in a single step.

Concrete Supply

Concrete Supply has one boiler producing steam to heat their equipment. This unit is fired with natural gas. Individual TAP emissions were estimated on an hourly and annual basis using DAQ spreadsheets for Natural Gas Combustion Emissions, based on AP-42 emission factors.

Exxon/Mobil Remediation Site

To provide a semi-annual indication of system effectiveness, source emission testing for total hydrocarbons and BTEX (benzene, toluene, ethylbenzene, and xylene) was conducted by ExxonMobil using EPA Method 18 with Tedlar™ bags in June 2001.[29] Given that this site operates continuously, the reported emission data in lb/hr was converted to annual emissions by multiplying it by 8760 hrs.

Southern States Remediation Site

For a similar reason and schedule, source emission testing for total hydrocarbons and BTEX was conducted by Southern States using EPA Method TO-14A with SUMMA™ stainless steel canisters in May 2001.[30] Because it operates continuously, the reported emission data in lb/hr was converted to annual emissions by multiplying it by 8760 hrs.

3.2.2 Source Emission Data For Hydrogen Sulfide

Emission tests were performed to quantify hydrogen sulfide emissions due to the absence of any known reliable data for H_2S emissions from liquid asphalt terminal or hot mix asphalt plant operations.

Associated Asphalt Emission Test

Source testing was performed at Associated on the major process operations under normal conditions in early September 2001 using EPA Method 15 for H_2S and other total reduced sulfur (TRS) compound (carbonyl sulfide, carbon disulfide, and methyl mercaptan) emissions.[31] Method 15 involves continuous sampling through a chilled buffered citrate solution with a sample aliquot analyzed for the target analytes by gas chromatography separation and flame photometric detection. The NC DAQ requested the testing, approved the test plan, audited the on-site measurements and process conditions during testing, and approved the test report with a permit-related clarification. Tests were conducted using standard EPA source test procedures on the existing release points (stacks) with three approved exceptions.

- A temporary fixture was mounted on the railcar hatch to simulate a regular stack in order to apply standard EPA test procedures.
- Since gas flowrates during storage tank unloading were below detection using standard EPA methods, flowrates were measured by collecting all of the exhaust in a plastic bag under measured time intervals, and then measuring the collected gas by a dry gas meter.
- Smoke tubes were used to qualitatively indicate the direction of air movement - whether flow direction was entering or leaving the container in question (railcar hatch, tank vent, or tanker truck hatch).[31]

All testing was performed from the same rail shipment of PG 64-22 liquid asphalt refined from a Venezuelan crude oil. Tests were conducted on the following sources and operating conditions:

Railcar heating. Three different railcars holding 90 tons of liquid asphalt after being heated to pumpable temperatures above 290°F were tested with no emission controls in place. Each test run time was 60-90 minutes in duration to allow for complete emptying of the railcar. A small amount of airflow out of the railcar was measured during heating. However, qualitative flow measurements during railcar unloading showed that the direction of airflow was negative – meaning that air was being induced into, and not out of, the railcar.

Storage tanks. Three different conditions with liquid asphalt heated to above 310°F were evaluated for a 400,000 gal storage tank vent emissions, each during normal operations: (A) During tank filling at a rate of ~1 ton/min from railcars with 1 ½ hour run times; (B) When the heated tank was idle (no incoming or outgoing liquid asphalt); and (C) During offloading to tanker trucks.

Truck loadouts. Testing during loading at a rate of 2.3 ton/min with 310°F liquid asphalt of eleven different trucks with run times between 12-14 minutes was conducted to measure emissions treated by a carbon bed. The test results are presented later.[31]

APAC HMA Preliminary Emission Data

EPA developed emission factors applicable to HMA plants for more than 40 criteria pollutants and VOC hazardous air pollutants. However, because H_2S levels were below the estimated detection limit of 100 ppm using Fourier transform Infrared Spectroscopy, EPA reported no H_2S emission data.[26] In an effort to help fill this data gap, DAQ used ambient monitoring methods to *estimate* - not EPA source test methods to officially determine - H_2S emission concentrations from four HMA batch mix operations. During the survey DAQ personnel collected gas samples using Drager tubes and a multi-gas electrochemical monitor manufactured by RAE Systems. Because these systems are not designed for use under source test conditions, their accuracy and precision in this application is considered to be limited for producing only semi-quantitative data.

Drager tube samples for H_2S were taken in duplicate with two different concentration ranges: 100 to 2,000 parts per million (ppm) and 2,000 to 70,000 ppm. The H_2S tubes have a cross-sensitivity to sulfur dioxide (SO_2). Based on the EPA AP-42 emission factor for SO_2 for the APAC natural gas fired dryer, the calculated SO_2 level was found to be very low (2 ppm), suggesting a negligible cross-reactivity bias from SO_2. The multi-gas monitor manufactured by RAE Systems is a MultiRAE PLUS model. It is a programmable monitor designed to provide continuous exposure monitoring of H_2S and other toxic gases of indoor or ambient air from 0 to 100 ppm.

Concentration measurements were performed during normal conditions and production/ operating levels on the exhaust gas stream from each of three operations at the noted locations: (1) Liquid asphalt storage tank filling at the exhaust of the condenser mounted atop of the tank, (2) Batch mix dryer baghouse exhaust in the duct immediately downstream of the induced draft fan, and (3) Mixed asphalt truck loadout in the space directly above the fuming asphalt. Gas flowrate data was obtained by various means:

(1) The volumetric liquid asphalt-pumping rate of 181 gallons per minute (gpm) into the storage tank displaces the same volumetric gas flowrate of 24 cfm out of the tank.

(2) The APAC-supplied gas flowrate of 32,700 actual cfm (acfm) at 270°F was converted to 24,000 wet cfm at 70°F because the concentration measurements were made near this temperature.
(3) An order-of-magnitude estimate was made for the gas flowrate from the truck bed.

The manufacturer tested the RAE H_2S monitor for interferences with sixteen gases (see http://www.raesystems.com/pdf/TN-114_Sensor_Specs.pdf). According to the manufacturer, no major interference effects from asphalt fumes are expected from the relatively low levels quantified in the EPA speciation profile for a wide range of compounds VOCs, semi-VOCs, and criteria pollutants. As previously indicated, there could be hundreds of compounds in asphalt fumes. However, the H_2S monitor manufacturer's data in combination with other available data for asphalt fumes show that:

A. High levels of polar organic compounds (alcohols, ketones, and amines) give a negative response (i.e., a low bias); however, the EPA data indicates the relative absence of polar compounds. Other organic compounds in asphalt fumes quantified by EPA have no effect (e.g., toluene) or are at sub-ppm levels -- too low to cause interference.
B. Likewise, methyl mercaptan causes interference at 100 ppm, but the Associated Asphalt test data show that methyl mercaptan was below the practical detection limit of 4 ppm.

Further discussion with the monitor manufacturer revealed that the non-condensing specification for humidity is primarily for long-term instrument protection. The approximate moisture and dew point conditions at the storage tank exhaust and the dryer / mixer exhaust were 5% H_2O / 90 °F and 20% H_2O / 140 °F, respectively (see Reference 31: TRC Environmental Corp., "Test Report - H_2S and TRS Emission Testing at the Salisbury Terminal Liquid Asphalt Transfer Station). Given the monitoring survey characteristics (moisture-related conditions, gas temperature, pollutants' concentrations, sampling configuration, duplicate measurements and stable monitor readings), the H_2S monitor manufacturer vouched for the integrity of the storage tank data (90 ppm H_2S) and judged only a 10% shift in response at the dryer / mixer due to the estimated temperature of 140 °F. This suggests a lower concentration at the dryer / mixer than originally reported (6 ppm – (10% of 6) = 5.4 ppm), reducing the emission rate from the reported value of 0.75 lb/hr to 0.68 lb/hr (rounded to one significant figure, 0.7 lb/hr).

Cambridge Environmental submitted review comments on the draft report in behalf of APAC arguing that the H_2S data discussed above was "unreliable, and … should not appear in the final report." After review of Cambridge Environmental's comments and DAQ's discussion with the H_2S monitor manufacturer, DAQ continues to believe that the data are reliable to one significant figure and should still be presented as "preliminary estimates" in the final report. The Cambridge Environmental review comment submittal and the corresponding DAQ response are contained in Appendix I.

3.3 DISPERSION MODELING

3.3.1 Stationary Source Dispersion Modeling

DAQ performed dispersion modeling to evaluate the incremental impacts of the emissions of 12 TAPs and 6 criteria pollutants for the individual sources at the two asphalt facilities, the concrete batch plant, and the two remediation sites. Modeling was limited to the 12 TAPs and 6 criteria pollutants on which emission factor data are available and represents the fullest extent of the response allowed within the constraints of DAQ authority. A total of 15 individual emission sources were modeled at the two asphalt facilities, concrete batch plant, and two remediation sites. The Industrial Source Complex Short Term Version 00101 (ISCST3) using 5 years of meteorological data recorded from Charlotte (surface) and Greensboro (upper air) airports was employed to evaluate impacts in simple and complex terrain from the combination of facilities.[32, 33] [*Note: In dispersion modeling, a simple terrain approach is applicable when the variation in ground elevation is less than the stack height; complex terrain modeling is applicable when the variation in ground elevation is more than the stack height*.]

Inputs to the dispersion model were the emission data (for VOC TAPs, H_2S and criteria pollutants), source specific release parameters (stack height and diameter, gas flowrate and temperature, and position coordinates), and meteorological data (wind speed and direction, temperature, moisture, barometric pressure, and solar radiation). Direction-specific building dimensions, determined using EPA's Building Profile Input Program (95086), were used as input to the model for building wake effect determination. [*Note: Building wake effect is a disturbance of air flow streamlines on the downwind side of buildings*.] Receptors, or discrete ground level points, were placed around the property boundaries of the two asphalt facilities and remediation sites at 25-meter intervals. Receptor locations were also extended outward to a distance of approximately 2 kilometers at grid resolutions of 50 meters (out to 500 meters distance), 100 meters (from 500 metes to 1 kilometer), and 250 meters (from 1 km to 2 km). [*Note: A grid is simply the integrated pattern of receptor locations evaluated for exposure.*] Property boundary coordinates were not obtained for the Concrete Supply facility; therefore, receptors were placed within the property owned by this company. Another dispersion model (SCREEN3 Version 96043) was also used to evaluate cavity impacts for several sources; however, cavity concentrations were less than ISCST3 simple terrain impacts and no further cavity impact analysis was necessary. [*Note: Cavity impacts are a part of the building wake effect, and is that portion in which pollutants are trapped and concentrated due to building wake effects.*]

3.3.2 Mobile Source Dispersion Modeling

A portable DOT traffic counter was setup on Jake Alexander Blvd near the two asphalt facilities to collect daily traffic data in the first part of the study. Traffic counts were taken from May 18-28 and from June 27 to July 17, 2001. The highest traffic count obtained was 29,500 vehicles per day on May 25.

Two mobile source modeling studies were utilized to predict the impact of VOC concentrations on the basis of this vehicular traffic data. The objective was to predict the dispersion beyond the roadway to characterize VOC concentration using worst-case meteorology, worst-case meaning those meteorological conditions that are least conducive to the dispersion of pollutants. The study used Mobile5a[34] and Caline4 models[35] to estimate VOC emissions from a one-mile stretch of the traffic on the 5-lane Jake Alexander Blvd. The following inputs and assumptions were included:

- A maximum of 2,800 vehicles per hour traveled the road.
- A 1995 NCDOT vehicle classification counts showing 80% cars, 10% pickup trucks, 4% single unit trucks, 5% tractor trailers, and 1% motorcycles.
- Typical operating modes and fleet emissions profiles were applied.
- Emissions were calculated for July 2002 with a temperature of 86°F and vehicle speed of 45 mph.

3.4 AMBIENT MONITORING METHODS

The three sites were established based on EPA regulations specifying the protocol to be used in the selection of monitoring sites for ambient air sampling for criteria pollutants.[36] The EPA guidelines were followed as closely as possible for:

- Maximizing unrestricted airflow by placing the monitors in a location that has an arc of at least 270° of unrestricted airflow from the source direction.
- Placing the air intake of the sampler in the breathing zone.

Figure 1 shows the location and orientation of the sites relative to the emission sources. Site 1 was on the end of a nearby *cul de sac* street and located downwind and off-axis of the prevailing wind direction. It represents a neighborhood exposure area. Site 2 was located roughly 50 feet from the Associated property line to represent a source-dominated location and was in proximity to an earlier multiple-source modeling study maximum point of impact. Site 3 was in an open area approximately 200 feet from a 5-lane highway (Jake Alexander Blvd) and approximately 100 ft. from the air effluent of a ground water remediation site. It represented a site that is upwind and off-axis of the prevailing wind direction from the area sources of interest. Each monitoring site was configured with one meteorology station, a VOC sampling system, and a hydrogen sulfide tape meter housed in a climate-controlled enclosure (4 ft wide, 4 ft deep, 8 ft high) surrounded by controlled access security fencing.

3.4.1 Meteorological Monitoring

The siting criteria and critical parameters for meteorological data sensors were in accordance with EPA protocols.[37, 38] The parameters measured at each site were wind speed, wind direction, wind direction standard deviation, temperature, relative humidity, and, at site 2 only, barometric pressure. Prior to field installation, the manufacturer calibrated all meteorological sensors deployed in this study. The field auditing and calibration verification of all sensors was performed at the beginning, intermittently as data review warranted and following the end of the study. Continuous meteorological measurements were recorded every 10 seconds and averaged every 15-minutes, every hour, and every 24-hours. These data were recorded and stored by Campbell Scientific

CR10X™ data loggers. The data were later downloaded to a lap top computer during periodic site visits. Meteorological parameters were measured at 6 meters above ground.

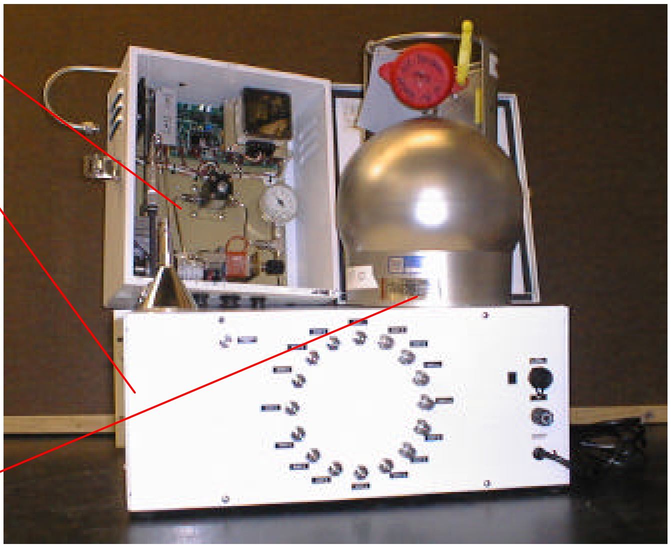
3.4.2 Volatile Organic Compounds Monitoring

Method: The Xontech™ 911/912 systems were assembled and operated to collect a 24-hour sample in a 6L stainless steel canister. The samplers collected whole air samples for subsequent laboratory analysis for VOCs via gas chromatography / mass spectrometry (GC/MS). The analyses were performed following EPA method guidelines.[39] The lower quantitation limit (LQL) for the instrumentation at the TPB lab was 0.250 ppb. Any values below the LQL is reported as BLQL (below LQL) in the data tables and for statistical purposes assigned a value of ½ LQL (0.125 ppb). This statistical treatment was also used for raw data obtained for comparison purposes from other states.

Time Frame: Sampling occurred over the course of the study on a 10-day schedule at the three sites from May 12 through July 26, 2001. However, due to unforeseen equipment difficulties and power outages, collected samples were analyzed only for the dates shown in **Section 4.2.3, Table 7**. Each 6-L canister collected air samples over a 24-hour period that began and ended at approximately 0:00 hrs (midnight).

Additionally, samples were taken from September 3-5, 2001 before and during source testing at the Associated asphalt terminal. These samples were collected over 12-hr intervals from 7:00 hrs to 19:00 hrs and from 19:00 hrs to 7:00 hrs to closely coincide with the hours of operation of the facility.

Figure 3. XontechÔ 911/912 Sampling Systems



Xontech™ 911 regulated air flow pump
Xontech™ 912 multi-port sampling device

Supply lines and fittings, ¼” stainless steel
Flowmeter

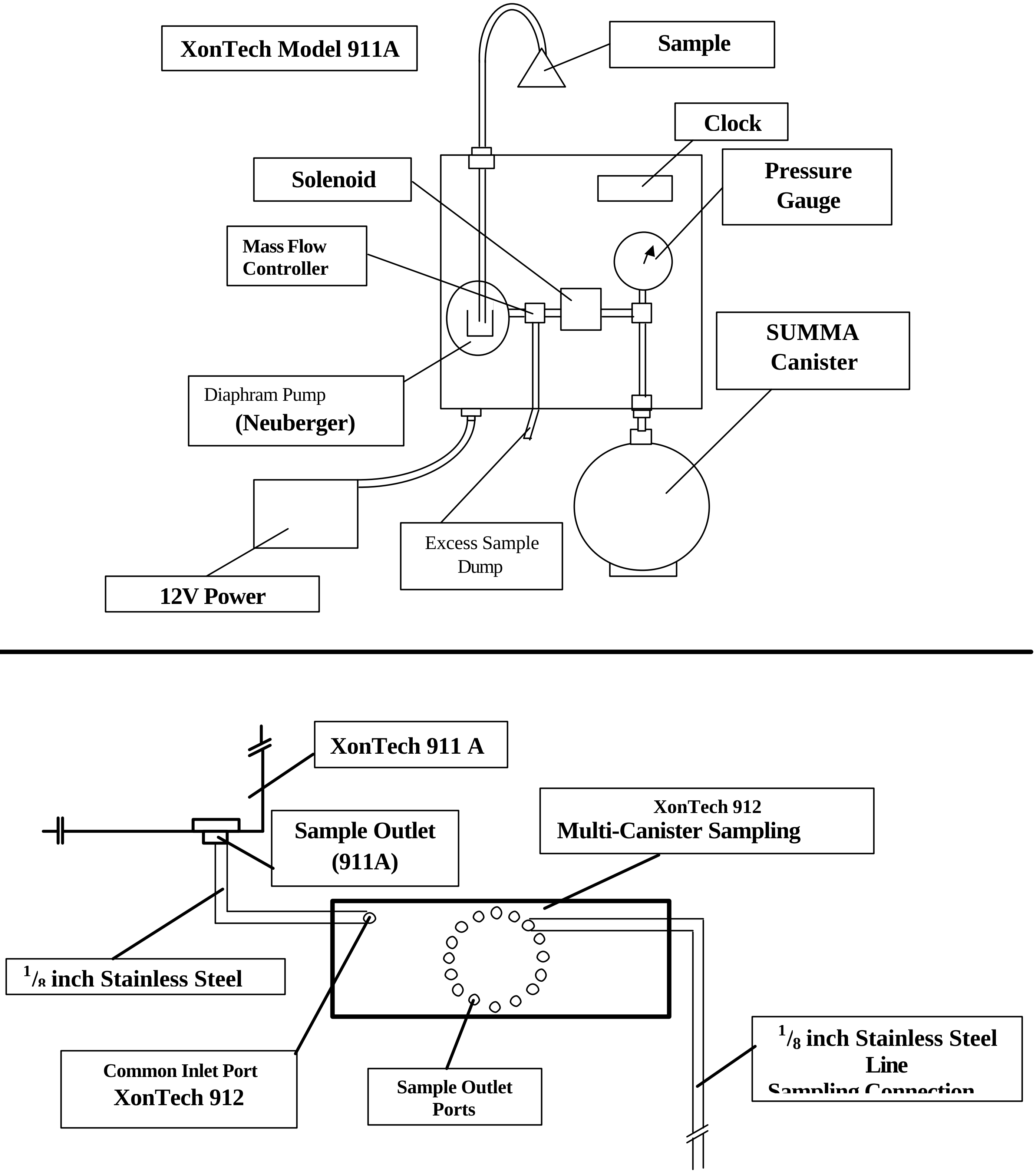
Stainless steel canisters, 6L, SUMMA™

Sampling Procedure: Each VOC sampling assembly was housed in a secured climate-controlled building and consisted of 10 SUMMA™ canisters, a Xontech™911 and Xontech™912 automated sampling system. Canisters, 911/912 combinations, and lines were certified as clean before field deployment following standard procedures for cleanliness certification.

Each sampling train was set up as shown in **Figure 4**. A "candy cane" sampling funnel was mounted outside the building at approximately 8ft above the ground. A stainless steel line extended from the sampling funnel to the 911 sampler, then connected to the multi-port 912 sample indexer by a single stainless steel line. The 912 sample indexer was subsequently connected to the 10 individual canisters. The 911 sampler ran continuously to pump air into a single canister through the 912 sample indexer. The pump was run at a flow rate of 9 mL/min to give a final canister pressure of approximately 22 psi. The 912 sample indexer was programmed to sample for 24 hours and then switch to the next sample canister. At the end of the 10 days a new set of canisters was placed in the system and collection was continued. Samples were transferred to the laboratory using the chain-of-custody procedures defined in the Quality Assurance Project Plan found in Appendix H.

Sample Analysis and Data Reduction: After sample collection, canisters were returned to the DAQ TPB lab for analysis by GC/MS using EPA Method TO-14A as a guide.[39] TO-14A is an accepted methodology for the identification of up to 41 VOCs. ATAST routinely analyzes for 40 of those compounds based on several criteria such as the stability of the compounds in the standard mixes, instrument sensitivity and performance criteria, and instrument capabilities at the time of analysis. Of these 40 compounds, 32 are listed on the Clean Air Act 1990 (CAA) HAP list and/or the NC TAP list.

Figure 4. Diagram of XonTech 911A Sampler System and 912 Sample Indexer



3.4.3 Hydrogen Sulfide Monitoring

H_2S data for ambient air levels were collected using Zellweger Analytics Single Point Monitors™, or Tapemeters obtained from ATSDR.[40] This instrument uses a lead acetate-treated cloth tape reel to analyze for H_2S. The chemically treated tapes react when exposed to H_2S with a colorimetric change occuring in proportion with the concentration. Optical sensors measure the degree of color change. The Tapemeter can measure a 2-90 parts per billion (ppb) range with precision +/-25% that is acceptable by the manufacturer. The unit has an internal sample pump which draws ambient air at a constant flow rate through the paper tape. At the end of each 15-minute sample period the concentration data are electronically stored on an attached data logger. The monitor, data logger, and other sampling equipment were housed within a climate controlled weather-resistant storage building. The monitor stores setup information and other functional information (i.e. flow rate, alarm levels, H_2S concentration with corresponding times). Sample tubing was equipped with a moisture knockout impinger and a funnel with a screen. To ensure quality the spare chemical tapes were stored in a cool atmosphere out of direct sunlight.

Calibration using known cylinder gas concentrations is considered unnecessary by the manufacturer. Each tape reportedly passed manufacturer calibration tests prior to sale to eliminate any need for instrument calibration in the laboratory or field. An ATSDR subcontractor (Texas Technology Institute) verified these claims of accuracy and reliability with known H_2S concentrations and various relative humidity levels.[41] The tapemeter has been tested for precision by collocating two tapemeters to measure ambient concentrations and its accuracy has been shown by collocating the tapemeter with other technologies. [42-45] The instrument does allow for a response verification using an optical test card. This test was completed each time the tape reel was changed during the DAQ/ATSDR study. The instrument can operate for approximately one month on a tape reel under normal monitoring conditions.

One Zellweger hydride tapemeter capable of measuring 60-1400 ppb was collocated with the H_2S tapemeter at the Access Road monitoring site. Other hydrides besides H_2S can react with its tape, but these hydrides (AsH_3, SiH_4, PH_3, et al.) are not likely to be found in asphalt facility or soil remediation emissions at quantifiable levels. There were several times when the hydrides tapemeter produced data that was inconsistent with the H_2S tapemeter data. Because of the potential uncertainty of its validity, data collected from the hydride tapemeter are not included in the results of the study. A tapemeter with a magnified detector is shown in **Figure 5.**

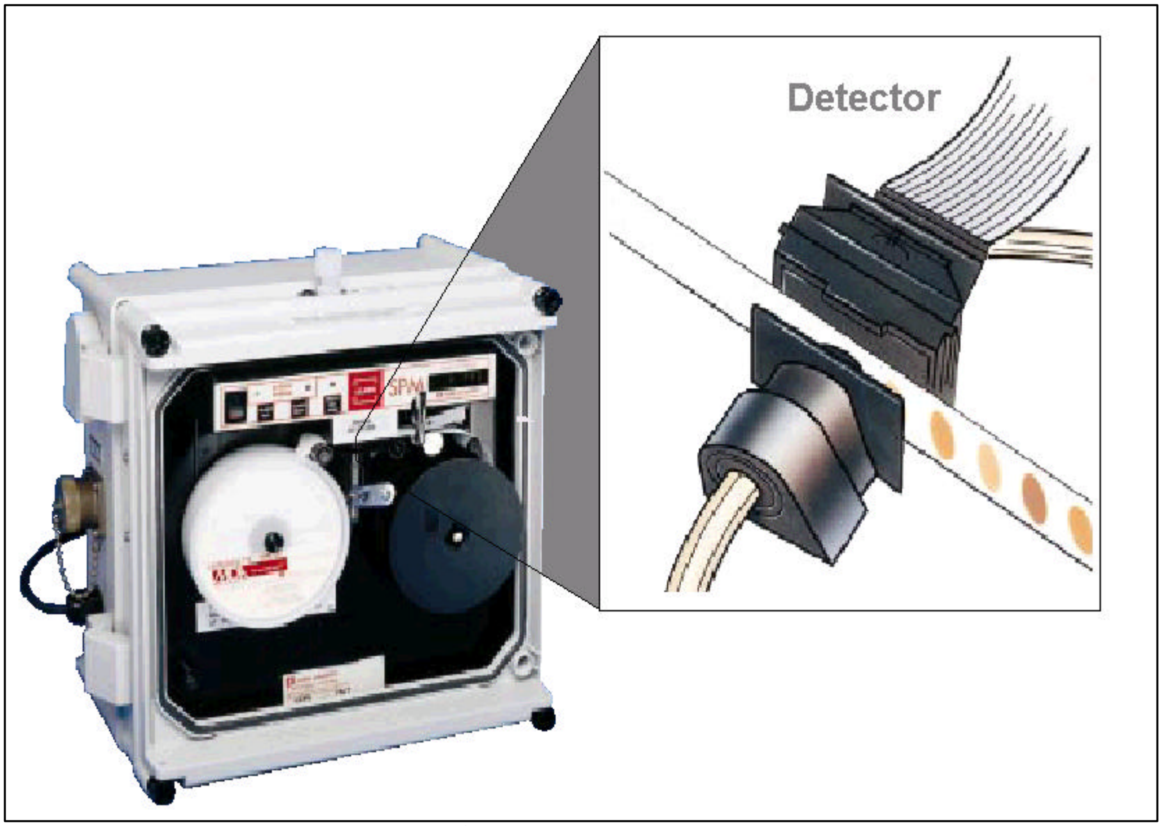


Figure 5. Zellweger Hydrogen Sulfide Sampling System

3.5 ODOR COMPLAINTS

Approximately 200 complaints were registered with the City of Salisbury over the twelve months prior to the study, and nearly 40 complaints were recorded during the study. [46] City officials developed an inspection / verification protocol to document objectionable odors. The procedure was as follows: When three or more citizens registered a complaint with the City Risk Department, the Codes Enforcement Office investigated the complaint as soon as possible. The strength of odor was determined at four locations thought the neighborhood. Each neighborhood location was chosen to represent the most frequent complainants. Finally the Access Road was visited, from there the investigator once again determined the strength of the odor and a production activities at each of the two asphalt facilities. If the odor were strong and either APAC and/or Associated were operating, the responsible facility or facilities was considered to be in violation of the City's Nuisance Odor ordinance and a civil penalty was assessed. All records of the reported odor complaints and citations during the study period were provided to the DAQ project team.

3.6 QUALITY ASSURANCE / DATA QUALITY MEASURES

3.6.1 Data Quality Objectives and Criteria for Measurement

The primary data quality objective of this study was to produce valid, representative data.

The EPA recommends using the Data Quality Objectives (DQO) Process outlined in *Guidance for the Data Quality Objectives Process* to develop data quality objectives for monitoring studies.[47] As stated in EPA's DQO guidance, "*every step of the DQO guidance may not be applicable to data collection activities where specific decisions cannot be identified, such as studies that are exploratory in nature...[P]art of the DQO Process includes formulating statistical hypotheses. If a statistical hypothesis is not linked to a clear decision in which the decision maker can identify potential consequences of making a decision error, then some of the activities recommended in this guidance [for the DQO Process] may not apply.*" Thus, although the entire DQO Process could not be followed for this study, the relevant steps were used.

3.6.2 Training Requirements

Field Operations

All personnel involved in the meteorological data collection, VOC sampling, and hydrogen sulfide sampling followed Standard Operating Procedures (SOPs) when carrying out their duties. **Appendix H** contains all SOPs used in this study. A minimum of three people from DAQ Toxics Protection Branch was trained to operate the sites. Other DAQ personnel were trained as needed. SOPs are provided for all field equipment operation and sample handling.

Laboratory Operations

Analysts involved in the study are certified in all of the laboratory methods and procedures used in the study for VOCs. Certification for the analytical method consisted of the analysis of Quality Control (QC) samples, the determination of the method detection limit, and the determination of the practical quantification limit. The number of samples used in certification was sufficient to verify the precision and accuracy of the analysis and to measure any bias between analysts.

Documentation and Records

Various types and levels of documentation are required for this study. Listed below is a summary of the field and laboratory documentation required:

- Activity log book maintained at each monitoring site
- Chain of custody forms
- Analytical instrument and analysis logbooks
- Inventory control (certified canisters/field samples) spreadsheets
- Meteorological equipment checklist for operations and audits

Examples and descriptions of miscellaneous forms and documentation are contained in **Appendix H**. Copies of all log sheets, forms, and checklists will be maintained in the project files throughout the study period, as long as deemed necessary by the Program Administrator.

The Data Managers maintained the validated, quality-coded meteorological and analytical data on a dedicated computer for their particular portion of the study.

Additionally, they placed this data on a reserved server in the DAQ local area computer network so that the data were available in a timely manner to the DAQ personnel for ready distribution to inquires for information. Copies of these validated, raw data were maintained on the Data Managers' computers and the reserved server throughout the study period, as long as deemed necessary by the Program Administrator.

Audit reports detailed the results of the field operations audits, analytical audits, and data management audits as needed were placed in the ATAST study file. This final report generated for the study includes the audited data, summary statistics, charts of the validated data if appropriate, and a discussion of the quality assurance audits. The Quality Assurance Project Plan (QAPP) is included in Appendix H and provides greater detail of the QA/QC procedures used in the study.

3.7 REGULATORY BACKGROUND ON TOXIC AIR POLLUTANTS

Of particular interest are the TAP levels observed in the study that were above the regulatory guidelines for TPERs and AALs. The following discussion presents DAQ regulatory definitions and concepts involved with TAPs.

3.7.1 Acceptable Ambient Level

At the outset of its air toxics program, North Carolina decided that the philosophy of the program would be based upon protection of public health. It established airborne concentration of chemicals "above which the substance may be considered to have an adverse effect on human health." The chemicals became known as toxic air pollutants or TAPs and the concentrations became known as acceptable ambient levels or AALs.

AALs are expressed in weight per unit volume, most often as milligrams per cubic meter of air (mg/m^3). North Carolina has developed AALs for 105 toxic air pollutants. By their nature, AALs are intrinsically distinct from measured air concentrations, and an understanding of this distinction is necessary to prevent misunderstanding and misapplication of AALs.

3.7.2 AAL Determinations

Historically, AALs were established by two means:

(1) For health effects other than cancer, the AALs were determined by taking occupational exposure standards and lowering exposure guidelines to acceptable concentration levels by safety factors of 10 to 160. Safety factors were used because the state recognized that chemical compounds differed in the nature and severity of the toxic effects and how much was known about the health effects of a chemical. Generally speaking, highly toxic chemicals such as mercury have larger safety factors and lower AALs. (Occupational exposure standards are essentially "no effect levels' and as such, safety factors tend to decrease those standards well below the levels at which adverse health effects have been seen in occupationally exposed humans).

(2) For substances known to cause cancer (carcinogens) in humans, AALs are set at levels calculated to represent an increment of "one in a million" risk. That is, if one million individuals are exposed continuously for 70 years, to a carcinogen

> at the concentration of the AAL, one person might be expected to contract cancer as a result of that exposure. For "probable" and "possible" human carcinogens, the risk levels increase to "one in one hundred thousand" and "one in ten thousand," respectively.

Currently, the NC DAQ maintains a scientific body of experts known as the Scientific Advisory Board (SAB) whose job it is to continually review the scientific information that forms the basis of the AALs. As this information changes, the SAB recommends updates to the AALs. The SAB reviews tend to be more complex that those used at the beginning of the Toxics program, but the objective is the same: to recommend safe exposure concentrations for toxic air pollutants that allow an ample margin of safety for potentially exposed people.

3.7.3 AAL Comparison to National Ambient Air Quality Standards (NAAQS)

North Carolina's air toxics program does not set state-wide or even community ambient standards for TAPs in the same sense as national air standards are set for familiar air pollutants such as ozone, nitrogen oxides or carbon monoxide, which are called "criteria air pollutants". National air quality standards set specific limits for ambient concentrations of pollutants (NOx, SO2, Pb, CO, VOC, and particulate matter) in the air we all breathe, and every state is expected to meet the national standards. States have extensive air monitoring programs designed to monitor for criteria air pollutants to ensure that compliance with the national standards is being maintained. Wide-ranging pollution control strategies and national rules have been adopted to enable states to meet the standards for the criteria pollutants. By contrast and although termed "acceptable ambient levels," North Carolina's AALs are used in pollution permitting to insure that toxic air pollutants from new or modified facilities do not make toxic air pollutant levels worse, on a case by case basis. Generally, monitoring for toxic air pollutants is limited to specific areas and specific pollutants.

When contrasted to the national standards, AALs are applied on a much smaller scale. Since there is not enough monitoring information to be able to know the general ambient concentrations for each of the 105 TAPs, the NC program focuses on what a facility <u>adds to the existing environment</u>. What a facility adds to the environment is determined in a two step process. First, the facility determines how much of a toxic air pollutant it emits. Determining emissions can be difficult, but generally there are standard techniques available. For example, a facility can perform testing at its emissions points to determine emission quantities and rates. If available, a facility may also use a published "emission factor" that has been determined to be a typical emission rate for a particular pollutant from a generic source such as a boiler. If the pollutant is determined to be emitted from the emission source at a rate above what is allowed by the toxics program (that is, the TPER), then an air dispersion computer model is run. If the air dispersion model results show that the toxic air pollutant emission is below the AAL, a conclusion is made that the facility has not <u>added concentrations of toxic air pollutants to the air</u> that are harmful to human health.

3.7.4 Air Dispersion Modeling

Air dispersion computer models use mathematical equations to simulate the real world. These equations attempt to account for all conditions affecting the release and dispersal of a pollutant, such as wind speed, wind direction, temperature, terrain, height of the emissions, how fast the emissions are released and so on. The model is used to predict the downwind concentrations or off-site concentrations of a given pollutant from the input information. Since air modeling is conducted only for the source of interest, the resulting modeled air concentration is directly comparable to the AAL.

3.7.5 AAL Relationship to Measured Ambient Air Concentrations

At first glance, AALs may appear to be directly comparable to air concentrations measured during ambient monitoring. However, such comparisons are misleading. Although a constituent of interest may be emitted from several different sources, its AAL is applicable only to the portion of the air concentration emitted from a specific industrial source. The NAAQS for the criteria air pollutants are established and monitored with total loading as a consideration. **A model predicts ambient air concentrations but does not account for contributions from other sources. The AAL is not to be exceeded at the closest property boundary.**

When monitoring for toxic air pollutants is conducted, the measured air concentration for a particular air pollutant can usually only be compared with its AALs if the source emitting that pollutant can somehow be isolated from all other sources. Such isolation is usually not possible or realistic. Furthermore, because air monitoring measures the total loading of a constituent from all emission sources, the resulting measurement is likely to be greater than the AAL for that constituent. It is not uncommon to find toxic compounds such as benzene and arsenic in a sample of ambient air in concentrations above the AAL. If such a sample were taken at the property line of a facility, it would not automatically imply that a given facility was in violation of the AAL. Additional information would be needed to draw appropriate conclusions about what the sample represented and its origin.

SECTION 4

RESULTS AND DISCUSSION

4.1 PROCESS DATA

4.1.1 Associated Asphalt Terminal

The production related data requested by DAQ and obtained from the asphalt terminal included documented invoices, computer-recorded data, and manually-recorded data collected during the study. The remaining process statistics were based on a single shipment of liquid asphalt weight of 90 ton/railcar and a single tanker truck loadout weight of 25 ton/truck. The study period covered 117 days or 32% of the year. **Table 3** presents the processing statistics from process data compiled on the Associated terminal during the study period. Note that the liquid asphalt sold in the study period reflects proportionally higher percentages than the time statistic percentage, verifying representative facility operation.

Table 3. **Asphalt Facilities' Process Statistics During Study**

Process Parameters	Study Period		2001 Fiscal Year
	Production Level	Percent of Annual Level	
Associated Terminal			
Liquid Asphalt Sold, Tons	42,800	36%	120,000
Liquid Asphalt Received, Tons	46,700	39%	~120,000
Number of Individual Railcars	519	39%	~1,330
Percent Liquid Asphalt Sold as PG 64-22	89%	a	~90
Percent Liquid Asphalt Sold as PG 70-22	11%	a	~10%
Number of Truck Loadouts	1,712	36%	4800
Percent of Truck Loadouts with anti-strip additive	65%	a	~65%
APAC HMA			
Tons of HMA Sold	48,000	48%	101,000
Number of HMA Truck Loadouts	3,000	48%	6,310
HMA Production Time, Hours	300	48%	630
Liquid Asphalt Used, Tons	2,060	48%	4,340

a: Process parameter level during study period similar to 2001 annual level.

4.1.2 APAC-Carolina Hot Mix Asphalt Plant

The process data requested by DAQ and obtained from the HMA plant were based on documented invoices and computer-recorded data collected during the study period. The remaining process statistics were based on a single HMA truck loadout weight of 16 ton/truck, normal HMA production rate of 160 ton/hr, and the annual average of

4.3% liquid asphalt in HMA. **Table 3** compares the production statistics compiled on the APAC Plant during the DAQ/ATSDR study period to its 2001 annual level. Each process parameter reflects higher percentages than the time statistic percentage, verifying representative facility operation.

4.2 VOLATILE ORGANIC COMPOUND SOURCE EMISSION DATA

4.2.1 Volatile Organic Compound Source Emission Data

As discussed in **Section 3.2**, VOC emission data for benzene, toluene, xylene, and formaldehyde were produced from two approaches:

1. Emission factors were applied to estimate VOC emissions from both asphalt facilities, the concrete batch plant, and Jake Alexander Blvd.
2. The most recent emission test data were used to present VOC emissions from both remediation sites.

Table 4 presents the benzene, toluene, xylene, and formaldehyde emission data in terms of hourly and annual emission rates for the thirteen types of emission points from the six emission sources. The data show that the benzene TPER guideline of 8.1 lb/yr was exceeded by benzene emission rates of 57 lb/yr and 28 lb/yr from the Southern States remediation site and the APAC dryer/mixer, respectively. Also included in **Table 5** is the relative percent of annual emissions contributed by each emission point, reflecting that:

- The Southern States remediation site was the principal emitter of VOC releases from the six sources, with benzene, toluene, and xylene accounting for the majority (65-72%) of the emissions from the source cluster.

- APAC was the second –most emissive source of VOCs, contributing 32%, 27%, and 30% of benzene, toluene, and xylenes emissions, respectively. In addition, APAC was the principal emitter of formaldehyde releases from the six sources, accounting for 82% of these emissions from the source cluster.

- Nearly all (> 97%) of the benzene, toluene, xylene and formaldehyde emissions stem from Southern States and APAC operations.

- The remaining four emission sources (Associated, Concrete Supply, ExxonMobil, and Jake Alexander Blvd.) contributed relatively minor emissions (< 3%) of benzene, toluene, xylene, and formaldehyde.

Table 4. Volatile Organic Compound Emission Estimates

	Benzene			**Toluene**			**Xylene**			**Formaldehyde**		
Facility	**lb/hr**	**lb/yr**	**%**	**lb/hr**	**lb/yr**	**%**	**lb/hr**	**lb/yr**	**%**	**lb/hr**	**lb/yr**	**%**
Associated Liquid Asphalt Terminal												
Storage tanks	5.4E-4	7.5E-1	1	1.0E-3	1.5E+0	0	4.3E-3	6.0E+0	1	1.2E-2	1.6E+1	6
Railcars	2.3E-6	5.3E-3	0	4.5E-6	1.0E-2	0	1.9E-5	4.2E-2	0	5.0E-5	1.1E-1	0
Truck loadouts	3.3E-4	7.5E-1	1	1.0E-3	1.5E+0	0	4.3E-3	6.0E+0	1	1.2E-2	1.6E+1	6
Steam boilers	2.6E-5	2.3E-1	0	4.2E-5	3.7E-1	0	0	0	0	9.3E-4	8.1E+0	3
Hot oil heaters	1.8E-5	1.6E-1	0	2.8E-5	2.5E-1	0	0	0	0	6.6E-4	5.8E+0	2
APAC HMA Plant												
Dryer Stack	5.0E-2	2.8E+1	32	1.8E-1	1.0E+2	27	4.9E-1	2.7E+2	30	1.3E-1	7.5E+1	28
Truck Loadout	4.0E-4	2.2E-1	0	1.6E-3	8.8E-1	0	3.7E-3	2.1E+0	0	6.7E-4	3.7E-1	0
Yard	2.9E-5	5.8E-2	0	1.2E-4	2.3E-1	0	2.7E-4	5.4E-1	0	5.0E-5	1.0E-1	0
LA Tank	1.8E-5	1.0E-2	0	3.6E-5	2.0E-2	0	1.4E-4	8.0E-2	0	2.5E-1	1.4E+2	54
Concrete Supply Batch Plant												
Boiler	4.7E-6	8.4E-4	0	7.7E-8	1.4E-5	0				1.7E-6	3.0E-4	0
Remediation sites												
Exxon / Mobil	6.9E-5	6.1E-1	1	6.9E-5	6.1E-1	0	3.5E-4	3.0E+0	0	0	0	0
South. States	6.6E-3	5.7E+1	65	3.1E-2	2.7E+2	72	7.1E-2	6.2E+2	68	0	0	0
Traffic												
J. Alex. Blvd	1.5E-5	1.3E-1	0	3.5E-5	3.1E-1	0	0					
Total	0.058	88.5	100	0.21	373	100	0.57	912	100	0.41	263	100
TPER		8.1		98 lb/day			16.4			0.04		

4.2.2 Volatile Organic Compound Dispersion Modeling

DAQ performed separate dispersion modeling for the stationary sources and the mobile sources to evaluate the incremental impacts of the emissions for these sources.

Stationary Source Dispersion Modeling Result for VOCs

Table 5 summarizes and **Figure 6** illustrates the stationary source dispersion modeling results for all the benzene emission sources. Included in **Table 5** are the averaging periods, maximum impact concentration, acceptable ambient level (AAL) guideline, and percent of the AAL for each of the 12 TAPs. The ISCST3 dispersion modeling results show that benzene was the only TAP that exceeded its respective annual AAL guideline of 1.2 x10^{-4} mg/m^3 (or 0.12 μg/m^3) as outlined in the North Carolina Administrative Code (NCAC) 2D.1104, Toxic Air Pollutant Guidelines. However, as the attached concentration isopleth analyses demonstrate, maximum impacts are centered solely around the Southern States remediation site and concentrations drop rapidly (<50 meters) outside the immediate vicinity of the source.

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Table 5. Maximum Modeled Impacts for Toxic Air Pollutants

Toxic Air Pollutant	**Averaging Period**	**Maximum Impact (μg/m^3)**	**AAL (μg/m^3)**	**Percent of AAL (%)**
Benzene	annual	1.02	0.12	850
Benzo(a)pyrene	annual	0.00002	0.03	0
Carbon disulfide	24-hour	0.38	186	0
Formaldehyde	1-hour	26.3	150	18
Hydrogen sulfide	1-hour	404	2,100	19
Methylene chloride	annual	0.00002	24	0
	24-hour	0.00140	1,700	0
n-Hexane	24-hour	3.88	1,100	0
Phenols	1-hour	0.793	950	0
Styrene	1-hour	0.14	10,600	0
Toluene	24-hour	120	4,700	3
	1-hour	1,706	56,000	3
Trichlorofluoromethane	1-hour	0.01	560,000	0
Xylene	24-hour	279	2,700	10
	1-hour	3,959	65,000	6

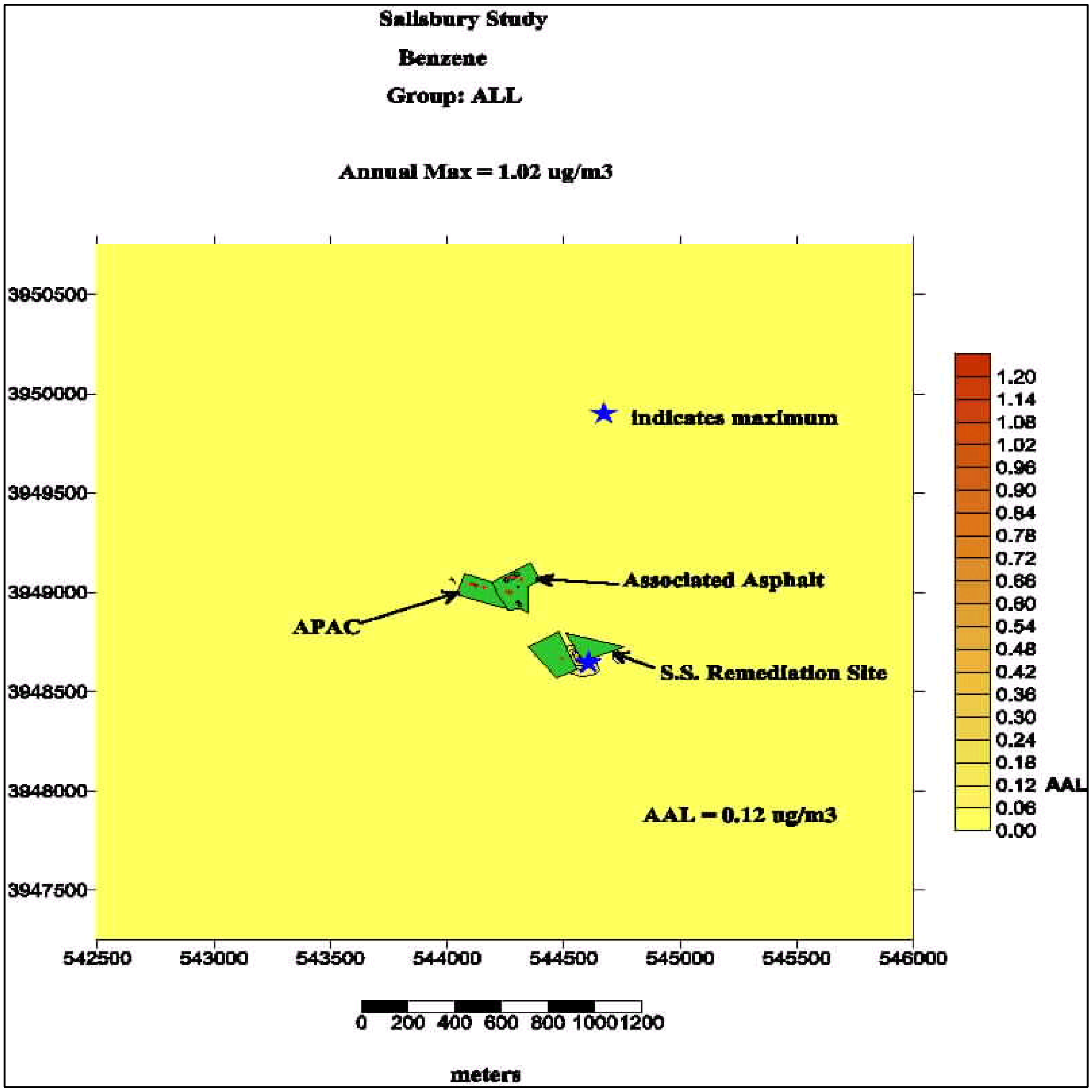


Figure 6. Dispersion Model Prediction of All Benzene Emission Sources.

Stationary Source Dispersion Modeling Result for Criteria Air Pollutants

Included in **Table 6** are the modeled concentrations for 6 criteria pollutants. Several statistical techniques depending on the pollutant are used to determine a maximum study impact (e.g. to determine the 24-hour PM10 study impact 5-years of daily PM10 concentrations are modeled at hundreds of receptors beyond the fence line. The five highest PM10 concentrations at each receptor are discarded for this statistical analysis. The highest remaining receptor concentration is the study impact). An identical data treatment method is applied to the most recent years data collected by the nearest state maintained monitoring location. The study impact is added to the observed background to determine a total impact. That total impact is compared with National Ambient Air Quality Standard (NAAQS) levels designed by the EPA to protect public health and public welfare within an adequate margin of safety. All modeled concentrations were below acceptable NAAQS levels. EPA criteria pollutant NAAQS limits are similar to North Carolina's TAP AAL.

Table 6. Maximum Modeled Impacts for Criteria Air Pollutants

Criteria Pollutant	Averaging Period	Study Impact (mg/m^3)	Background Concentration (mg/m^3)	Total Impact (mg/m^3)	NAAQS (mg/m^3)	Percent of NAAQS (%)
Carbon monoxide	8-hour	241	3.6	244.6	10,000	2.5
	1-hour	1,441	7.6	1448.6	40,000	3.6
Nitrogen Oxide	Annual	15.7	0.018	15.7	100	16
TSP	Annual	1.3	48.0	49.3	75	66
	24-hour	12.0	73.0	85.0	150	57
PM10	Annual	1.3	30.0	31.3	50	63
	24-hour	7.90	47.0	54.9	150	37
Sulfur Dioxide	Annual	0.09	0.004	0.1	80	0.1
	24-hour	0.99	0.014	1.0	365	0.3
	3-hour	3.0	0.066	3.1	1,300	0.2
VOCs	Annual	9.2	NA	9.2	NA	NA
	1-hour	397	NA	397	NA	NA

4.2.3 Volatile Organic Compound Stationary Source Ambient Monitoring Data

The VOC portion of the study was conducted from May 12 through July 26, 2001 with a collection of samples from the sites every eleven days. This sampling schedule would have given 70 sampling days that would have resulted in field collection of 210 samples (1 sample per day per site). However, due to unforeseen sampling equipment difficulties and random power outages at the monitoring sites, the number of valid samples collected from the field and returned to the DAQ lab for analysis was 109 (52%). Of these 109 samples, 34 (31%) were analyzed within a 30-day holding period. Delays in analyses were primarily due to the installation of a replacement gas chromatograph-mass spectrometer (GC/MS) and the requisite time required to install, optimize, and calibrate the new system.

In addition to the 24-hr samples, 12-hr samples were collected September 3-5, 2001. These samples were collected at all three sites during the period of the stack testing being conducted at the Associated facility. This resulted in 18 valid samples (2 samples per day per site) being collected and analyzed (100%). **Table 7** summarizes the spatial and temporal distribution of the valid samples that were collected and analyzed in the study.

VOC sample analysis was performed by the DAQ/TPB lab via GC/MS using EPA specifications for Method TO-14A as a guide.[39] The lab routinely analyzes for 40 of those compounds, 32 of which are on the EPA HAP list and/or the NC TAP list, as identified in **Table 8**.

Table 7. VOC Analyzed Sample Dates

24-hr samples			
Date	**Cul-de-Sac**	**Access Rd**	**Remediation**
Jun-06-01	no sample	X	no sample
Jun-07-01	X	X	no sample
Jun-08-01	X	X	X
Jun-09-01	X	X	X
Jun-10-01	X	X	no sample
Jun-13-01	X	X	X
Jun-14-01	X	X	X
Jun-15-01	X	X	no sample
Jun-17-01	X	X	no sample
Jun-18-01	X	X	no sample
Jun-19-01	X	X	no sample
Jun-22-01	X	X	X
Jun-23-01	X	no sample	X
Jun-24-01	X	no sample	X
Jul-08-01	X	no sample	X
Subtotal	14	12	8
24hr Sample Total	34		
12-hr samples			
Sept-03-01	X	X	X
Sept-03-01	X	X	X
Sept-04-01	X	X	X
Sept-04-01	X	X	X
Sept-05-01	X	X	X
Sept-05-01	X	X	X
Subtotal	6	6	6
12hr Sample Total	18		
X – Samples were successfully collected and analyzed from this site on the date indicated.			

Table 8. List of Analyzed Volatile Organic Compounds

Compound Name (Synonym)			
Benzene	(1)	Hexachlorobutadiene	(2)
Benzyl chloride	(1)	Methyl bromide (Bromomethane)	(2)
Carbon tetrachloride	(1)	Methyl chloride (Chloromethane)	(2)
Chlorobenzene	(1)	Methyl chloroform (1,1,1-Trichloroethane)	(1)
Chloroform (Trichloromethane)	(1)	Styrene (Vinyl benzene)	(1)
1,2-Dibromoethane	(1)	1,1,2,2-Tetrachloroethane	(1)
p-Dichlorobenzene	(1)	Tetrachloroethylene (Perchloroethylene)	(1)
1,1-Dichloroethane	(2)	Toluene (Methyl benzene)	(1)
1,2-Dichloroethane	(1)	1,2,4-Trichlorobenzene	(2)
Dichloromethane (Methylene chloride)	(1)	1,1,2-Trichloroethane (Vinyl trichloride)	(2)
1,2-Dichloropropane	(2)	Trichloroethylene (Trichloroethene)	(1)
Ethyl chloride (Chloroethane)	(2)	Vinyl chloride (Chloroethylene)	(1)
Ethylbenzene	(2)	Vinylidene chloride (1,1-Dichloroethene)	(1)
Freon 11 (Trichlorofluoromethane)	(3)	m,p-Xylene (1,4 & 1,3-Dimethylbenzene) (chromatographically indistinguishable)	(1)
Freon 113 (1,1,2Trichloro1,2,2trifluoroethane)	(3)		
Freon 12 (Dichlorodifluoromethane)	(3)	o-Xylene (1,2-Dimethylbenzene)	(1)
(1) EPA HAP and NC TAP	(2) EPA HAP only	(3) NC TAP only	

Analytical Results

Table 9 provides the summary of the results obtained from the 24hr-collected samples analyzed in this study. The average, standard deviation, and the maximum concentration in the study are given. Compounds that have BLQL listed for the average and maximum concentrations and zero for the standard deviation are compounds that were not quantifiable and/or not detected.

Table 9. Summary of 24-hr Volatile Organic Compound Analysis Results

Compound (Synonym)	Avg (ppb) n=34	Std Dev (ppb) n=34	Max (ppb) n=34
Benzene (Cyclohexatriene)	0.163	0.079	0.374
Benzyl chloride (a-chlorotoluene)	BLQL	0.000	BLQL
Carbon tetrachloride (Tetrachloromethane)	BLQL	0.000	BLQL
Chlorobenzene (Phenyl chloride)	BLQL	0.000	BLQL
Chloroform (Trichloromethane)	BLQL	0.000	BLQL
1,2-Dibromoethane (Ethylene dibromide)	BLQL	0.000	BLQL
p-Dichlorobenzene (1,4-dichlorobenzene)	BLQL	0.000	BLQL
1,1-Dichloroethane (Ethylidene dichloride)	BLQL	0.000	BLQL
1,2-Dichloroethane (Ethylene dichloride)	0.129	0.026	0.275
Dichloromethane (Methylene chloride)	BLQL	0.000	BLQL
1,2-Dichloropropane (Propylene dichloride)	0.133	0.049	0.412
Ethyl chloride (Chloroethane)	0.213	0.284	1.763
Ethylbenzene	0.134	0.053	0.433
Freon 11 (Trichlorofluoromethane	Note 1	--	--
Freon 12 (Dichlorodifluoromethane)	Note 1	--	--
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	BLQL	0.000	BLQL
Hexachlorobutadiene	BLQL	0.000	BLQL
Methyl bromide (Bromomethane)	BLQL	0.000	BLQL
Methyl chloride (Chloromethane)	0.485	0.266	1.094
Methyl chloroform (1,1,1-Trichloroethane)	BLQL	0.000	BLQL
Styrene (Vinyl benzene)	0.129	0.024	0.264
1,1,2,2-Tetrachloroethane	BLQL	0.000	BLQL
Tetrachloroethylene (Perchloroethylene)	BLQL	0.000	BLQL
Toluene (Methyl benzene)	0.421	0.214	0.977
1,2,4-Trichlorobenzene	BLQL	0.000	BLQL
1,1,2-Trichloroethane (Vinyl trichloride)	BLQL	0.000	BLQL
Trichloroethylene (Trichloroethene)	BLQL	0.000	BLQL
Vinyl chloride (Chloroethylene)	BLQL	0.000	BLQL
Vinylidene chloride (1,1-Dichloroethene)	BLQL	0.000	BLQL
m,p-Xylene (1,4 & 1,3-Dimethylbenzene)	0.142	0.074	0.529
o-Xylene (1,2-Dimethylbenzene)	BLQL	0.000	BLQL

Note 1: The results for Freon 11 and Freon 12 are not presented because of a contamination problem at the DAQ lab facility caused by a refrigerant leak in the air conditioning system. This was observed in blank samples that were run as part of the QA/QC criteria. The nature and degree of contamination was non-uniform; therefore data for these two compounds are not considered to be reliable representations of ambient air concentrations.

4.3 DISCUSSION OF VOLATILE ORGANIC COMPOUND DATA

4.3.1 Volatile Organic Compound Source Emission Results

The data in **Table 4** show that the benzene TPER guideline of 8.1 lb/yr was exceeded by benzene emission rates of 57 lb/yr and 28 lb/yr from the Southern States remediation site and the APAC dryer/mixer, respectively. DAQ was aware that the APAC benzene data was above the TPER and also that it modeled *below* the AAL. However, prior to this study, DAQ was not aware that the Southern States (or other remediation sites) benzene data was above the TPER and also that it would model *above* the AAL. Likewise, it was considered new information to DAQ that the Southern States was the principal emitter of benzene, toluene, and xylenes from the six sources, accounting for the majority (65-72%) of these emissions from the source cluster.

In December 1988 DAQ revised its policy on remediation sites using various air stripping techniques in that they would be required to register these projects but were no longer required to receive a permit. In August 1995 the policy was revised somewhat in that air strippers were to be permitted unless they were found to be exempt as an insignificant activity under 15A NCAC 2Q .0102(b)(2)(E)(i). This exemption covers sources with potential emissions before any control of (A) criteria pollutants below 5 ton/year, (B) a single hazardous air pollutant (HAP) below 10 ton/year, or (C) a combination of HAPs below 25 ton/yr. Because nearly all remediation sites qualify for this exemption, the NC Division of Water Quality (DWQ) now has oversight responsibility for remediation sites with contaminated water and soil, based on an administrative decision made by the Department of Environment and Natural Resources.

4.3.2 Volatile Organic Compound Dispersion Modeling Results

In regards to emission dispersion from the stack of a source, the taller the stack and the greater the distance between the stack and property line has the effect of lowering its predicted ground-level concentration. Similarly, higher exit stack gas velocity and gas temperature will result in a greater *effective stack height*, likewise reducing its ground-level concentration.

The maximum one-hour ground-level benzene concentration predicted by dispersion modeling is 0.32 ppb (1.02 ug/m^3) for Southern States, as shown in **Table 5** and **Figure 6**. Note that the ground-level maximum occurred within 150 ft of its southern property line. The Southern States benzene emission rate is 7-times the TPER (57 lb/yr versus 8.1 lb/yr), with the corresponding maximum impact level being 8.5-times above the AAL. **Table 10** presents four contributing factors that account for the maxima impact concentration, which were used as inputs in dispersion modeling. For comparison, a corresponding range of typical values is also shown in **Table 10.** Comparison of the first three parameters in the table shows that each of Southern States source characteristics is lower than typical values for air pollution sources. Collectively, these atypical source parameters produce abnormally low dispersion characteristics.

Table 10. Southern States Source Dispersion Characteristics

Parameter, Units	Southern States	Typical Facility
1. Stack exit velocity, ft/min	900	3000-4000
2. Stack height, ft	10	30-300
3. Proximity to Property Line, ft	< 50	100-1000
4. Source emission concentration, ppb	1,800	Varies

Examination of the area with predicted levels above the AAL (within 150 ft of the southern property line) show that the affected area (approximately 1 acre in size) encompasses four tracts of property. These properties include Southern States itself and three adjacent tracts: Leeds Building Products, Jake Alexander Blvd., and the former ExxonMobil Terminal. Assessment of the three adjacent tracts indicates that above-AAL levels in the affected area pose little/no long-term exposure potential for any individuals. Furthermore, Southern States voluntarily decided in March 2002 to discontinue operation of the air sparging / soil-vapor extraction system and is currently in the process of evaluating alternative technologies to minimize or eliminate benzene and other VOC emissions. Exxon/Mobil made a similar voluntary change from soil-vapor extraction to bioventing at its remediation site in December 2001, also eliminating the concentrated release of benzene and other VOC emissions.

4.3.3 Volatile Organic Compound Ambient Monitoring Results

The compounds in **Table 9** with quantifiable concentrations were compared to data from other sites in North Carolina and other states. Efforts were made to obtain data from other sites that were similarly indicative of the area in Salisbury, NC. Comparison data was obtained from other NC locations, Georgia (GA), and Louisiana (LA). All samples used in the comparison were collected over a 24-hr period. **Table 11** shows these comparisons. *Note: There is one exception to the 24-hour samples: two 12hr samples taken each of three days in Salisbury, NC (during the Associated source emission test) for this study. These were averaged to obtain a 24hr sample value and these values were subsequently averaged to obtain what is referred to in* ***Table 11*** *as the "12hr Composite Sample Average."*

In **Table 11**, it can be seen that the average VOC values obtained at the "suburban" Salisbury sites were comparable to those obtained from rural sites in NC, GA, and LA as well as a suburban site in GA. And in some cases the Salisbury VOC values were lower than those found at rural sites. For example, the average 24-hour benzene concentration for Salisbury was 0.16 ppb, within the range of 0.13 - 0.24 ppb measured in other suburban and rural sites during 24-hour periods. The concentrations measured and reported from the Salisbury sites will be assessed in terms of health effects and risk assessment in a separate report through the NC Department of Health and Human Services (DHHS) and ATSDR.

Table 11. Comparison of 24-hr and Composite 12-hr Salisbury Results with Other Sites

Compound Name (Synonym)	**NC TAP**	**Average Concentrations in parts per billion (ppb)(1)**						
		Salisbury,NC Study Avg. 24hr samples (n=34)	**Salisbury,NC Study Avg. 12hr Composite samples (n=18)**	**Lincoln Co, NC Rural Site (n=89)(2,3)**	**Conyers, GA Suburban site Avg (n=31)(2,4)**	**Dawsonville, GA Rural site Avg (n=20)(4)**	**Douglas, GA Rural site Avg (n=10)(4)**	**Pride, LA Rural site Avg. (n=68)(5)**
Benzene (Cyclohexatriene)	**X**	0.16	0.25	0.16	0.24	0.13	0.23	0.20
1,2-Dichloroethane (Ethylene dichloride)	**X**	0.13	0.13	--	--	0.13	0.13	0.13
Dichloromethane (Methylene chloride)	**X**	0.12	0.14	--	--	0.20	0.24	0.17
1,2-Dichloropropane (Propylene dichloride)		0.13	0.13	--	--	0.13	0.13	0.13
Ethyl chloride (Chloroethane)		0.21	0.13	--	--	0.13	0.13	0.14
Ethylbenzene		0.13	0.13	0.06	0.06	0.13	0.56	0.13
Methyl chloride (Chloromethane)		0.48	0.13	--	--	0.64	0.73	0.60
Styrene (Vinyl benzene)	**X**	0.13	0.13	--	--	0.13	0.13	0.13
Toluene (Methyl benzene)	**X**	0.42	0.56	0.38	0.38	0.13	1.71	0.13
m,p-Xylene (1,4 & 1,3-Dimethylbenzene)	**X**	0.14	0.15	0.18	0.36	0.13	2.01	0.13
o-Xylene (1,2-Dimethylbenzene)	**X**	0.13	0.13	0.07	0.08	0.13	0.50	0.13

Notes:

1. Raw data was obtained from the respective states and the data sets were statistically treated in the same manner as the data set from Salisbury see **Section 3.4.2**
2. “--“ indicate that these compounds were not analyzed for in the samples from these sites.
3. Data from Paw Creek Study, Charlotte, NC – Lincoln Co. rural site May 6 - August 11, 1997.
4. Data from Georgia Department of Natural Resources, 1999 PAMS (Photochemical Assessment Monitoring Stations) Network and Toxics Network .
5. Data from Louisiana Department of Environmental Quality, Air Toxics Summary 2001.

Site Comparison Data for Benzene

Of particular interest to the City of Salisbury are the benzene concentrations observed in the study, especially as it relates to the AALs. **Table 12** shows the number of samples, the average 24hr sample benzene concentrations, and the standard deviation for each site in the Salisbury study, the total for all sites in the study, and the Lincoln county (rural) site. When the average for each site was statistically compared to each of the other sites in the study, it was found that at the 95% confidence interval that the averages were not statistically different.

Given that measured benzene levels at the three monitoring stations were not statistically different and the stations are located upwind and downwind from the cluster of emission sources, the data suggest that there was little/no impact from the emission sources. This suggestion of limited effect from nearby sources is also supported by the dispersion modeling results, which indicated that that only a relatively small 1-acre area was predicted to have maximum ground level impacts above the AAL.

Additionally, statistical comparison of the total Salisbury Study average to the Lincoln County rural site at the 95% confidence interval also found that these averages were not statistically different. The equations and the values used for these statistical comparisons [48, 49] are given in the QAPP (see Appendix). The reader is advised to refer back to the discussion of AALs in **Section 3.7** to provide appropriate context for this discussion.

Therefore, given the comparisons shown in **Tables 11** and **12** and the regulatory background on AALs, DAQ concludes that the Salisbury air quality is typical of similar areas. As noted earlier, the concentrations measured and reported from the Salisbury sites will be assessed in terms of health effects and risk assessment in a separate report through the NC Department of Health and Human Services (DHHS).

Table 12. Benzene Statistical Summary

Site	**Number of Samples (n)**	**Average (ppb)**	**Standard Deviation**
Cul-de-sac (site 1)	14	0.187	0.090
Access Road (site 2)	12	0.146	0.072
Remediation (site 3)	8	0.149	0.066
Total Salisbury (all sites)	34	0.163	0.079
Lincoln County site	86	0.159	0.347

4.4 PRESENTATION OF HYDROGEN SULFIDE RESULTS

4.4.1 Hydrogen Sulfide Source Emission Results

Associated Terminal Emission Results

As discussed in **Section 3.2**, emission test data were the basis utilized to present H_2S emissions for the two asphalt facilities. Detectable results in the Associated source emission testing were only produced for H_2S, as concentrations of the other TRS compounds were below detection. Gas flowrates were reported in standard cfm (scfm) and H_2S emission data were reported for concentrations in ppm by volume, dry basis (ppmvd) and for emission rates in lb/hr. Tests were conducted under normal operations in terms of process and air pollution control device conditions. A summary of the process conditions with corresponding emission test results is presented in **Table 13**. The significant aspects of the Associated H_2S test from the three types of emission points are as follows:

- 2,400 ppm concentration and emission rate of 0.30 lb/hr from the storage tank vent controlled by the Ecosorb® scrubber;
- 0.2 ppm and emission rate of 0.000017 lb/hr from the truck loadout vent controlled by the carbon bed; and
- 150 ppm and emission rates for one railcar of 0.0061 lb/hr and for an 18 car shipment of 0.11 lb/hr without any form of air pollution control.

APAC HMA Plant Emission Results

DAQ used ambient monitoring methods to *estimate* - not EPA methods to officially determine - H_2S emission concentrations from four HMA batch mix operations: (1) Liquid asphalt storage tank, (2) Liquid asphalt truck unloading, (3) Batch mix dryer, and (4) HMA truck loadout. With the expressed *caveat* that these are considered preliminary semi-quantitative data, a summary of the process conditions with corresponding H_2S emission estimates are also presented in **Table 13**.

Preliminary data collected at the APAC hot mix asphalt plant suggest H_2S emission concentrations of 90 ppm and 6 ppm emitted from liquid asphalt storage tank filling and the dryer/mixer, respectively. Facility wide emission rates are estimated to be 0.7 lb/hr, a level above the TPER guideline of 0.52 lb/hr. (Subsequent dispersion modeling shows a permissible AAL; see discussion below).

Table 13. Asphalt Facilities H_2S Emission Results

Process Operation	**PG 64-22 Liquid Asphalt Parameters**		**Gas Flowrate**	**H_2S Emission Data**		
	Quantity or Rate	Temperature, °F	Scfm	Concentration ppmvd	Rate lb/hr	Emission factor, lb/ton [a] [b]
Associated Terminal						
Railcar heating	90 ton in railcar	294	7.7	154	0.0061	NA
Railcar unloading	90 ton in railcar	294	Negative	NA	NA	NA
Storage tank filling	61 ton/hr (237 gpm)	315	24	2370	0.30	0.0049 [a]
Storage tanks heating	~1700 ton in 2 tanks	310	2	0.07	8.1E-06	NA
Storage tank unloading	~910 ton in one tank	313	Negative	NA	NA	NA
Truck loadout	138 ton/hr (536 gpm)	313	709	0.20	0.00075	1.7E-05 [a]
APAC HMA Plant						
LA storage tank filling	0.8 ton/min	~ 275	~ 24	~ 90	~ 0.01	~ 0.0002[a]
LA tanker truck unloading	0.8 ton/min	~ 275	~ 0	<10	0	0
HMA Dryer/ mixer	160	~ 280	~ 24,000	~ 6	~ 0.7	~ 0.005 [b]
HMA truck loadout	2 ton/min	~ 280	~ 50	0	0	0

a: units of lb H_2S / ton of liquid asphalt.
b: units of lb H_2S / ton of hot mix asphalt.

4.4.2 H_2S Dispersion Modeling Results

Modeling in 2001

The ISCST3 dispersion modeling results showed that H_2S was predicted to be below its respective annual AAL of 2.1 $x10^{-4}$ mg/m^3 (~ 1.5 ppm) as outlined in NCAC 2D.1104. Isopleths for Associated and APAC are shown in **Figures 7** and **8,** respectively. Generally, the H_2S isopleth analyses for both facilities also show that maximum impacts are distributed at and along the northern property boundary of the Associated facility and drop rapidly moving away from the facility. The highest one-hour H_2S concentration of 290 ppb (0.404 mg/m^3) for Associated occurred just outside its property line less than

55 feet from the Access Road sampling site. The highest one-hour H_2S concentration of 4.3 ppb (0.006 mg/m^3) for APAC occurred about 300 ft outside its northern property line.

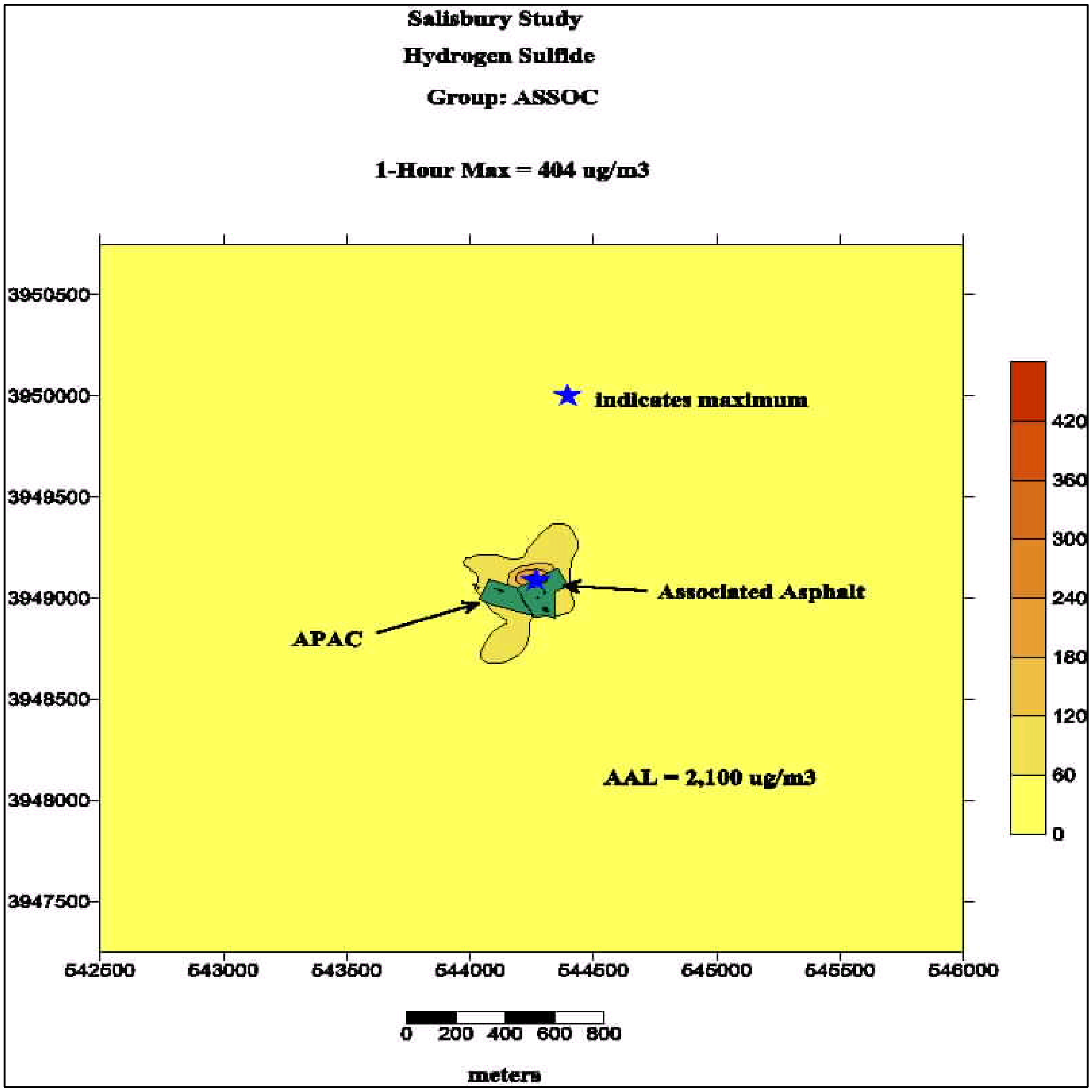


Figure 7. Associated Dispersion Model Prediction for H_2S.

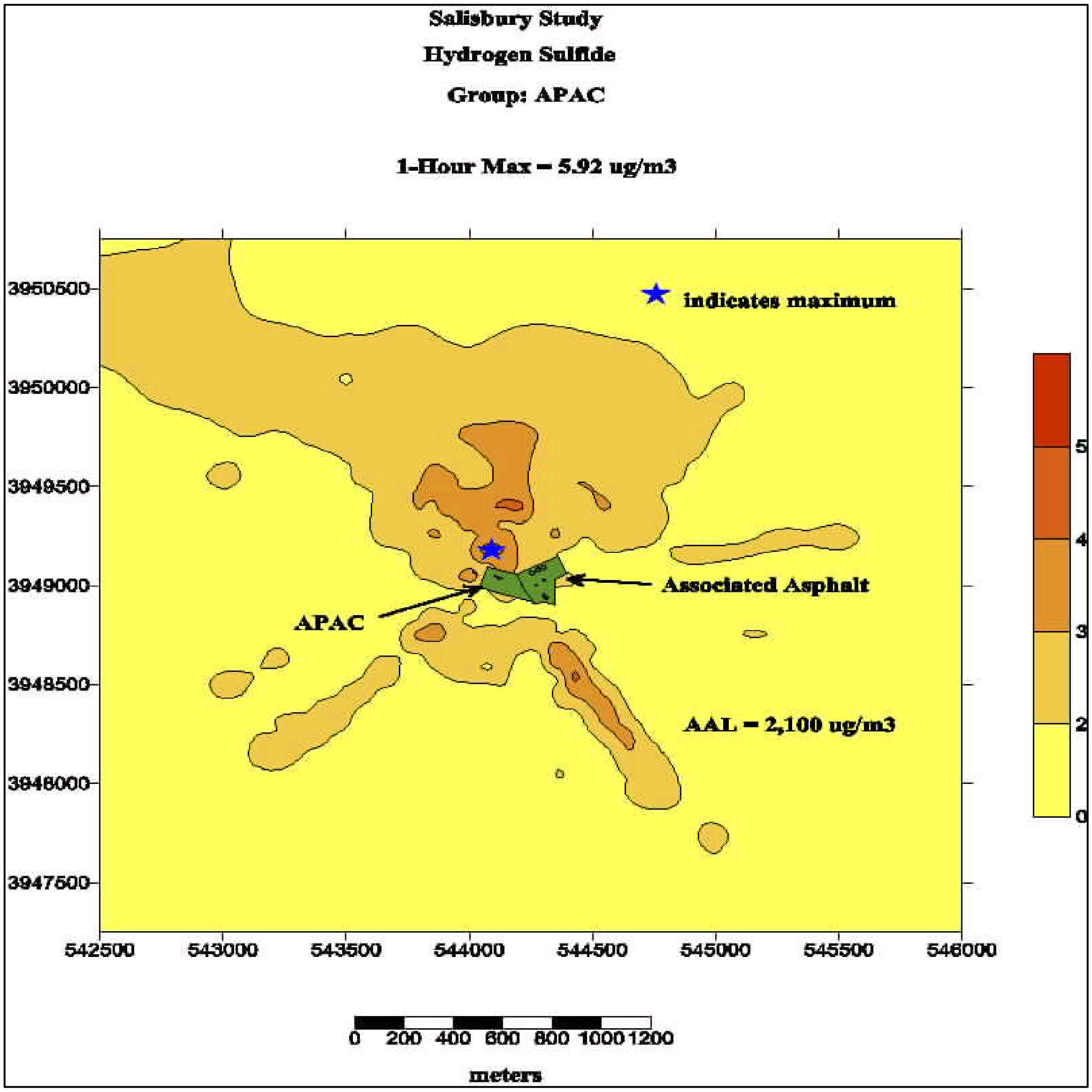


Figure 8. APAC Dispersion Model Prediction for H_2S.

Both Associated and APAC own rectangular shaped properties and have one common property boundary (Associated's west property line is APAC's east property line as shown in **Figure 1**). For the seven boundaries, maximum concentrations at the property line predicted by the model ranged from 0.83 ppb to 290 ppb. **Table 14** presents the modeled concentrations at each asphalt facility property line midpoint. In addition, concentrations above the odor threshold (8 ppb) throughout the Milford Hills subdivision were predicted from modeling the Associated terminal emissions determined during the study.

Table 14. Modeled H_2S Levels at Asphalt Facility Property-Lines

Asphalt Facility	Property line	H_2S Concentration, ppb
Associated	North	290
	East	106
	South	30
	West (common to both)	65
APAC	North	1.5
	East (common to both)	3.4
	South	3.0
	West	0.8

Modeling in 2003

Due to over 400 odor complaints and H_2S emission testing indicating the ineffectiveness of the Ecosorb® system in reducing odorous emissions, in January 2002 DAQ withdrew Associated's temporary permit which previously allowed use of the Ecosorb® scrubber. Associated then replaced the Ecosorb® scrubber controlling storage tank vents with activated carbon beds by the end of March 2002. Nonetheless, concerned citizens and ATSDR were still concerned about the corresponding exposures to ambient H2S concentrations from this emission control configuration. In response to citizen's and ATSDR request, DAQ performed dispersion modeling of emissions incorporating the latest emission control changes. The Asssociated facility emission control practices have changed over the 2000-2002 period as a result of experimenting with what was later determined to be ineffective control technology. Presented below are descriptions of two key emission control scenarios that were modeled by DAQ and presented in **Table 15**:

Emission Control Scenario 1. As discussed in Section 2.1, during the study an Ecosorb® scrubber treated the storage tank vent streams and activated carbon beds controlled the truck loadout vent streams. Emission source testing in September 2001 showed relatively high concentrations of 2,370 ppm H_2S exiting the Ecosorb® scrubber treating the tank vents and only 0.2 ppm H_2S exiting the carbon bed treating the truck loadout vents.

Emission Control Scenario 2. Carbon beds were re-installed on all 3 storage tank system vents in late March 2002; the carbon beds treating the truck loadouts stayed. This control configuration has remained in place since March 2002.

Using Associated source data and vapor space properties assumptions emission factors were calculated; each is presented below in **Table 15**. Neither facility production rates nor property boundaries changed over time. Both of the above scenarios were modeled using the ISCST3 model.

Table 15. Asphalt Terminal H_2S Emission Data

Source Description	Asphalt Quantity or Rate	H_2S Emissions	
		lbs / ton asphalt	lbs / hr
Tank filling Uncontrolled (no fan)	61 ton/hr (237 gpm)	0.0049 (a)	0.300 (a)
Tank filling Controlled (no fan)		0.000017 (b)	0.001 (b)
Truck loadout Controlled	138 ton/hr (536 gpm)	0.000017 (a)	0.0008 (a)
Railcar heating Uncontrolled	90 tons in railcar	#N/A	0.0061 (a)

(a) Associated source test in September 2001.
(b) Vapor space properties assumptions.

The modeling results for predicted maximum impacts and approximated impact radii are presented in **Table 16**. The following assumptions were made for modeling. First, plant wide throughput was assumed to be though Tank System 2 with three 1-million gallon tanks (see **Table 1**). Submitted process records show Tank System 2 was used the majority of the time. The second assumption was that two threshold values (56 ug/m^3 and 33 ug/m^3) were chosen to define the radius of the area with concentrations above the thresholds. The two values correspond with the NC Scientific Advisory Board (SAB) recommended revisions in the H_2S AAL. (A third threshold value of 120 ug/m^3 with a 24-hr average period was also proposed by the SAB. However, based on modeling neither Associated scenario is expected to cause an offsite 24-hr concentration greater than 120 ug/m^3.) Impact radius is not a normal AQAB modeling product, but one used to estimate the area and corresponding persons exposed for this situation.

The most significant observation is that the actual annual emission (lb/yr) has decreased. The modeling predictions (1-hr max and 24-hr max) follow a similar pattern. Associated in its present configuration would comply with all the proposed AAL guidelines.

The radius of impact in **Table 16** has no direct regulatory relevance and is presented only to estimate the extent of community exposure. The radius of impact describes an approximated circular area, centered at the Associated terminal, in which residents would be exposed to a concentration higher than a proposed guideline. For example, Table 16 shows an impact radius of 0.25 miles for the 56ug/m^3 one-hour H2S guideline under the September 2001 emission control scenario; this impact radius covers approximately 0.20 square miles encompassing 70 people. The following two assumptions regarding population density were made:

- The modeled area included parts of four census tracks; population density across those tracks was assumed to be constant.

- Occupational exposure was not considered; a Food Lion administrative building and a military reserve post are nearby and within the impact radius, but an actual number of employees has not been determined

Table 16. Asphalt Terminal H_2S Modeling Results

Associated Conditions	Sept. 2001	April 2002 to present
Tank Filling	Uncontrolled w/o fan	Controlled w/o fan
Truck Loadout	Controlled	Controlled
Railcar Heating	Uncontrolled	Uncontrolled
Estimated years of operation (years)	1	1
Actual Annual Emissions (lb/yr)	718	132
Relevant Proposed Guideline; 56 ug/m^3 1-hr average (human-airway resistance)		
1-hour max impact (ug/m^3)	404	9.2
Radius of impact (miles) Concentration greater than 56 ug/m^3	0.25	0
Area (miles square)	0.20	0
Persons exposed (a)	70	0
Relevant Proposed Guideline; 33 ug/m^3 24-hr average (human-eye pain)		
24-hour max impact (ug/m^3)	59	1.3
Radius of impact (miles) Concentration greater than 33 ug/m^3	0.031	0
Area (miles square)	0.003	0
Persons exposed (a)	0	0

(a) Persons exposed values determined by NC Department of Health and Human Services.

4.4.3 H_2S Ambient Monitoring Data

The original H_2S ambient monitoring data were produced with 15-minute averages at each monitoring site. In total, more than 31,000 data points representing 15-minute averages were produced. Tapemeter concentrations less than the 2 ppb were below the lower quantitation limit (BLQL). All ensuing statistics were based on using BLQL concentrations converted to ½ of the limit (or 1 ppb) using common EPA practice. The H_2S ambient monitoring data served a central role for evaluating its connection with asphalt facilities' process data, wind directional data, and odor complaints.

The original 15-minute H_2S concentration data were converted to 1-hour averages to synchronize it for comparison with: 1) the hourly process data, 2) the one-hour ambient regulatory level (NC DAQ Acceptable Ambient Level as an acute irritant) for H_2S, and 3) dispersion model concentrations. Hourly averages were considered above detection if the average of the four sample periods was greater than or equal to 1.25 ppb. The distribution of 1-hour H_2S measurements for each monitoring site is presented in **Table 17**.

Table 17. Number of 1-hour H_2S Concentration Measurements for Each Site

H_2S Concentration Range, ppb	Access road site	Cul-de-sac site	Remediation site
Below Detection Level, < 1.25	1,825	2,185	2,795
1.25 – 10	717	120	13
10.25 – 30	25	4	0
30.25 – 50	3	0	0
Invalid [a]	238	499	0
Total Measurements	2,808	2,808	2,808

a: Each site experienced some difficulty due to power disruption.

Data in **Table 17** shows that the monitoring site at the Access Road (located 50 ft to the north of Associated's northern property-line) observed more frequent and intense peaks for H_2S than the other two sites. In fact, the Access road site tapemeter produced more than five-times more detectable concentrations than the other two sites combined. Given that there are no other H_2S sources nearby, interpretation of the analysis of the distribution of the 1-hour data strongly suggests that one or both of the asphalt facilities is (are) the source of the fluctuating H_2S levels.

The following five graphs in **Figure 9** graphically present 1-hour average H_2S levels at each site for each separate month (May-September) during the study. These figures illustrate the extent and variability of the H_2S ambient monitoring data.

Figure 9. Summary of 1-hour H_2S Ambient Concentration Data

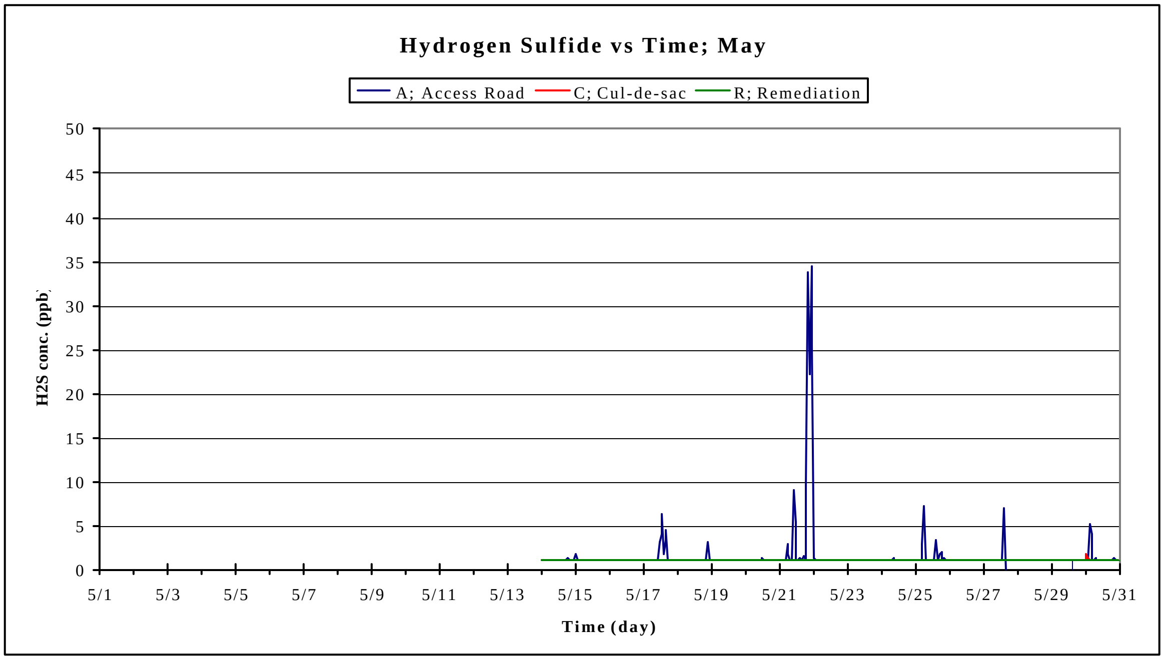
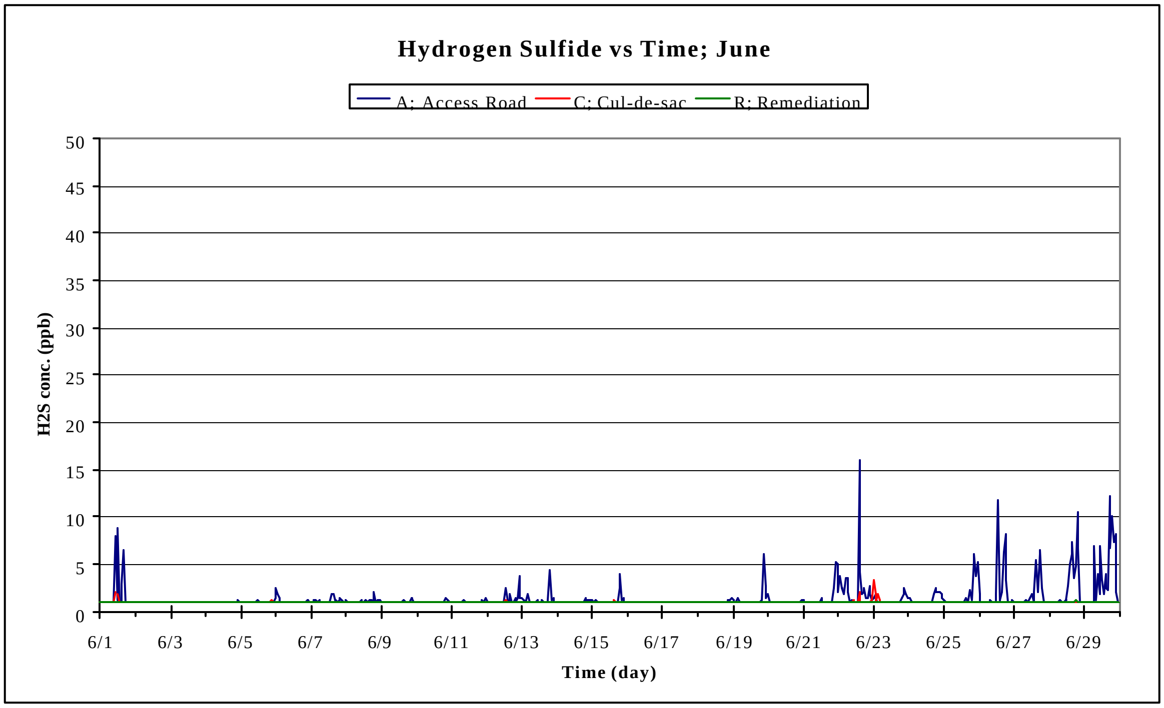


Figure 9 (con'd). Summary of 1-hour H_2S Ambient Concentration Data



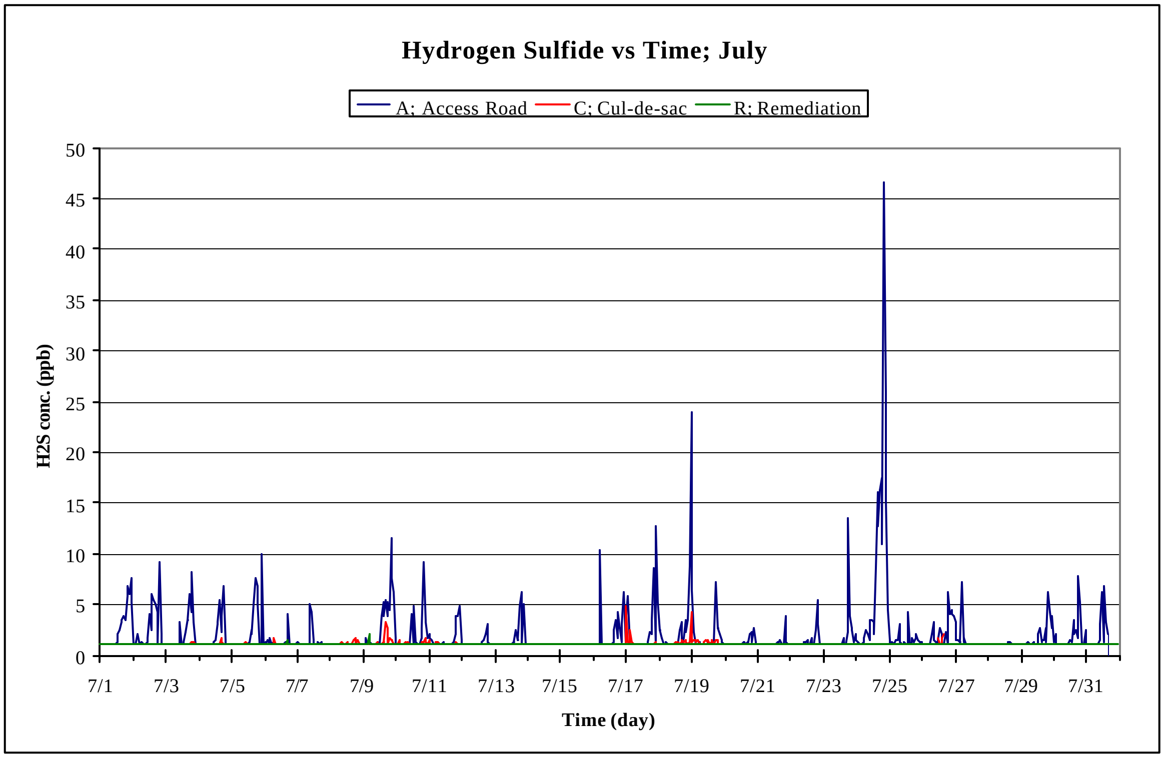
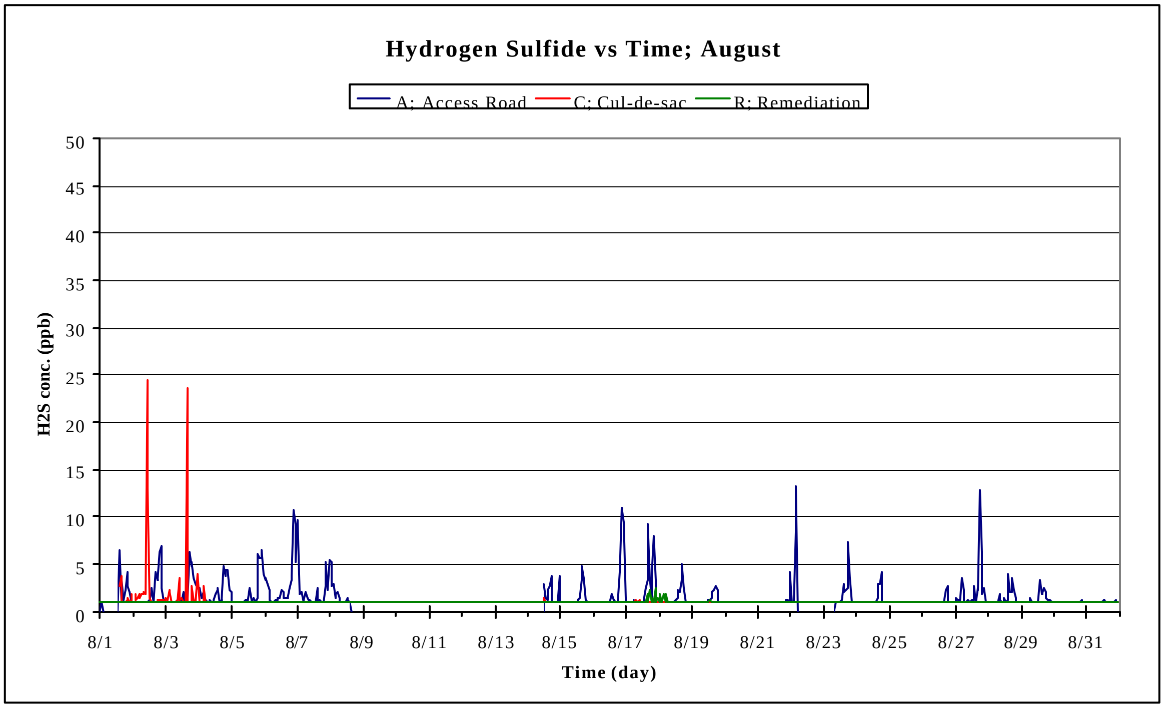
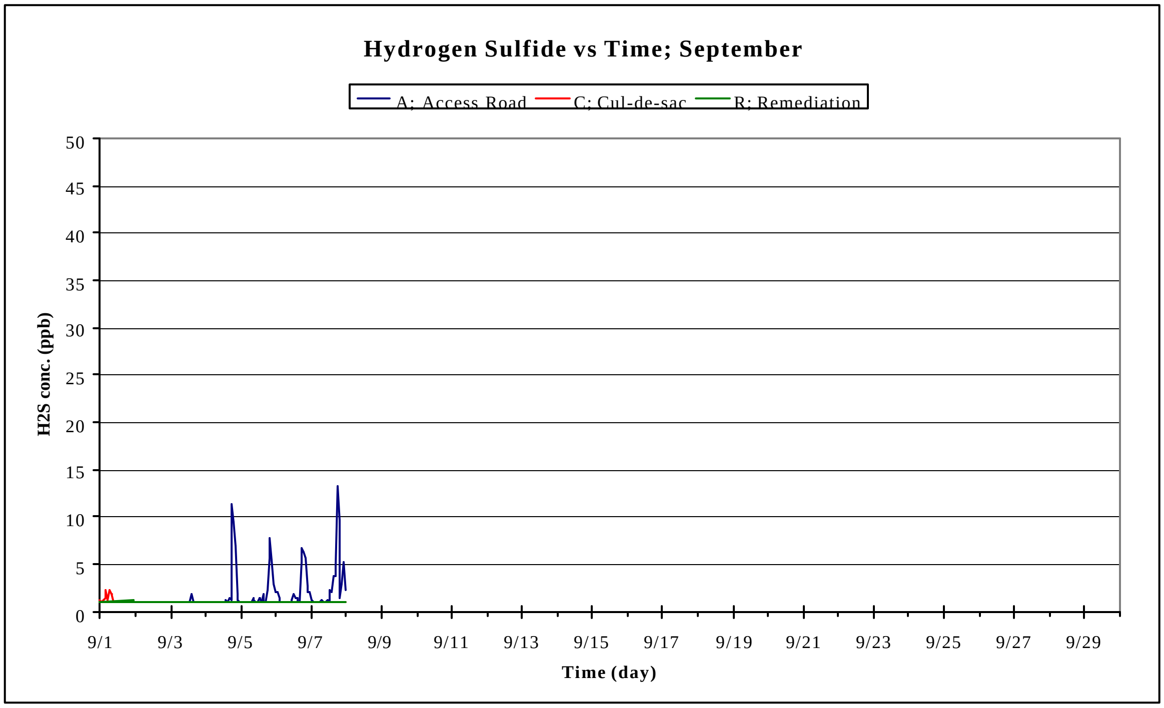


Figure 9 (con’d). Summary of 1-hour H_2S Ambient Concentration Data





4.4.4 Odor Complaints

During the study there were 24 unique odorous events reported by 39 citizens.[46] Of these events 88% coincided with or occurred less than 4 hours after either APAC HMA production or Associated storage tank filling. In the opinion of the city risk manager the intensity of the odor on four occasions warranted citation. All four citations that occurred during the study period were issued to Associated because it was the only facility operational at the time of the odor complaint.

4.5 DISCUSSION OF HYDROGEN SULFIDE RESULTS

4.5.1 Discussion of Hydrogen Sulfide Source Emission Data

Associated Asphalt Hydrogen Sulfide Source Emission Data

The following discussion puts the significance of the new H_2S emission test results for Associated into context:

Discovery that H_2S is by far the most emissive toxicant measured from liquid asphalt. The test results from the storage tank vent during filling showed that the measured H_2S concentration was 2,400 ppm with an emission rate of 0.30 lb/hr. Facility-wide H_2S emissions using current emission controls are estimated at roughly 700 lb/year, considerably more than the last two estimates of 4 lb/year and 23 lb/year formally submitted by Associated to DAQ. It is expected that many of the other (approximately 13) liquid asphalt terminals in NC have also underestimated their H_2S emissions.

Furthermore, a comparison of uncontrolled emissions was made between measured H_2S emissions and estimates for individual VOC species using EPA emission factors and EPA TANKS software for the Associated terminal annual throughput of 120,000 ton. The results show that:

- H_2S at 1200 lb/yr is more than 15-fold more emissive than the next most emissive compound, 2-Methylnaphthalene at 68 lb/yr.
- H_2S is 2800-fold more emissive than benzene at 0.4 lb/yr.
- H_2S, as a single inorganic compound, is emitted at nearly the same level as all total organic compounds, including volatiles and semivolatiles, at 1300 lb/yr.

H_2S Controllability. There is a 4 order-of-magnitude contrast in emission concentration between the storage tank (2,400 ppm) controlled by the Ecosorb® scrubber and the truck loadout (0.2 ppm) controlled by activated carbon. The results indicate that activated carbon treating the truck loadout vent was highly effective (~ 99.9+ % efficiency) and that the Ecosorb® scrubber treating the storage tank vent was ineffective in H_2S control for this application. As stated in their manual, "Ecosorb® is not designed to control emissions in compliance with federal or state regulations."[24]

It can be argued that the H_2S concentration treated by each control devices is expected to be essentially the same. This is based on the assumption in the EPA TANKS software (and in other applications) that a tank's headspace is saturated, meaning that volatile compounds above the same liquid at the same temperature have identical concentrations.

Railcar heating emissions. While the H_2S emission rate for one railcar is relatively low at 0.0061 lb/hr, emissions for a shipment of 18 cars become more significant at 0.11 lb/hr.

Odor and worker exposure issues. Average H_2S concentrations of 2,400 ppm in the storage tank vent near ground level are nearly a million-fold above the odor threshold, generally set at 8 ppb,[50] and more than 20-fold above the Immediately Dangerous to Life and Health (IDLH) set at 100 ppm for 30-min exposure by the National Institute for Occupational Safety and Health.[51] Such statistics support the potential for odor complaints and support the rationale for the strong precautionary language in asphalt Material and Safety Data Sheets. DAQ has referred this information to DHHS for consideration.

APAC Preliminary Hydrogen Sulfide Source Emission Data

While the H_2S data for the HMA plant are preliminary, three points are of interest:

1. The actual source of the H_2S emissions from the combined dryer/mixer exhaust are released only by mixing operations; there is no opportunity of any H_2S release from the aggregate or fuel fired in the dryer.
2. The estimated emission rate from the mixer of 0.7 lb H_2S/hr is above the TPER level of 0.52 lb/hr.
3. A comparison of emissions was made between measured H_2S emissions and estimates for individual VOC species using EPA emission factors (see **Table 5**, Ref. 25) for the 2001 APAC HMA plant annual production of 101,000 ton/yr. The comparison suggests that H_2S is the most emissive toxic compound from hot mix asphalt operations. Use of the 0.005 lb H_2S/ton HMA emission factor for a typical 100,000 ton HMA/yr produces 500 lb/yr H_2S. This is higher than the second-most emissive toxic compound level of 270 lb/yr for xylene and the third-most emissive toxic compound level of 220 lb/yr for ethylbenzene.
4. Previous permit applications submitted by APAC and other HMA companies to DAQ do not include any estimated emissions for H_2S due to the absence of any EPA emission factor data for H_2S.

4.5.2 Discussion of Hydrogen Sulfide Dispersion Modeling Results

The dispersion of emissions from the stack of a source can be described and visualized as a conical-shaped plume. As it travels downwind, the plume progressively spreads and expands in both the vertical and crosswind dimensions. While the plume retains all of the emissions released from the source, pollutant concentrations rapidly diminish as the plume expands in three directions. This means that the further downwind the plume travels, the more it will expand, resulting in a lower pollutant concentration. Additionally, the taller the stack, the further the plume must travel before it reaches ground level. Again, this has the effect of lowering its predicted ground-level concentration. Similarly, higher exit stack gas velocity and increased buoyancy from higher gas temperature will result in a greater *effective stack height*, likewise reducing its ground-level concentration.

The maximum one-hour ground-level H_2S concentration predicted by dispersion modeling is 290 ppb (0.404 mg/m^3) for Associated and 4.3 ppb (0.006 mg/m^3) for APAC. Note that each ground-level maxima occurred outside its northern property line, with APAC's maxima at 300 ft away being considerably more distant from the property line than Associated's maxima at 55 ft away. While the APAC H_2S emission rate (based on preliminary data) is almost twice as high as Associated (0.7 lb/hr versus 0.41 lb/hr), there are at least four contributing factors that account for the formers much lower maxima impact concentration. The four factors, which were used as inputs in the dispersion modeling, are shown in **Table 18.**

Table 18. APAC and Associated Source Dispersion Characteristics

Parameter, Units	APAC Dryer/mixer	Associated Storage Tank Vents
Source emission concentration, ppm	6	2,400
Stack exit velocity, Ft/min	4,250	120
Stack height, ft	30	10
Temperature, °F	270	140

The primary reason for APAC's lower maxima is that its emission concentration is 60-times lower than Associated. In addition, each of three factors (stack height, gas velocity, and gas temperature) also contributes to a taller effective stack height. Collectively, there is a compounding effect from these factors that cause APAC's source characteristics to produce a much lower H_2S concentration at ground level relative to Associated's plume. Further evidence of this relative advantage in source characteristics is comparison of the isopleths, each showing lines with H_2S concentration (analogous to a topographical map showing lines with the same elevation). As seen from the two isopleths in **Figure 7** and **Figure 8**, there is much more area, and at higher H_2S concentration, affected by Associated source characteristics than APAC characteristics.

4.5.3 Discussion of Hydrogen Sulfide Ambient Monitoring Results

Continuous monitoring of the H_2S ambient levels was intended to serve two objectives:

- Characterize the airborne concentrations in the area, and
- If measurable levels were observed, then attempt to resolve the question as to which facility(s) was responsible for contributing to the measured levels.

The issue as to which facility(s) was responsible for any elevated airborne concentrations is known as "source apportionment." In order to investigate source apportionment, asphalt facility process and wind directional data were also collected to evaluate any relationships among monitored H_2S ambient concentration, asphalt facility operation, and wind direction.

The monitoring data in **Table 17** and **Figure 9** show the following results from the measured 1-hour average H_2S data:

- Access Road site located within 30 meters of the asphalt terminal exceeded odor threshold levels 28 times and approached or exceeded odor nuisance levels (40 ppb) only 3 times in 4 months.
- Cul-de-sac site located 200 meters from the asphalt terminal were above odor threshold levels only 4 times in 4 months, but did not approach odor nuisance levels.
- Remediation site located 400 meters from the terminal neither exceeded odor threshold levels nor approached odor nuisance levels.

While the H_2S ambient monitoring data are generally low most of the time, there are important facts to consider, including:

(A) Each asphalt facility only operates intermittently (nominally 20% of the time),
(B) Wind direction is aligned with the asphalt facilities and the Access Road monitoring site only occasionally (nominally 30% of the time), and
(C) A and B must occur *concurrently* in order for a monitor to detect H_2S levels.

In such a situation with intermittent facility operations and periodic wind direction alignment, conditions are suitable or available for H_2S detection only 6% of the time (0.2 times 0.3 = 0.06, or 6%). Recognition of this fact shrinks the *apparent availability* for H_2S detection from an ideal 100% down to a *realistic availability* of merely 6%. Even if 16 monitors could be stationed in all directions (16 sectors) completely surrounding the facilities, then there would still only be a realistic opportunity for H_2S detection 20% of the time collectively from all 16 monitors. Recognition of the compressed opportunity was the first key in gaining insight on source apportionment.

The second key was to recognize that an alternative approach to the conventional pollutant-rose approach would be helpful in evaluating any relationships with other data, as done in another similar source apportionment study.[52] This was achieved by subdividing and converting the original wind directional data (produced in degrees from 0-360 degrees) into sector data (arranged in 16 sectors, each of which is 22.5 degrees). This method takes advantage of the higher resolution provided by wind directional data in order to characterize and correlate wind pattern with other selected parameters, such as H_2S monitoring data and process data.[53] The following is a discussion of a series of results produced from evaluating relationships among monitored H_2S ambient concentration, asphalt facility operations, and wind direction.

Relationship of H_2S Monitoring Data and Asphalt Process Data

The H_2S monitoring data were evaluated to determine whether a relationship could be established with the time periods when the asphalt facilities were operating. To simplify and focus such analysis, the most H_2S emissive operations at each asphalt facility were identified using the data in **Table 13**. This table identifies ten separate H_2S emission points within the two asphalt facilities. However, the APAC dryer/mixer (HMA production) and the Associated tank filling operations account for nearly all (99%) H_2S emissions. Given this fact, the following analysis and statistics are based on documented time periods for these two operations and the time-corresponding ambient H_2S

concentrations observed by the Access Road tapemeter. The following data were matched with the 1-hour periods during which they occurred:

- Ambient H_2S concentrations (ppb),
- APAC HMA production, and
- Associated tank filling.

Documented records clearly show that APAC HMA production and emissions occur almost exclusively on weekdays during normal business hours (7:00 to 18:00 hrs). Associated railcar offloading (storage tank filling) activities may occur at any hour of the day. The study period was 117 days (2,808 hours) long. Of those 2,808 total hours 649 of them APAC was producing HMA. Associated filled tanks 742 hours of the study period. Review of the data showed that the elevated ambient concentrations measured at the Access Road site followed a pattern relative to time. During the DAQ study period 71% of the concentrations over 10 ppb occurred after 17:00 hours, the time when APAC was not operating. The number of hours each facility was operating and the corresponding H_2S ambient concentrations for those time periods are presented in **Table 19**. The analysis of the process data with the 1-hour H_2S monitoring data clearly show that the majority of the detected H_2S levels are during unique time periods when only Associated is conducting H_2S emissive operations.

H_2S ambient levels at the Access Road site were highest and occurred most frequently in the late evening hours when only Associated was unloading railcars, its most H_2S emissive operation. This occurrence of peak H_2S ambient levels in the late evening is consistent with two other similar investigations performed by ATSDR.[42-45] During summer days (when the study was performed), sunlight produces ozone (O_3) which causes oxidation reaction of H_2S to sulfur dioxide (SO_2). In addition, the dispersion caused by radiation is lowest at night. It is postulated that these two effects contribute to this occurrence of peak H_2S ambient levels in the late evening hours.

Table 19. Process Activity Versus Number of Access Road 1-hr H_2S Data

Six-hour Time Periods	Hours with APAC HMA Production	Hours with Associated Tank Filling	1-Hour Ambient H_2S Concentration (ppb)		
			1.25-10	10.25-30	30.25-50
0:00 – 5:59	1	115	103	2	-
6:00 – 11:59	324	187	91	-	-
12:00 – 17:59	319	226	256	6	-
18:00 – 23:59	5	214	267	17	3
Total	649	742	717	25	3

DAQ staff reviewed the H_2S ambient monitoring data in **Figure 9** and identified time periods with the noticeably highest concentrations. There were two particularly high peaks with 1-hour averages at / above 35 ppb H_2S. The corresponding time periods with these peak H_2S concentrations were in the late evening on May 21 (35 ppb H_2S 1-hour average peak) and July 24 (47 ppb H_2S 1-hour average peak), each occurring at the Access Road site. Asphalt facility process data records were reviewed to determine which, if any, plant was operating. In both cases, Associated was unloading railcars and filling storage tanks, its most emissive operations. **Table 20** presents the data for the date, time, monitoring site, H_2S ambient monitoring data, and operational plant. This table shows that the 15-minute average data is 2 - 4 times higher than the 1-hour average data and that Associated was the only practical source of emissions responsible for the elevated H_2S concentrations.

Table 20. Highest H_2S Monitoring Data and Asphalt Facilities Process Data

Date	Time	Site	H_2S, ppb		Plant Operational
			15-min avg	1-hr avg	
May 21	8 – 9 pm	Access Road		34	Associated
	9 – 10 pm			22	
	10 –11 pm			35	
	11-12 pm			26	
	8:30 pm		45		
	8:45 pm		64		
	10:00 pm		40		
	11:15 pm		40		
July 24	8 – 9 pm	Access Road		47	Associated
	9 – 10 pm			26	
	8:30 pm		47		
	8:45 pm		90		

Relationship of Asphalt Facilities' Process Data, Wind Direction Data, and H_2S Monitoring Data

The final data analysis was designed to determine whether a correlation existed with the two asphalt facilities' process data, wind direction data, and H_2S monitoring data. How the data was handled to see whether such a relationship existed is discussed below.

Process Data. There were several time periods in which each asphalt facility operation occurred concurrently during the study. To separate the effect of common operating times, four specific operating scenarios were identified. The scenario-numbering scheme starts with least frequent script and progresses up to the most frequent.

- In scenario one, which occurred only 8% of the time, APAC was producing HMA and Associated was filling storage tanks. This scenario represents worst-case emissions or the greatest potential amount of H_2S entering the area. This scenario is presented in the dispersion model above.
- Scenario two, APAC producing HMA and Associated not filling storage tanks. This specific scenario accounted for 14% of the study period.
- Scenario three is just the opposite, Associated filling tanks and APAC not producing HMA; it occurred 17% of the time.
- The fourth and final scenario is when neither facility was operating, which was 53% of the time.

The number of hours during the study, the matching time percentage, and the average emission rates are presented in **Table 21** for each corresponding scenario.

Table 21. Asphalt Process Scenarios Versus H_2S Emission Rates

Process Operation Scenario		Historical Scenario (hrs)	Historical Probability (Percent)	Average Emissions [a] (lb/hr)
1	Both facilities operational	226	8%	0.61
2	Only APAC HMA Produced	385	14%	0.37
3	Only Associated Tank Filled	473	17%	0.31
4	Neither operational	1,494	53%	0.00
Total		2,808	100%	0.16

a: Average emissions based on Table 13 emission factors with process data collected during study.

Wind Data. Wind direction data was subdivided and identified into one of the 16 sectors of the compass, *i.e.*, sector one is defined as the north; sector two is north-northeast, and so on in clockwise fashion. Each of the 16 sectors represents 22.5 degrees of the total 360 degrees in a circle. Sector one equals zero plus or minus 11.25 degrees, or 348.75 degrees to 11.25 degrees. The identified time periods for each process operation scenario were then sorted by wind direction, and an average ambient H_2S concentration calculated.

H_2S Monitoring Data. The H_2S monitoring data was then sorted by operating scenario and then by wind direction; after sorting each data set was averaged and graphed into Figure 10.

Correlation. **Figure 10** presents the average H_2S ambient 1-hour concentrations for the above four scenarios as a function of wind direction. As seen in the figure, most of the plotted points are less than the LQL of 2 ppb. Process scenario 4 (neither asphalt facility operational) is the study baseline. Note that Scenario 2 (APAC only operational) is virtually indistinguishable from the baseline data across all wind directional sectors. However, the combination of Scenario 3 (only Associated operational) and wind sector 8 (southerly wind) results in a H_2S average concentration significantly (more than 4 times) above the baseline. Once again, the analysis strongly suggests that Associated is largely responsible for the elevated H_2S levels from the connection among the ambient H_2S data, the process data, and wind directional data.

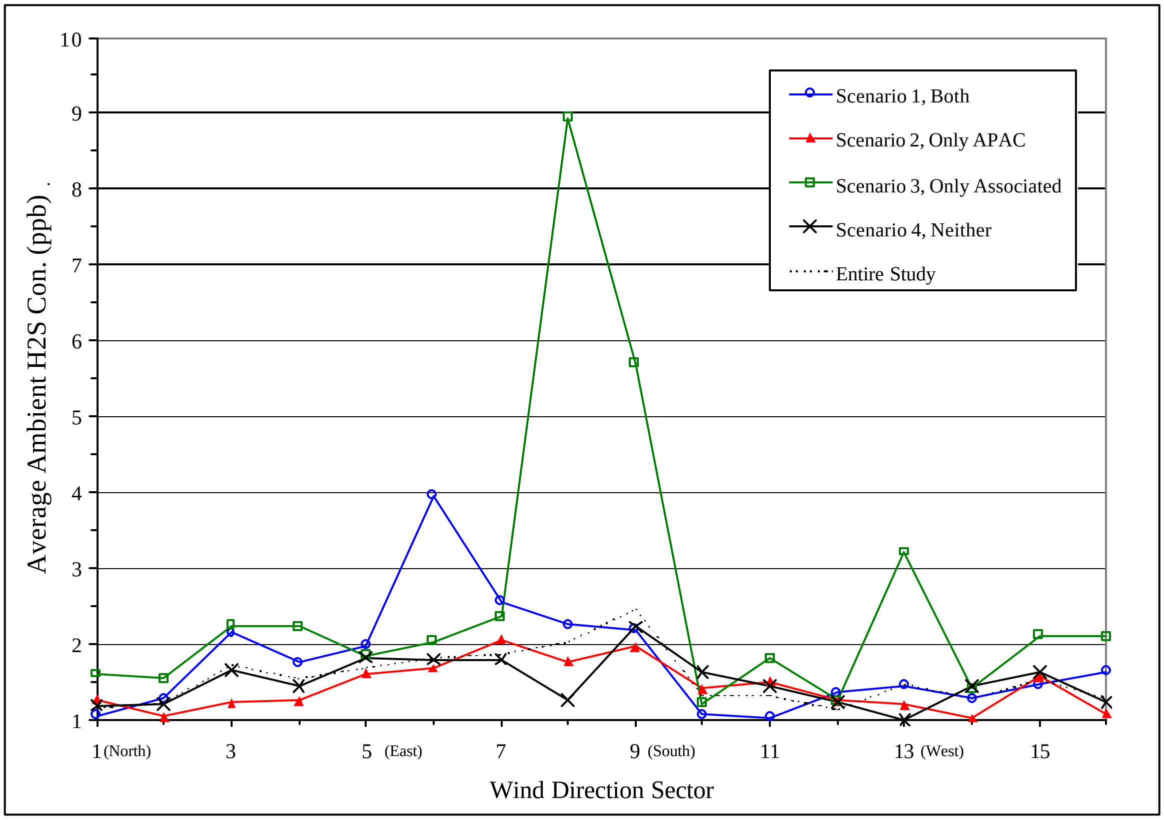


Figure 10. Access Road 1-hour H_2S Concentrations vs. Wind Sector and Process Scenario

4.5.4 Discussion of Odor Complaints and Related Data

There are several elements of related data and odor complaint information that, when taken in combination, form a large information base. This body of related data includes:

- Odor complaints,
- Source H_2S emission concentrations nearly a million-fold above the odor threshold,
- Source emission rates above the H_2S TPER,
- Dispersion modeling predictions well above the odor threshold at all the Associated asphalt facility property lines,
- Dispersion modeling predictions above the odor threshold throughout the surrounding area, and
- H_2S ambient monitoring data well above the odor threshold.

The study data do confirm that, at least on a periodic basis, H_2S levels at the residential monitoring site were in excess of the odor threshold and exceeded levels designated as odor nuisance levels.[50] It is also worth noting that H_2S measurements reflect an average level detected during a 15-minute timeframe and then four 15-minute data periods were combined to produce a 1-hour average. Given the highly variable pattern of atmospheric H_2S levels seen *between* 15-minute measurements in this study, it seems likely that significant variability would also exist *within* each 15-minute period, as was the case at two ATSDR studies where 1-minute averages were as much as 10-times higher than 15-minute averages.[44,45] These peak exposures could result in the perception of highly offensive odors at annoyance levels. However, because H_2S monitoring data are limited to 15-minute segments of time, it remains speculative as to what peak levels of short-term exposure (less than 15-minute average) might have occurred in this area on any shorter timeframe.

4.5.5 Summary of Hydrogen Sulfide Related Data

Nine sets of information related to H_2S were collected and examined to characterize the nature and source of the odor problem in Milford Hills. Each set of information led to the same finding, as seen below:

1. Emission data in Table 13 showed 2,370,000 ppb H_2S (2,370 ppm) released from the storage tanks located near the property line, nearly a million times the 8 ppb H_2S odor threshold. This established the potential for Associated as the source of the odors.
2. Dispersion modeling predicted a maximum concentration of 290 ppb H_2S 1-hour average at Associated's property line, as shown in Table 14. Computer modeling calculated levels well above the odor threshold released from Associated into Milford Hills.
3. H_2S ambient monitoring data in Table 17 showed that the Access Road site, located near Associated's property line and the point of maximum concentration, observed significantly more frequent and more intense H_2S peaks in terms of concentration than the other two sites. This confirmed the computer modeling that H_2S levels near Associated were above the odor threshold.
4. H_2S ambient levels at the Access Road site were highest and occurred most frequently in the late evening hours when only Associated was unloading railcars, as shown in Table 19. This data suggests that Associated released H_2S measured at levels above the odor threshold. Peak occurrence in the late evening is consistent with the fact that poor dispersion occurs at night.
5. The time periods with the noticeably highest concentrations were investigated and found to occur in the late evening while only Associated was operating its most emissive processes. The data showed that the highest concentration were 47 ppb H_2S on a 1-hour average and 90 ppb H_2S on a 15-minute average. This data confirms that Associated released H_2S across its property line at levels above the odor nuisance level.
6. Figure 10 shows that the highest H_2S ambient levels at the Access Road site occurred when Associated was the only asphalt facility operating and when the wind direction was coming from Associated. This is considered very convincing data showing a direct link between Associated's operations, wind direction coming from Associated to the monitoring site, and elevated H_2S ambient levels.
7. During the study period four odor citations were issued to Associated because of the intensity of the odor and Associated was the only asphalt facility operational at the time of the odor complaint. This data suggests that Associated was responsible for releasing H_2S above the odor threshold.

   Since the study was completed and Associated installed carbon beds on all its storage tank vents in late March 2002, two additional sets of information became available; updated dispersion modeling and odor complaints.

8. DAQ performed modeling with carbon beds on all Associated's storage tank vents predicting a maximum concentration of 7 ppb H_2S 1-hour average at Associated's property line, as shown in Table 16. This indicates that Associated released H_2S at levels below the odor threshold after the additional carbon beds installation.
9. In 24 months prior to the additional carbon beds installation in late March 2002, there were 451 odor complaints received from area residents and four odor citations were issued to Associated. In the 17 months since the additional carbon beds installation, there were only 57 complaints and no odor citations, reflecting a dramatic reduction in the extent and frequency of the odor problem.

Nine sets of information independently suggest the same argument that Associated was the primary contributor to the odor problem. Collectively, the weight of evidence from this broad body of information corroborates the Associated Asphalt terminal was largely responsible for the odor problem in Milford Hills.

SECTION 5

CONCLUSIONS

5.1 VOLATILE ORGANIC COMPOUNDS

Benzene is the only VOC TAP of potential regulatory concern in the study. This is because the TPER guideline of 8.1 lb/yr was exceeded by benzene emission rates of 57 lb/yr and 28 lb/yr from the Southern States remediation site and the APAC asphalt plant, respectively. The remaining four emission sources combined only emit 2.5 lb/yr benzene. However, dispersion modeling results show that benzene from Southern States is the only TAP that exceeds its respective AAL guideline of 1.2 x10^{-4} mg/m^3 (0.038 ppb), annual basis, with maximum impacts centered only in the immediate vicinity of the source. Its predicted ground level maximum impact was 1.02 x10^{-3} mg/m^3 (0.32 ppb), a level 850% of the AAL. However, the predicted maximum impacts rapidly drop below AAL concentrations and pose little/no long-term exposure potential to any individual.

Benzene data for the three sites in the study were statistically compared to each other with the results showing that the averages were not statistically different. Benzene and other VOC concentrations measured in the study were also compared to data from other sites similar to Salisbury. The average 24-hour benzene concentration for Salisbury was 0.16 ppb, within the range of 0.13 - 0.24 ppb measured in other suburban and rural sites during 24-hour periods. Given that measured benzene levels at the three monitoring stations were not statistically different and the stations are located upwind and downwind from the nearby emission sources, the data suggest that there was little/no impact from the sources. This limited effect suggestion from nearby sources is also supported by the dispersion modeling results, which indicated that only a relatively small 1-acre area was predicted to have maximum ground level impacts above the AAL. Southern States voluntarily decided in March 2002 to discontinue operation of the air sparging / soil-vapor extraction system and is currently in the process of evaluating alternative technologies to minimize or eliminate benzene and other VOC emissions. Exxon/Mobil made a similar voluntary change from soil-vapor extraction to bioventing at its remediation site in December 2001, also eliminating the concentrated release of benzene and other VOC emissions.

DAQ concludes that in terms of ambient air quality, benzene and other VOC concentrations measured in the Salisbury study are typical of air in similar rural and suburban areas. Given that emission reduction efforts at the two remediation sites have eliminated, or are in the process of eliminating, the concentrated release of VOCs, DAQ believes that there are no additional VOC emission reduction activities available within the constraints of our authority.

5.2 HYDROGEN SULFIDE

The results from this study provide an interesting discovery and new insight into the emissive behavior and profile of toxic compounds released from liquid asphalt.

Comparison with other data reveals that H_2S is by far the most emissive toxicant known from storage tank filling at this particular liquid asphalt terminal. Initially it seems counter-intuitive that an inorganic compound in trace levels (<1%), contained in a predominantly organic (99%) mixture, is the most emissive toxic compound from liquid asphalt. However, the fact that H_2S vapor pressure is 15,000-fold greater than the organic mixture provides the rationale in the relative difference in their emissive behavior. New emission test data showing 2,400 ppm H_2S from paving-grade liquid asphalt is in reasonable agreement with Owen Corning data for levels as high as 1,700 ppm from roofing-grade liquid asphalt. Dispersion modeling results using a facility-wide emission rate of 0.41 lb/hr H_2S predict a 1-hour maximum impact of 290 ppb H_2S, a level below the 1,500 ppb AAL guideline but well above the odor threshold of 8 ppb.

Preliminary data indicate that H_2S emission rates of 0.7 lb/hr are released from the APAC hot mix asphalt plant, a rate above the H_2S TPER guideline of 0.52 lb/hr. However, dispersion modeling results using this emission rate predict a 1-hour maximum ground-level impact of 5 ppb H_2S, just below the odor threshold. Relatively favorable source dispersion characteristics (low concentration, high stack height and exit velocity) account for the acceptable dispersion modeling prediction.

Measured H_2S in the residential areas surrounding the asphalt operations occasionally exceeded odor threshold levels and very likely reached or exceeded odor nuisance levels on a periodic basis. Given that several sets of information independently support this argument, the weight of evidence is considered conclusive that Associated was the central cause to the Milford Hills odor problem.

In June 2000 DAQ issued Associated Asphalt a temporary permit to replace the activated carbon beds on the storage tanks with an Ecosorb® scrubber to control odors. The temporary permit allowed Associated Asphalt to evaluate Ecosorb's® effectiveness. Due to numerous odor complaints and emission testing indicating the ineffectiveness of the Ecosorb® system in reducing odorous emissions, DAQ withdrew the temporary permit in January 2002. DAQ directed Associated Asphalt to remove the Ecosorb® system and to reinstall the activated carbon canisters by March 31, 2002 on the storage tank vents. Reinstalling the carbon canisters on the storage tanks was expected to reduce facility-wide H_2S and VOC emissions by an additional 85%. In early April 2002 DAQ confirmed Associated had complied with the directive to reinstall the carbon canisters.

In November 2002 DAQ revised the Associated Asphalt air permit, No. 08428R03. The new permit not only requires carbon beds on all storage tank and truck loadout vents, but also includes provisions to assure that good inspection and maintenance practices are in effect. Noteworthy provisions include:

- Monitor and record H_2S emission levels from each carbon bed 3 times a week.
- If these monitored levels exceed 10 ppm H_2S, then discontinue the corresponding asphalt handling operation until a new carbon bed replaces the spent one.
- Always maintain spare carbon beds on site for replacing spent ones.
- Verify and record the functionality of the H_2S monitor weekly; and do a performance inspection annually by a qualified instrument technician.

- Perform and record annual inspections of the carbon bed system, including ductwork and fans.
- Submit quarterly reports on the above provisions to DAQ.

Because of the required emission reductions and the inspection and maintenance practices performed by Associated, H_2S levels in the local ambient air, as monitored by citizen complaints, have improved.

SECTION 6

RECOMMENDATIONS

Recommendations presented below are in response to two different situations arising from this study. The first set of recommendations deal with situations that directly involve DAQ action. These involve permitting points and statewide interagency policies with toxic air pollution control issues. The second set of recommendations involve considerations for expanding the information obtained in this study on emissions from liquid asphalt terminals and hot mix asphalt plants that could be pursued as possibilities for further study. While considered logical extensions of the study's findings, DAQ believes that the asphalt industry and its trade group(s) are in better position to decide what is the most cost-effective and appropriate way of obtaining additional emission data for H_2S from asphalt and new emission data from anti-strip asphalt additives. Mention of these recommendations does not constitute a commitment that DAQ will undertake or sponsor such additional studies. However, DAQ intends to openly share our new findings from this study and to encourage other organizations or agencies to undertake or sponsor further studies. An example is that DAQ presented a paper on the Salisbury study for the National Air & Waste Management Association Conference held in Baltimore in June 2002.[54]

6.1 RECOMMENDATIONS FOR DAQ ACTION

1. Based on the premise that the remediation sites in this study are representative of hundreds of others across NC, it is recommended that DAQ work with other state agencies to evaluate an alternative approach for environmental oversight of remediation sites. This process is underway.

2. A few would-be recommendations from this study have also already been implemented. These include the confirmed installation of carbon beds on Associated's storage tanks which reduce H_2S and VOC emissions, and use of alternative technologies to reduce benzene and other VOC emissions from the two remediation sites.

6.2 RECOMMENDATIONS FOR INDUSTRY ACTION

1. It is recommended to study the chemistry driving the behavior and fate of hydrogen sulfide in and from liquid asphalt. Recommendations to consider include:

- Determine sulfur content and H_2S content in current types of liquid asphalt in NC and evaluate the effect of these factors for hot mix asphalt plant operations (batch and drum plants) and distribution terminals.
- Identify other cost-effective H_2S emission controls for liquid asphalt operations.
- Develop pollution prevention measures to improve the environmental performance (i.e., reduce H_2S content and/or H_2S emissions) of liquid asphalt.

2. It is recommended to consider studying the behavior and fate of anti-strip additives in asphalt. There are indications from anecdotal and scientific information that odors and VOCs are emitted in asphalt facility operations using certain brands of these NC DOT required additives.

SECTION 7

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