Health Consultation

APAC CAROLINA INC. AND ASSOCIATED ASPHALT INC. JAKE ALEXANDER BOULEVARD

SALISBURY, ROWAN COUNTY, NORTH CAROLINA 28144

EPA FACILITY ID: NCD095458204

FEBRUARY 14, 2007

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES Public Health Service Agency for Toxic Substances and Disease Registry Division of Health Assessment and Consultation Atlanta, Georgia 30333

Health Consultation: A Note of Explanation

An ATSDR health consultation is a verbal or written response from ATSDR to a specific request for information about health risks related to a specific site, a chemical release, or the presence of hazardous material. In order to prevent or mitigate exposures, a consultation may lead to specific actions, such as restricting use of or replacing water supplies; intensifying environmental sampling; restricting site access; or removing the contaminated material.

In addition, consultations may recommend additional public health actions, such as conducting health surveillance activities to evaluate exposure or trends in adverse health outcomes; conducting biological indicators of exposure studies to assess exposure; and providing health education for health care providers and community members. This concludes the health consultation process for this site, unless additional information is obtained by ATSDR which, in the Agency's opinion, indicates a need to revise or append the conclusions previously issued.

You May Contact ATSDR Toll Free at 1-800-CDC-INFO or Visit our Home Page at: http://www.atsdr.cdc.gov

HEALTH CONSULTATION

APAC CAROLINA INC. AND ASSOCIATED ASPHALT INC. JAKE ALEXANDER BOULEVARD

SALISBURY, ROWAN COUNTY, NORTH CAROLINA 28144

EPA FACILITY ID: NCD095458204

Prepared By:

Exposure Investigation and Site Assessment Branch Division of Health Assessment and Consultation Agency for Toxic Substances and Disease Registry

Table of Contents

| Summary and Statement of Issues | 1 |
|---|-----|
| Background | 3 |
| Community Health Concerns | 5 |
| Discussion | |
| Results | 7 |
| Child Health Considerations | 9 |
| Conclusions | .10 |
| Recommendations | .12 |
| Authors | .14 |
| References | .15 |
| Acronyms | .17 |
| Figures | |
| Figure 1 Salisbury Study Area | .19 |
| Appendices | |
| Annandiy A ATSDD'S Multi Site Evolution of Hot Mix Aenhalt Dionte and Similar | |

Appendix A. ATSDR'S Multi-Site Evaluation of Hot Mix Asphalt Plants and Similar Facilities

Appendix B. ATSDR's Evaluation of HMA Plants using AP-42 Parameters

Appendix C. Odors Discussion

Appendix D. Explanation of Comparison Values

Summary and Statement of Issues

Over a six year period, people living near several asphalt plants throughout the U.S., requested the Agency for Toxic Substances and Disease Registry (ATSDR) to investigate the potential health impact of asphalt emissions on their communities. Although the operations in each location varied (e.g., one community had three companies), all of the locations handled the constituent ingredients of asphalt – stone, sand, and liquid asphalt (aka asphalt cement). Community members most frequently expressed health concerns about respiratory distress and eye irritation and associated the symptoms with asphalt production because the symptoms may be exacerbated by the chemicals associated with asphalt, in response to the community requests, ATSDR investigated the airborne exposures at 7 locations between 1998 and 2004 in Arizona, California, Georgia, New York, North Carolina, and Utah (ATSDR 1999, 2001a, b, 2003, 2004, 2005).

One of the seven requests came from the Rowan Citizens Against Pollution. This group asked ATSDR to evaluate people living near 26 North Carolina Department of Transportation (NCDOT) asphalt company test sites. Two of the 26 sites were Associated Asphalt and APAC-CAROLINA, Inc. in Salisbury, NC. The group compiled a list of health concerns for the Salisbury location which included unexpected gastrointestinal illness, respiratory problems, cancer clusters, higher suicide rates, and death. ATSDR partially accepted the North Carolina petition request for the 26 facilities as we were already assessing some of the sites on the list and had made assessments on several others in other parts of the country.

In 2001, the Salisbury Air Quality Monitoring Study was conducted. ATSDR, the NC Division of Air Quality (NCDAQ) Mooresville Regional Office, and the city of Salisbury collaborated with the NCDAQ to complete the study. The study included ambient air monitoring and emission tests to estimate concentrations of several toxic pollutants in residential suburban areas adjacent to a liquid asphalt distribution terminal (Associated Asphalt, Inc.) and a hot mix asphalt plant (APAC-CAROLINA, Inc.). Between May and September 2001, data were collected for hydrogen sulfide (H₂S), volatile organic compounds (VOCs), and meteorological conditions. The Salisbury Air Quality Monitoring Study, Final Report was completed in August 29, 2003 (NCDAQ 2003) and the full report is available online at www.daq.state.nc.us/toxics/studies/salisbury/Salisbury final report.pdf.

This consultation will summarize those findings and report on ATSDR's multi-site evaluation of the seven locations referenced above. We acknowledge that this data represents a brief period in time and historical air contaminant levels are not represented.

Summary of Findings

Salisbury Specific

ATSDR determined the following from the data:

• The available data from Salisbury and near other asphalt plants suggests that

concentrations of polycyclic aromatic hydrocarbons (PAHs) and volatile organic carbons (VOCs) pose <u>no</u> acute (i.e., short-term) or chronic (i.e., long-term) public health hazard.

- \circ Although limited to two days of sampling, Salisbury particulate levels for one day (respirable dust as PM_{2.5}) were above regulatory standards and could cause asthmatics and sensitive individuals to experience respiratory irritation. Most of both days' particulate levels (i.e., total dust, respirable dust and quartz) were higher than the background levels.
- The data from Salisbury are similar to those found at other asphalt sites.

The Salisbury Air Quality Monitoring Study determined the following:

Hydrogen Sulfide (H₂S)

- H₂S was the toxic compound emitted in the largest amount from the Associated Asphalt liquid asphalt terminal and it appears to be emitted at significant levels from hot mix asphalt plants.
- Monitoring data, process data, citizen complaints, and dispersion modeling support the conclusion that the liquid asphalt terminal is the primary contributor to H_2S levels above the odor threshold in the nearby area.
- Although measured H₂S 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, H₂S did not likely reach levels (concentrations) known to pose a long-term health hazard.

VOCs and PAHs

• Monitoring data and dispersion modeling show that ambient concentrations of benzene and VOCs in Salisbury are typical of air in similar communities with asphalt facilities.

ATSDR Multi-Site Evaluation

VOCs, PAHs, H₂S, Particulates

• ATSDR sampling from seven sites (including Salisbury) in the communities surrounding asphalt facilities showed that there do <u>not</u> appear to be any chemicals or compounds at levels that would pose a public health hazard. VOCs and PAHs were detected in very low concentrations, and only H_2S , and particulate matter (PM) – as respirable particulates or PM_{10} and $PM_{2.5}$ – were slightly elevated.

Sulfur dioxide (SO2), Nitrogen oxides (NOx), and Metals

- *Evaluation of Air Pollution (AP) Emission Factors*: ATSDR also reviewed the Environmental Protection Agency's (EPA's) AP-42 emission factors¹ for Hot Mix Asphalt (HMA) plants to determine if our detected sample constituents matched what was predicted. We had the following conclusions:
 - Based on both the emission rates and toxicities of the 159 chemicals
 reportedly emitted from asphalt plants, the compounds most capable of posing
 a health hazard in communities were sulfur dioxide (SO₂) and nitrogen oxides
 (NOx). Under some circumstances, carbon monoxide (CO), aldehydes (such
 as acrolein), particulates (such as quartz, dust) and some metals might also
 pose some concern, but they are much less likely to produce actual health
 effects in those exposed off-site.
 - Chemicals such as SO₂ and the aldehydes are highly reactive and at sufficiently high levels can cause irritation to the eyes and upper respiratory system. Particulates (such as quartz), which are released by HMA plants, can penetrate the lungs and cause inflammation and fibrosis if inhaled at sufficiently high levels.
 - Although scientists and regulators tend to associate H₂S as a major pollutant from asphalt facilities, SO₂, NOx, and many metals ranked higher than H₂S in their degree of toxicity, potential health risk and/or odor.
- We did not detect hazardous levels of VOCs, PAHs, or particulates at the seven asphalt sites we sampled. There remains a data gap for evaluating metals, aldehydes, SO₂, NOx, and CO. ATSDR is filling that data gap with subsequent sampling at facilities we are requested to evaluate.

Odor Responses

• Many compounds have odor thresholds that are lower than the levels thought to be hazardous. However, these warning odors may, by themselves, provoke odor-related symptoms such as fast heart rates, dizziness, nausea, sweating, and anxiety in sensitive individuals.

Background

How Are Asphalt Fumes Produced?

Liquid asphalt's composition varies each time it is made. Liquid asphalt is made in petroleum facilities; it is the distillate left over after oil is refined. Asphalt's chemical composition depends on the chemical complexity of the original crude petroleum as well as the manufacturing process.

¹ An emissions factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. Emission factors for Hot Mix Asphalt Plants are listed in AP 42, Fifth Edition: Volume I, Compilation of Air Pollution Emission Factors, Stationary Point and Area Sources – January 1995

A full discussion on the chemical variability of asphalt can be found in the *Health Effects of Occupational Exposure to Asphalt* (CDC 2000).

For distribution and use, the liquid is loaded onto rail cars and sent to regional tank farms where the cars are heated and the liquid is pumped into the tanks (heated to 190-450° F). During tank loading, condensers are used to prevent escape of vapors. From the tank farms, the heated liquid is loaded onto trucks and transported to the mix facilities where it is loaded into smaller tanks. Although fuel transfer stations are equipped with re-capture systems to prevent fumes from escaping, asphalt transfer stations are not.

The manufacturing process of asphalt can also affect its composition. Hot mix asphalt paving materials can be manufactured by the following: (1) batch mix plants, (2) continuous mix (mix outside drum) plants, (3) parallel flow drum mix plants, and (4) counterflow drum mix plants. This order of listing generally reflects the chronological order of development and use within the HMA industry (EPA 1976).

To produce the asphalt mix that is used for paving surfaces, the asphalt liquid is heated in an asphalt kettle and then poured into a mixing box where stone and sand (i.e., aggregate) are added and blended. The stone is ground in a manner that produces many surfaces for improved packing. A liquid hardener (sometimes called asphalt cement) made from petroleum distillates is also used.

Hot-mix asphalt (HMA) plants use aggregate that has been processed in a dryer to remove the moisture before it is mixed with liquid asphalt. HMA paving materials are a mixture of well-graded, high-quality aggregate (which can include reclaimed asphalt pavement (RAP)) (EPA 2004). Heating the aggregate generates fumes and the rotary drum dryer is the most significant source of emissions. The aggregate and liquid asphalt cement is heated and mixed in measured quantities to produce HMA. In most cases, the mixing plants need to be ducted and permitted as an emission source of both particulates and volatile organic compounds (VOC). Particulate emissions are reduced by a baghouse, cyclone or other emission control device. Particulate matter from other emission sources at the plant may also contribute fugitive emissions and require a permit (Ohio EPA 1996).

What Chemicals and Other Hazards are in Asphalt Fumes?

The most significant ducted source of emissions for all four types of HMA plants is the rotary drum dryer (EPA 1976, 1977, 2004). Batch mix processes have the greatest emission factors; parallel process and counter flow process plants have the same emission factors; however counter flow plants release the least VOC emissions (EPA 2004). The cleanest fuel for heating the asphalt is natural gas; between 70-90% of HMA plants use natural gas to dry and heat the aggregate (EPA 2004).

The rotary drum dryer emits the following compounds:

- o water
- o particulate matter (PM)
- products of combustion

- carbon dioxide (CO₂)
- nitrogen oxides (NO_x) e.g., nitrogen dioxide
- sulfur oxides (SO_x) e.g., sulfur dioxide
- carbon monoxide (CO)
- volatile organic compounds (VOCs)
- \circ methane (CH₄)
- hazardous air pollutants (HAPs) (EPA 2004)

Specific compounds released in fumes include hydrogen sulfide (H_2S), formaldehyde, naphthalene, methylnaphthalene, toluene, hexane, and phenol (EPA 2004).

Many of these chemicals also are also emitted by other combustion sources such as exhaust from motor vehicles, fireplaces and wood stoves, wildfires, and industries.

Salisbury Site Description and History

Jake Alexander Boulevard in Salisbury, NC has many current and former industrial properties. Four of the five current or past industries involved petroleum products. The past operations included two bulk petroleum storage facilities currently undergoing soil and water remediation. The current operations include a concrete batching plant and two asphalt-related businesses – a liquid asphalt distribution terminal (Associated Asphalt, Inc.) and a hot mix asphalt plant (APAC-CAROLINA, Inc.). Residents adjacent to those businesses requested a study. The Milford Hills community was the site of an ambient air monitoring study and emission tests conducted to estimate concentrations of several toxic pollutants (NCDAQ 2003). See Figure 1.

Community Health Concerns

Community members have been and are concerned about groundwater and air pollution from the asphalt facilities in Salisbury. Community members most frequently expressed health concerns about respiratory distress and eye irritation. They also expressed concerns about gastrointestinal illness, cancer clusters, higher suicide rates, and death. (Please note that this consultation only addresses possible health effects from air pollution. The groundwater issues are addressed in another ATSDR consultation.)

Discussion

Most of the data to evaluate ambient air exposure were collected during a four month period in 2001. These data represent conditions occurring only during that timeframe. Many process changes occurred during the operational lifetimes of the facilities. For example, in the past, Associated (then Chevron) reportedly produced cut-back asphalt, a product that is made with up to 45% solvent (by volume). Additionally, the facilities' equipment and pollution controls changed over the years. Those process and equipment changes likely resulted in less releases of pollutants into the community.

ATSDR's Involvement in the Sampling at Salisbury

ATSDR conducted sampling and analysis of particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs), and crystalline silica over a two-day period in 2001. That data is summarized in Appendix A. The Salisbury Air Quality Monitoring Study does not address the ATSDR effort. ATSDR also provided NCDAQ some of the air sampling equipment and comments on their sampling plan.

Salisbury Air Quality Monitoring Study – Sampling Summary

Data were collected at three monitoring sites from May through September 2001 for meteorological parameters, H₂S, and VOCs. The three monitoring sites were the Cul-de-sac site, the Access Road site, and the Remediation site denoted by A, B, and C respectively on Figure 1. Site A, the Cul-de-sac NCDAQ Monitoring Site, represented the neighborhood exposure site and was located 200 meters from the asphalt terminal. Site B, the Access Road NCDAQ Monitoring Site (Source Dominated Site), was within 30 meters of the asphalt terminal. Site C, the Remediation NCDAQ Monitoring Site, represented the upwind site was 400 meters from the asphalt terminal.

In addition, data were collected on process operations from both paving asphalt facilities, nearby road traffic, and odor complaints to characterize key parameters. These data were analyzed to evaluate relationships between each asphalt facility's process operations, remediation activities, wind direction, odor complaints and the H₂S and VOC concentrations. Direct H₂S and related odorous sulfur compounds measurements were also taken at the source of emissions at the liquid asphalt terminal (NCDAQ 2003). Finally, dispersion modeling using emission data and emission factors was performed to determine compliance with NC regulatory acceptable ambient levels (AALs) (NCDAQ 2003).

The monitoring sites and industrial sites in Figure 1 are numbered according to the following legend:

- A. Cul-de-sac NCDAQ Monitoring Site [Neighborhood Exposure Site]
- B. Access Road NCDAQ Monitoring Site [Source Dominated Site]
- C. Remediation NCDAQ 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

Salisbury Air Sampling Strategy and Procedures

Three monitoring sites were selected to characterize ambient air pollutant concentrations and meteorological data. Each monitoring site was configured with one meteorology station, one VOC sampling system, and one H_2S tape meter housed in a climate-controlled enclosure. The following is a list of the specific measurements:

- 1. Meteorological parameters included 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. NCDAQ 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 (NCDAQ 2003);
- H₂S ambient air levels data were collected using Zellweger Analytics Tapemeters[™]. This instrument uses a lead acetate-treated cloth tape reel to analyze for H₂S across a 2-90 parts per billion (ppb) range. After each 15-minute sample period the concentration data were stored on an attached data logger (NCDAQ 2003).

Asphalt facility process records were important for evaluating relationships with monitoring data. Process data from each asphalt facility were collected throughout the 117-day study period. Process data – collected weekly and organized into a computerized database – accounted for 90% of asphalt facility emissions. Process records and emissions for each asphalt facility varied over time.

Source testing was performed at the Associated Asphalt distribution terminal under normal operating conditions using EPA Method 15 for H₂S. In addition, NCDAQ staff collected preliminary H₂S data at the APAC hot mix asphalt plant and the two companies undergoing remediation (ExxonMobil and Southern States) performed VOC emission tests during the study (NCDAQ 2003).

The Salisbury Air Quality Monitoring Study final report contains more details on the sampling (NCDAQ 2003).

ATSDR's Multi-site Evaluation and Evaluation of HMA Plants using AP-42 Parameters

ATSDR's multi-site evaluation and evaluation of HMA plants using AP-42 parameters can be found in Appendices A and B.

Results

Salisbury Specific Results

Below is an excerpt from the Salisbury Air Quality Monitoring Study. For the August 29, 2003 complete report, access <u>www.daq.state.nc.us/toxics/studies/salisbury/Salisbury_final_report.pdf</u>

Hydrogen Sulfide

<u>H₂S Emissions</u>: Comparison with VOC data shows that H_2S was by far the toxic compound emitted in the largest amount from this particular liquid asphalt operation. New emission test data from Associated Asphalt showing 2,400 parts per million (ppm)

H₂S 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 H₂S/ton of liquid asphalt. Facility wide emission rates for Associated were determined to be 0.41 lb/hr H₂S for normal operating conditions. Using a facility-wide emission rate of 0.41 lb/hr, the predicted H₂S 1-hour maximum impact concentration was 290 ppb, a level below the 1,500 ppb permissible acceptable ambient levels (AAL) guideline, but well above the odor threshold of 8 ppb.

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 near liquid asphalt storage tank filling and the dryer/mixer, respectively. Facility wide emission rates are estimated to be 0.76 lb/hr, a level above the toxic pollutant emission rate (TPER) guideline of 0.52 lb/hr. (Subsequent dispersion modeling showed levels at 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.

<u>H₂S Dispersion Modeling</u>: Dispersion modeling results showed that the ground level maximum impact for H₂S was predicted to be below its respective hourly AAL of 2.1 mg/m³ (~ 1500 ppb) for APAC (0.006 mg/m³ or 4.3 ppb) and for Associated (0.404 mg/m³ or 290 ppb), individually. The H₂S isopleth analyses showed 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. Ground level maximum impact concentrations above the odor threshold (0.011 mg/m³, 8 ppb) were predicted for much of the area inside the Milford Hills subdivision. More favorable source characteristics² accounted for a lower and more distant (100 m from its property line) predicted maximum impact point for APAC as compared to Associated.

<u>H₂S Ambient Monitoring</u>: Measured 1-hour average H₂S 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 H₂S 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 H₂S data at the remediation site located 400 meters from the terminal neither exceeded odor threshold levels nor approached odor nuisance levels. Evaluation of the H₂S 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

² 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 (NCDAQ 2003).

 H_2S ambient levels in the late evening is consistent with three 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 associated with late evening circumstances.

PAH and VOCs

<u>VOC Emissions:</u> Two of the six emission sources were found to release benzene emissions above the NCDAQ permitting threshold, or toxic pollutant exemption 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 emissions were estimated from modeling then applying EPA Emissions Factors from AP-42)

<u>VOC Dispersion Modeling</u>: Dispersion modeling prediction results show that benzene from Southern States is the only Toxic Air Pollutant (TAP) in this study predicted to exceed its respective annual AAL guideline $(1.2 \times 10^{-4} \text{ mg/m}^3, 0.12 \text{ ug/m}^3, \text{ or } 0.038 \text{ ppb})$. Its predicted ground level maximum impact was $1.02 \times 10^{-3} \text{ ug/m} (0.32 \text{ ppb})$, a level 850% of the NC regulatory acceptable ambient levels (AAL). However, the predicted maximum impacts are centered in the immediate vicinity (within 50 m) of the emission source and rapidly drop below AAL concentrations posing 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.

<u>VOC Ambient Concentrations</u>: 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. NCDAQ 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.

Odors

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

Child Health Considerations

In communities faced with air, water, or food contamination, the many physical differences between children and adults demand special emphasis. Children could be at greater risk than are adults from certain kinds of exposure to hazardous substances. Children play outdoors and sometimes engage in hand-to-mouth behaviors that increase their exposure potential. Children are shorter than are adults; this means they breathe dust, soil, and vapors close to the ground. A child's lower body weight and higher air intake rate results in a greater dose of hazardous substance per unit of body weight. If toxic exposure levels are high enough during critical growth stages, the developing body systems of children can sustain permanent damage. Finally, children are dependent on adults for access to housing, for access to medical care, and for risk identification. Thus adults need as much information as possible to make informed decisions regarding their children's health.

ATSDR's health comparison values take children's susceptibility into account. Some of the highest values of contaminants at Salisbury may produce respiratory irritation in children and other more sensitive populations (e.g., elderly, people with pre-existing respiratory conditions, etc).

Conclusions

Salisbury Specific Conclusions

ATSDR's Conclusions

- 1. The available data from Salisbury and near other asphalt plants suggests that concentrations of polycyclic aromatic hydrocarbons (PAHs) and volatile organic carbons (VOCs) pose <u>no</u> acute (i.e., short-term) or chronic (i.e., long-term) public health hazard.
- 2. Although limited to two days of sampling, Salisbury particulate levels for one day (respirable dust as PM_{2.5}) were above regulatory standards and could cause asthmatics and sensitive individuals to experience respiratory irritation. Most of both days' particulate levels (i.e., total dust, respirable dust and quartz) were higher than the background levels.
- 3. Over the operational lifetime of the Salisbury asphalt plants, process and equipment changes likely resulted in less releases of pollutants into the community. If the ambient air pollutant concentrations were measured prior to those changes, they would likely have been higher.

Salisbury Air Study Conclusions

4. Volatile Organic Carbon (VOC) and Polycyclic Aromatic Hydrocarbons (PAH) Ambient Concentrations. Benzene, toluene, xylene and other VOC concentrations measured in the Salisbury study were compared to 24-hour data from other sites similar to Salisbury and found to be in the same range. NCDAQ concluded 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 (NCDAQ 2003). Although the VOCs and PAHs (including Asphaltines) are not at levels known to pose a long-term health hazard, the health risk from the mixture of these and other chemicals is not well understood so it is prudent to reduce the levels where possible.

5. *H*₂*S Ambient Monitoring*. H₂*S* was the toxic compound emitted in the largest amount from the Associated Asphalt liquid asphalt terminal and appears to be emitted at significant levels from hot mix asphalt plants. Monitoring data, process data, citizen complaints, and dispersion modeling argue strongly that the liquid asphalt terminal is the primary contributor to H₂*S* levels above the odor threshold in the nearby area (NCDAQ 2003). Although measured H₂*S* 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, H₂*S* did not likely reach levels known to pose a long-term health hazard.

ATSDR Multi-Site Investigation Conclusions

*VOCs, PAHs, H*₂*S, and Particulates*

- ATSDR sampling from seven sites in the communities surrounding asphalt facilities showed that there does <u>not</u> appear to be any chemicals or compounds at levels that would pose a public health hazard. VOCs and PAHs were detected in very low concentrations and only H_2S , and particulate matter (PM) as respirable particulates or PM_{10} and $PM_{2.5}$ were slightly elevated. (See Table A2 in Appendix A).
- *NIOSH Asphalt Review:* In the December 2000 NIOSH report on the *Health Effects of Occupational Exposure to Asphalt*, NIOSH found no worker exposures to be hazardous in their five studies, but they encouraged more studies. Benzene soluble particulates (a.k.a. PAHs) were elevated (CDC 2000).

Sulfur dioxide (SO₂), Nitrogen oxides (NOx), and Metals

- *Evaluation of Air Pollution (AP) Emission Factors*: ATSDR also reviewed the AP-42 emission factor for Hot Mix Asphalt (HMA) plants to determine if our detected sample constituents matched what was predicted. We had the following conclusions:
 - Based on both the emission rates and toxicities of the 159 chemicals reportedly emitted from asphalt plants, the compounds most capable of posing a health hazard in communities were sulfur dioxide (SO₂) and nitrogen oxides (NOx). Under some circumstances, carbon monoxide (CO), aldehydes (such as acrolein), particulates (such as quartz, dust) and some metals might also pose some concern, but they are much less likely to produce actual health effects in those exposed off-site.
 - Chemicals such as SO₂ and the aldehydes are highly reactive and at sufficiently high levels can cause irritation to the eyes and upper respiratory system. Particulates (such as quartz), which are released by HMA plants, can

penetrate the lungs and cause inflammations and fibrosis if inhaled at sufficiently high levels.

- Although scientists and regulators tend to associate H₂S as a major pollutant from asphalt facilities, SO₂, NOx, and many metals ranked higher than H₂S in their degree of toxicity, potential health risk and/or odor.
- We did not detect hazardous levels of VOCs, PAHs, or particulates at the seven asphalt sites we sampled. There remains a data gap for evaluating metals, aldehydes, SO₂, NOx, and CO. ATSDR is filling that data gap with subsequent sampling at facilities we are requested to evaluate.

Odors

- Many compounds have odor thresholds that are lower than the levels thought to be hazardous. However, these warning odors can, by themselves, provoke odor-related symptoms such as fast heart rates, dizziness, nausea, sweating, and anxiety in sensitive individuals.
- The AP-42 compounds likely to have the highest degree of significant/sustained odor at HMA plants* would be the following:

| 1. | Sulfur Dioxide | 6. | Xylene (m-/p-) |
|----|----------------|-----|----------------|
| 2. | Acetaldehyde | 7. | Heptane |
| 3. | Naphthalene | 8. | Ethylene |
| 4. | Toluene | 9. | Acrolein |
| 5. | Crotonaldehyde | 10. | Acetone |
| | | | |

*Note: Although H_2S did not rank high on this list because it did not have a significant emissions factor, it does have a low odor detection threshold of around 8 ppb in the general population and should be considered for sampling.

Recommendations

General Recommendations for Reducing Emissions from Asphalt Facilities

- 1. Install closed-system transfer units (likes those used at fuel transfer facilities) to reduce fugitive emissions.
- 2. Employ techniques to reduce particulate matter (e.g., wetting)

Salisbury-Specific Recommendations

NC Division of Air Quality (NCDAQ) Recommendations

A few recommendations from this study have 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 (NCDAQ 2003).

Note: Since the report was written, Associated Asphalt has reportedly gone out of business and is in the process of being sold.

NC Division of Air Quality (NCDAQ) Recommendations for Hot Mix Asphalt Plant Industry Action

- 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.
- \circ Identify other cost-effective H₂S emission controls for liquid asphalt operations.
- Develop pollution prevention measures to improve the environmental performance (i.e., reduce H₂S content and/or H₂S emissions) of liquid asphalt (NCDAQ 2003).

It would be useful to have more information on 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 (NCDAQ 2003).

ATSDR General Recommendations for Evaluating Emissions from HMA Plants

- 3. At future asphalt facilities where an ATSDR evaluation is requested, include sampling for sulfur dioxide (SO₂), nitrogen dioxides (NOx), carbon oxides (CO, CO₂), and some metals. Continue to sample for particulates, VOCs, and PAHs.
- 4. Include sampling for compounds with the highest degree of significant/sustained odor at HMA plants such as sulfur dioxide, acetaldehyde, naphthalene, toluene, crotonaldehyde, xylene (m-/p-), heptane, ethylene, acrolein, acetone and hydrogen sulfide.
- 5. Consider how site-specific chemical mixtures may react and form other hazards such as acid gases and possibly include pH measurements where applicable.

Authors

Diane Jackson, BSCHE

Greg Zarus, MS

Technical Advisors

Frank Schnell, PhD

Lourdes Guevara- Rosales, MD

Betty Willis, MS (retired)

James Parker, EPA Summer student

References

- AIHA (American Industrial Hygiene Association). 1997. Odor Thresholds for Chemicals with Established Occupational Health Standards 1997, Fairfax, VA
- ATSDR (Agency for Toxic Substances and Disease Registry) 1999. Exposure Investigation for Mission Valley, San Diego, CA. November 4, 1999. U.S. Department of Health and Human Services, Atlanta.
- ATSDR 2001a. Exposure Investigation for Prima Asphalt Concrete, Holtsville, NY. April 1, 2001. U.S. Department of Health and Human Services, Atlanta.
- ATSDR 2001b. Exposure Investigation for Staker Paving Asphalt Production Plant, Erda, UT. May 17, 2001. U.S. Department of Health and Human Services, Atlanta.
- ATSDR 2003. Exposure Investigation for Brimhall Sand and Gravel, Indian Wells, AZ. April 8, 2003. U.S. Department of Health and Human Services, Atlanta.
- ATSDR 2004. Exposure Investigation for Meredith Williams Co, East Point, GA. September 29, 2004. U.S. Department of Health and Human Services, Atlanta.
- ATSDR 2005. Health Consultation for Valley Asphalt, Spanish Fork, UT. December 8, 2005. U.S. Department of Health and Human Services, Atlanta.
- Brunekreef B, Dockery DW, and Krzyzanowski M, 1995. Epidemiologic Studies on Short term Effects of Low Levels of Major Ambient Air Pollution Components. Environ Health Perspect 103(Suppl 2):3 13.
- CDC (Centers for Disease Control and Prevention). 2000. Hazard Review. NIOSH Health Effects of Occupational Exposure to Asphalt. U.S. Department of Health and Human Services, Atlanta. Available online at <u>http://www.cdc.gov/niosh/pdfs/01-110.pdf</u>
- EPA (Environmental Protection Agency), 1976. Preliminary Evaluation Of Air Pollution Aspects Of The Drum Mix Process, EPA-340/1-77-004, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1976. Available online at <u>http://www.deq.state.ms.us/MDEQ.nsf/pdf/epd_AsphaltEmissionsFactors/\$File/04Gener</u> <u>al.pdf?OpenElement</u>
- EPA. 1977. Z.S. Kahn and T.W. Hughes, Source Assessment: Asphalt Paving Hot Mix, EPA-600/2-77-107n, U.S. Environmental Protection Agency, Cincinnati, OH, December 1977.
- EPA 1999a. Criteria Pollutants. http://www.epa.gov/oar/oaqps/greenbk/o3co.html

EPA 1999b. Air Quality Trends 1994, Particulate Matter (PM 10). http://www.epa.gov/oar/aqtrnd94/six_pm10.html

EPA 2004.Emission Factor Documentation For AP-42 Section 11.1, Hot Mix Asphalt Production, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 2004. http://www.epa.gov/ttn/chief/ap42/ch11/related/c11s01.html

Hazardous Substance Data Bank - http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB

- McClellan R, 1997. Use of Mechanistic Data in Assessing Human Risks from Exposure to Particles. Environ Health Perspect 105(Suppl 5):1363 1372.
- NC DAQ 2003. North Carolina Division of Air Quality, Toxics Protection Branch, Air Toxics Analytical Support Team (ATAST) ATAST Investigation Numbers 01007 and 01008. Final Study Report Salisbury Air Quality Monitoring Study. August 29, 2003 available online at <u>http://www.daq.state.nc.us/toxics/studies/salisbury/Salisbury_final_report.pdf</u>
- Neas LM, Schwartz J, and Dockery D, 1999. A Case Crossover Analysis of Air Pollution and Mortality in Philadelphia. Environ Health Perspect 107:629 631.
- Schiffman S, Williams, C.M. 2005. Science of Odors as a Potential Health Issue. J Environmental Quality 34:129-138
- Shusterman D, Lipscomb J, Satin K, Neutra R. 1991. Symptom prevalence and odor-worry interaction near hazardous waste sites. Environ Health Perspect 94:25-30.
- Shusterman D. 1992. Critical Review: The health significance of environmental odor pollution. Arch Environ Health 47:76-91.
- Ohio EPA.1996 Fact Sheet: Information Regarding Asphalt Concrete Plants, Number 5, November 1996, Ohio EPA, Division of Air Pollution Control -<u>http://www.epa.state.oh.us/dapc/sba/asp_con.html</u>.
- Van Gemert , L.J., Compilations of odor threshold values in air, water and media 2003, Boelens Aroma Chemical Information Service (BACIS)

Acronyms

| AAL | Acceptable Ambient Level |
|-------------------|--|
| APAC | APAC-CAROLINA, Inc. Hot Mix Asphalt Plant |
| ATSDR | Agency for Toxic Substances and Disease Registry |
| CDC | Centers for Disease Control and Prevention |
| CH_4 | Methane |
| СО | Carbon monoxide |
| CO_2 | Carbon dioxide |
| CV | Comparison value |
| EPA | U.S. Environmental Protection Agency |
| HAP | Hazardous Air Pollutant |
| HMA | Hot Mix Asphalt |
| H_2S | Hydrogen Sulfide |
| NCDAQ | North Carolina Division of Air Quality |
| NCDOT | North Carolina Department of Transportation |
| NIOSH | National Institute for Occupational Safety and Health |
| NOx | Nitrogen Oxides |
| PAH | polycyclic aromatic hydrocarbons |
| PM | Particulate matter |
| PM _{2.5} | Particulate Matter with aerodynamic diameter less than 2.5 microns |

| PM ₁₀ | Particulate Matter with aerodynamic diameter less than 10 microns |
|------------------|---|
| ppb | Parts per billion |
| SO ₂ | Sulfur dioxide |
| SVOC | Semi-volatile organic compounds |
| ТАР | Toxic Air Pollutant |
| TPER | Toxic Pollutant Exemption Rate |
| VOC | Volatile organic compounds |

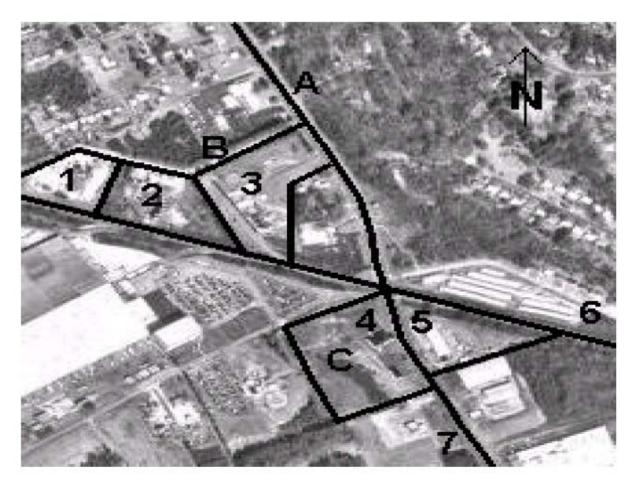


Figure 1. Salisbury Study Area. Aerial View of the Salisbury Monitoring study area showing the monitoring stations (A [Cul-de-sac], B [Access Road], C[Remediation site]), asphalt facilities (2, 3), concrete plant (1), remediation sites (4, 5), Southern Railway (6), and Jake Alexander Boulevard (7).

Appendix A

ATSDR's Multi-Site Evaluation of Hot Mix Asphalt Plants and similar facilities

ATSDR's Multi-Site Evaluation Process

In response to community requests, ATSDR has conducted sampling in different communities across the country where asphalt was being produced. Because our sampling represented a relatively short time period – days to weeks – we also conducted a more in-depth evaluation using the emission factors for Hot Mix Asphalt (HMA) plants to determine what compounds you would expect to find in communities near those facilities. That evaluation is in Appendix B.

ATSDR Sampling and Analysis Methods for Community Exposure

ATSDR evaluated seven communities where asphalt was used. Those included communities in Arizona, California, Georgia^{*}, North Carolina, New York, and two in Utah. One control "community" was also sampled. Upwind samples were collected in each community and served at the background comparison.

The operations and sampling methodology were unique at each site. Most samples were collected downwind. There were a few upwind samples and there were occasions when the wind changed to place the sampler downwind for only a portion of the sample duration.

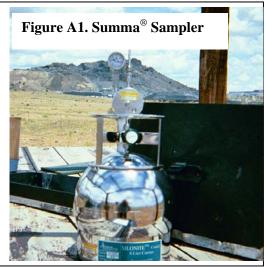
ATSDR sampled for compounds known to be released from the facilities and considered measurable in the community. Those included Volatile Organic Compounds (VOCs), Semi-VOCs (i.e., polycyclic aromatic hydrocarbons (PAHs)), and particulates. Particulates were sampled in six communities. PAHs and VOCs were only sampled in three communities. Hydrogen sulfide and asbestos was sampled in two communities. Carbon monoxide was sampled in one community.

Volatile Organic Compounds – VOCs

Liquid asphalt or asphalt cement is derived from petroleum distillates which contain VOCs. ATSDR chose methods proven to provide reliable results for those chemicals

considered to be highly toxic and or carcinogenic by ATSDR, EPA, or NIOSH. ATSDR chose one of the following methods at each site for our VOC analysis.

VOCs were collected using three methods, as whole samples (SUMMA[®]), adsorbed onto charcoal tubes, or adsorbed onto compound tubes. SUMMA[®] samples were collected by attaching a restrictive orifice onto an evacuated stainless steel canister. The orifices maintain a constant flow rate for up to 8hours.



^{*} In Georgia, the creosote facility we were evaluating was adjacent to the GA asphalt mix plant.

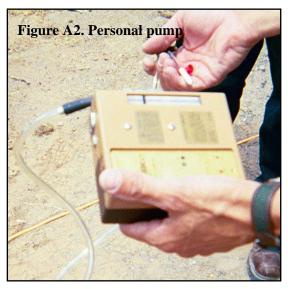
SUMMA[®] samples were collected and analyzed following the EPA Method TO-14/TO-15 for VOCs. (TO-14/15). Samples were analyzed at a laboratory using gas chromatography/mass spectroscopy (GC/MS [ion trap]) with a cryogenically cooled trap to reduce the water vapor and concentrate the VOCs.

Other VOC samples were collected and analyzed according to the NIOSH Methods 1500, 1501, and 1003 for VOCs [7]. The sampling equipment consisted of a charcoal or carbon sorbent tube connected to a personal sampling pump. The sampling pumps were calibrated to collect approximately 1.5 liters of air through the sorbent tube and filter. The samples were collected over an 8-hour period (pre programmed into the samplers).

Some VOC samples were collected and analyzed following the EPA Method TO-17 for VOCs and SVOCs (TO-17).

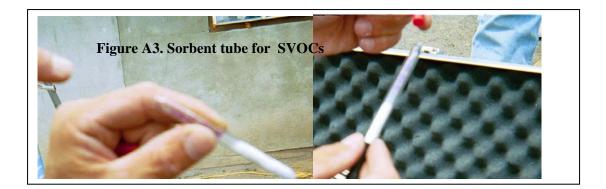
Semi Volatile Organic Compounds – SVOCs

Asphalt cement is derived from petroleum distillates which contain SVOCs. The SVOC methods provide chemical specific analyses of PAHs. The methods chosen reliably detect chemicals considered to be highly toxic and or carcinogenic, but do not detect minimally toxic and heavy PAHs like asphaltines. NIOSH samples "benzene soluble particulates" as a group instead of individually, because NIOSH focuses on worker exposures to the spattered asphalt cement. Because community exposures occur farther downwind after the spattered asphalt (droplet) has an opportunity to either



volatilize creating separate vapor-phased and particle-phased PAHs or drop out due to gravity, ATSDR uses chemical-specific analysis.

SVOCs including PAHs were collected using two methods, one that separated the particulate phase and one that did not.



SVOCs were collected and analyzed according to procedures consistent with NIOSH Method 5506 for PAHs. Samples were collected using a personal sampling pump and a filter head. The samples were collected over an 8 to 10-hour period (while the plant operations were occurring). The sampler head has two components: a polytetrafluoroethylene (PTFE) membrane to collect and retain particulate matter and a sorbent tube washed in XAD-2 resin to collect and retain gaseous phase compounds. Analytical detection procedures involved liquid chromatography and a fluorescence/ultraviolet detector.

Samples were collected and analyzed consistent with the modified NIOSH Method 5515 for PAHs. The sampling equipment consisted of an XAD-2 sorbent tube and a PTFE filter connected to a personal sampling pump. The sampling pumps were calibrated to collect approximately 1.5 liters of air through the sorbent tube and filter. The samples were collected over an 8 to 10-hour period.

Silica and Total Particulates

Asphalt mix used for paving is 95% crushed rock. Asphalt plants that have rock-crushing and sieving on-site make a lot of dust. Most of the earths crust contains silica and silica and quartz deposits are found in most bedrock. Natural weathering breaks down more of the softer minerals into dirt and dust leaving the harder minerals behind in the rock. Quartz is abundant and with a rating of 8 (of 10) on Moe's Hardness scale, it is hard to break down into small particulates (i.e., respirable) by natural weathering. However, stone crushers are strong enough to break quartz into finer particles not otherwise found naturally. Some workers exposed to fine particulate of silica-quartz experience silicosis. Most data on silicosis is found in workers who sandblast; however asphalt technology has recently changed to maximize the content of aggregate rock – which requires more crushing and sieving than before. Furthermore, local and state governments are utilizing asphalt more frequently.

Airborne particulates were collected using a sampling pump. The pump drew air through a tube connected to the specific collection device. Total suspended particulates were collected directly on a pre-weighed filter. Respirable particulates were first separated by size with a cyclone separator. The cyclone separator captured particles that were 4.5 microns or smaller ("respirable"), and a pre-weighed filter collected the particles. Particulate measurements were made by weighing the filters (NIOSH Method 0500), and then the particulate samples were analyzed for silica using x-ray powder diffraction (NIOSH Method 7500). Samples were collected for 8-10 hours. Particulate monitors were attached to a data logger to characterize the peak particulate exposures.

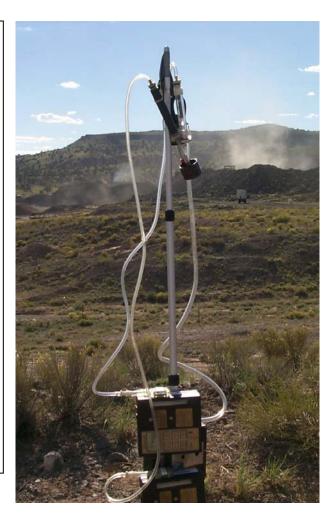


Figure A4. Respirable dust sampling train





Figure A5. Assembled samplers for dusts and SVOCs



Asbestos

Natural asbestos is not abundant like quartz, but there are certain geological formations which contain high levels of asbestos. Gypsum rock has a lot of asbestos. ATSDR considers asbestos sampling near asphalt facilities because aggregate rock may be used from some regions of the county with natural asbestos formations. There are very specific methods for conducting asbestos sampling and the sampling method must match the exposure criteria. ATSDR developed a sampling criterion for communities after the World Trade Center disaster.

Asbestos fibers were collected with AirMetric miniVOL samplers. Samplers were programmed to run between nine and twelve hours with flow rates of approximately 4.2 liters per minute (lpm). Pre-loaded filter cassettes (25 mm dia, 0.45 um pore size, mixed cellulose ester (MCE)) assembled with a cowl, tapered-style for TEM analysis. Samples were submitted to EMSL Analytical Inc (Westmont, NJ) for asbestos fiber analysis by transmission electron microscopy (TEM) according to EPA Level II Method.

Carbon Monoxide (CO)

Asphalt is the waste product of petroleum distillation. It contains large amounts of carbon monoxide and carbon dioxide (CO and CO₂). The AirMetric MiniVol is standard equipment used by enforcement agencies

CO was sampled by using AirMetric MiniVOL. For scheduled run days, samplers were set to collect CO for 8- 12 hours 6:00 a.m. to 2 p.m. Samples were collected in 6-liter Tedlar bags connected to the sampler. Following sample collection, samples were analyzed using Thermo Environmental Instruments, gas-correlation CO analyzer, model 48. The analyzer was challenged with known concentrations of span and precision CO gases (percent deviation less than 4% from known concentration). Concentrations were reported in parts-per million (ppm) averaged over the 8 or 12-hr quartz near the asphalt sites.

| Chemical or Compounds | Sampling Equipment | Analytic Method | Accuracy | | |
|---|---|---|--|--|--|
| Volatile Organic Compounds (VOCs) | SUMMA [®] canisters | EPA TO-14 & 15 NIOSH 1500 | Not available | | |
| | Compound tubes | NIOSH 1500 NIOSH 1501 NIOSH 1003 EPA TO-17 | | | |
| Semi-Volatile Compounds (SVOCs) including PAHs | Sampler head with polytetrafluoroethylene (PTFE) membrane Sorbent tube with XAD-2 resin | NIOSH 5515 modified | Not available | | |
| Total particulates | Filter Cyclone separator (Respirable < 4.5 microns) | 0500 7500 (silica) | Range studied: 8-28 mg/m ³ BIAS: 0.01% OVERALL PRECISION (S^rT): 0.056 [1] ACCURACY: ± 11.04% | | |
| Asbestos | Filter cassettes | EPA Level II Method (transmission electron microscopy (TEM)) | Not available | | |
| Carbon Monoxide | Tedlar bags | Thermo Environmental Instruments, gas- correlation CO analyzer, model 48 | Not available | | |

Table A1. ATSDR Sampling Equipment and Methods

ATSDR Multi-Site Sampling Results

Although the operations and sampling methodology were unique at each site, the results are similar *—measurable levels of contaminants were lower than those expected to cause health effects.* Table 2 displays the measured levels in the seven communities and the (composite) backgrounds.

PAHs

Acenapthene was sampled at five sites and found at three sites; however significant measurements were only measured at one site (and only in a few of the samples at that site). The highest measurement was much lower than EPA's Risk Based Concentration (RBC).

Odors

Hydrogen sulfide was only measured at two sites. It contributes a significant portion of the characteristic odor at asphalt facilities with an odor detection threshold of around 8 parts per billion (ppb) (11 ug/m³) in the general population. From more than 2,800 hours of sampling at the two sites, H₂S was only exceeded ATSDR's health comparison value (30 ug/m³) for 5 hours (NCDAQ 2003). H₂S samples were collected continuously throughout the day and converted to 1-hour averages at each monitoring site (NCDAQ 2003). We will discuss odors in more detail in the section on AP-42 parameters (Appendix B).

Particulates

Particulate matter measured downwind of asphalt sites averaged three times the average levels upwind of all the sites sampled.

PM-10 (particles with an aerodynamic diameter smaller than 10 μ m) particles are responsible for most adverse health effects associated with airborne contaminants because of their ability to reach the lower regions of the respiratory tract (EPA 1999a; McClellan 1997). EPA's health based national air quality standards for PM 10 is 150 μ g/m³ when measured as a daily average (EPA 1999b).

Epidemiologic studies conducted in several metropolitan areas have shown adverse health effects associated with exposure to total suspended particulate (TSP) levels $<100 \ \mu g/m^3$ (Brunekreff et al, 1995; Neas et al, 1999).

Respirable dust averaged 1¹/₂ times more downwind of asphalt sites than upwind.

Quartz: No comparison could be made with quartz because few measurements were much higher than the detection levels. However, the total airborne quartz and respirable quartz were each found at half of the asphalt sites and not found in the background samples. This is significant in that ATSDR and EPA rarely detect quartz above the detection levels. We measured quartz in the soil near asphalt sites and found it was $\underline{6}$ times higher than the level in the background. The high levels of quartz in the soil

indicates deposition of quartz, therefore, the re-suspension of quartz may account for some of the airborne measurements of quartz near the asphalt sites.

Sampling Limitations

Sampling equipment

SUMMA canisters and compound sorbent tubes give very similar responses with a few exceptions. Compound tubes are best for semi-volatiles, but separate OSHA PAH samplers are needed if a wide range of PAHs (other than those we detected) are expected. Compound tubes stabilize some reactive compounds better. However, if there are compounds that do not adhere to the sorbent, the SUMMA canister must be used along with rapid analysis. In summary, although the methods give similar responses, some compounds will be captured more accurately with one method vs. the other. We found one important advantage to using the compound sorbent tubes; they detected some Tentatively Identified Compounds (TICs) that helped us identify the existence of a contributing source of PAHs at one site.

Sampling length and timeframe

ATSDR's sampling efforts are generally short-term (i.e., days to weeks). Our sampling efforts may or may not be conducted during critical times (upsets, higher production periods, worst waste stream processing). This makes the sampling a snapshot in time although we are often comparing the results to longer-term averages.

Since VOCs volatilize quickly, if they are released sporadically, they are experienced as peaks or spikes in the environment. However, if the equipment is set to capture a sample volume over a specified timeframe, the concentration detected would be averaged for the total volume analyzed thus reducing the peak concentrations. If the sample volume or timeframe is very long, VOCs are often in too low in concentration to be detected by analysis equipment.

| | | CV [¥] Source | Averages (and Maximum) Level Detected | | | | | | | |
|-------------------------------|--------|---------------------------|---------------------------------------|----------|------------|-----------|-----------------|---------------|------------|-----------------|
| Chemical | | | Sampling Locations | | | | | | | |
| | CV | | СА | NY | UT-1 | UT-2 | NC | GA | AZ | Back- ground |
| Acetone | 30,000 | i-EMEG | NS | NS | 8.5(22) | ND | NS | ND | 2.0(5.6) | 2.4(8.0 |
| Benzene | 20 | i-EMEG | NS | NS | 1.5 (3.4) | 0.12(.13) | 0.79 (1.7) | 2.9(14) | 0.6(1.1) | 1.1(5.4 |
| Carbon | | | NS | NS | 0.04 (41) | 0.10(00) | 0 (2(0 70) | ND | ND | 0.0/1.0 |
| Tetrachloride | 200 | i-EMEG | NS | NS | 0.24 (.41) | 0.18(.22) | 0.63(0.79) | 12(10) | ND | 0.8(1.0 |
| Ethylbenzene | 4000 | i-EMEG | NS | NS | 0.59(2.7) | ND | 0.41(1.9) | 12(18) ND | ND | 1.1(2.7 |
| Methylene Chloride | 1000 | i-EMEG | NS | NS | 0.77(2.4) | 0.26(.32) | 2.2 (3.8) ND | 1.7(3.3) | ND | 0.5(2.7 |
| Tetrachloroethene | 300 | c-EMEG | NS | NS | 0.054(.09) | ND | | 32(38) | 1.0(1.4) | 0.5(2.4 |
| Toluene 1,1,1- | 300 | c-EMEG | NS | NS | 2.1 (3.9) | ND | 1.9(4.3) | ND | ND | 2.6(8.6 |
| Trichloroethane | 4000 | i-EMEG | IND | IND | 0.13(2.7) | 0.15(.18) | 0.28(0.38) | ND | ND | ND |
| m,p-Xylene | 3000** | i-EMEG | NS | NS | 1.0(2.3) | ND | 0.60(2.3) | 33(48) | ND | 2.2(7.1 |
| o-Xylene | 3000** | i-EMEG | NS | NS | 0.39(0.98) | ND | 0.49(1.0) | 6.5(8.7) | ND | 1.2(3.6 |
| | | | | | | | | | | |
| Carbon Disulfide | 900 | c-EMEG | NS | NS | 1.0(3.6) | ND | NS | ND | 1.2(12.4) | ND |
| Hydrogen Sulfide | 30 | i-MRL | NS | NS | NS | NS | 9(65.5) | NS | 0.1(2) | ND |
| Carbon Monoxide | | NAAQS | NS | | | 1580(298 | | NS | | |
| (ppb) | 10,000 | (8 hr) | | NS | NS | 0) | NS | | NS | NS |
| | | | | | | | | | | |
| Acenaphthene | 210 | RBC | NS | NS | 1.3(2.9) | 1.3 | ND | ND | 26 (70) | ND |
| Benzo(a)anthracene | 200 | OSHA PEL | NS | NS | 0.14(0.44) | ND | ND | ND | 0.02(.031) | ND |
| Benzo(b)fluoranthe | 200 | OSHA | | | | ND | ND | ND | | ND |
| ne | 200 | PEL | NS | NS | 0.14(0.44) | | | | ND | |
| Benzo(k)fluoranthe ne | 200 | OSHA PEL | NS | NS | 0.07(0.13) | ND | ND | ND | ND | ND |
| Fluoranthene | 150 | RBC | NS | NS | 0.30 (1.0) | 0.08 | ND | ND | ND | ND |
| Fluorene | 150 | RBC | NS | NS | 0.30 (1.0) | 0.00 | ND | ND | 0.09(0.1) | ND |
| Pyrene | 110 | RBC | NS | NS | 0.09(0.15) | ND | ND | ND | ND | ND |
| I yrene | 110 | KDC | 115 | 110 | 0.09(0.12) | ND | ND | 112 | 112 | 1.2 |
| | | EPA | | | | | | | | |
| | | PM10 | 53 (75) | 19(22) | 50((0)) | 14 (14) | 140(150) | NS | 22(28) | 1((21) |
| Total Dust | 150 | (24 hr) EPA | 52(75) | 18(33) | 50(60) | 14 (14) | 140(150) | | 22(38) | 16(21) |
| | | PM2.5 | | | | | | NS | | |
| Respirable Dust | 35 | (24 hr) | 28(49) | 8.1(19) | 23(30) | 13(21) | 30(40) | 145 | 19(30) | 13(30) |
| | | | | | | | | | | |
| T . 10 . | • | | 4 4(7 1) | ND | 0.2(12) | ND | ND | NC | 4(4.0) | ND |
| Total Quartz Respirable | 200 | NIOSH | 4.4(7.1) | ND | 9.3(13) | ND | ND | NS NS | 4(4.0) | ND |
| Quartz | 5*** | NIOSH | 3.1(4.9) | ND | ND | 4 (4) | 2(4) | 140 | ND | ND |
| Soil Quartz | - | | | | | . (.) | -(•) | | | 1.2 |
| (percent) | None | None | 19% | 24% | NS | NS | NS | NS | 29% | 4% |
| | | | | | | | | | | |
| Asbestos (s/mm ²) | 20 | AHERA | NS | 1.8(4.4) | NS | ND | NS | NS | NS | 1.5(4.3 |
| . , , | | | | | | | | | | |

Measurements in **bold** are those that are higher than the background value.

Chemicals listed in *italics* are those that were higher than the background at three asphalt sites.

Background samples were collected upwind from several of the asphalt sites.

ND = Not detected. (detection levels varied)

NS = Not Sampled or Not Analyzed

- ${}^{\text{¥}}$ = For an explanation of terms used for CV Sources, see Appendix D.
- § = Half the detection limits were used to calculate the averages when an analyte was not detected in the downwind samples.

* = The CV for 1,2,4-Trimethylbenzene was adopted from that of 1,3,5-Trimethylbenzene based on NIOSH's treatment of these two chemicals as equals in terms of their Recommended Exposure Limit of 125,000 μ g/m³ for a 10-hr Time-Weighted Average (TWA).

- ** = m,p-xylene and o-xylene were assigned a comparison value for total xylenes due to a lack of individual comparison values.
- ***= NIOSH's REL is 50 ug/m³. Since this is for occupational exposure, we divided the REL by a safety factor of 10 for community exposure.

Published documents with this air data include: ATSDR 1999, 2001a,b, 2003, 2004, 2005

References

- ATSDR (Agency for Toxic Substances and Disease Registry) 1999. Exposure Investigation for Mission Valley, San Diego, CA. November 4, 1999. U.S. Department of Health and Human Services, Atlanta.
- ATSDR 2001a. Exposure Investigation for Prima Asphalt Concrete, Holtsville, NY. April 1, 2001. U.S. Department of Health and Human Services, Atlanta.
- ATSDR 2001b. Exposure Investigation for Staker Paving Asphalt Production Plant, Erda, UT. May 17, 2001. U.S. Department of Health and Human Services, Atlanta.
- ATSDR 2003. Exposure Investigation for Brimhall Sand and Gravel, Indian Wells, AZ. April 8, 2003. U.S. Department of Health and Human Services, Atlanta.
- ATSDR 2004. Exposure Investigation for Meredith Williams Co, East Point, GA. September 29, 2004. U.S. Department of Health and Human Services, Atlanta.
- ATSDR 2005. Health Consultation for Valley Asphalt, Spanish Fork, UT. December 8, 2005. U.S. Department of Health and Human Services, Atlanta.
- Brunekreef B, Dockery DW, and Krzyzanowski M, 1995. Epidemiologic Studies on Short term Effects of Low Levels of Major Ambient Air Pollution Components. Environ Health Perspect 103(Suppl 2):3 13.
- EPA 1999a. Criteria Pollutants. http://www.epa.gov/oar/oaqps/greenbk/o3co.html
- EPA 1999b. Air Quality Trends 1994, Particulate Matter (PM 10). http://www.epa.gov/oar/aqtrnd94/six_pm10.html
- McClellan R, 1997. Use of Mechanistic Data in Assessing Human Risks from Exposure to Particles. Environ Health Perspect 105(Suppl 5):1363 1372.
- Neas LM, Schwartz J, and Dockery D, 1999. A Case Crossover Analysis of Air Pollution and Mortality in Philadelphia. Environ Health Perspect 107:629 631.
- NC DAQ 2003. North Carolina Division of Air Quality, Toxics Protection Branch, Air Toxics Analytical Support Team (ATAST) ATAST Investigation Numbers 01007 and 01008. Final Study Report Salisbury Air Quality Monitoring Study. August 29, 2003 available online at <u>http://www.daq.state.nc.us/toxics/studies/salisbury/Salisbury_final_report.pdf</u>

Appendix B

ATSDR's Evaluation of HMA Plants using AP-42 Parameters

AP-42 and HMA Plant Emissions Factors

ATSDR reviewed the emission factors for Hot Mix Asphalt (HMA) Plants to determine if our predicted sample constituents matched what was detected in our own sampling. We also evaluated which chemicals may pose the greatest hazard.

What is potentially released from HMA plants?

EPA has estimated emissions factors for many industries, including Hot Mix Asphalt Plants. AP 42 (Volume I, Fifth Edition: Stationary Point and Area Sources – January 1995) has chapters on <u>External Combustion Sources, Solid Waste Disposal</u>, <u>Stationary Internal Combustion Sources, Evaporation Loss Sources, Petroleum</u> <u>Industry, Organic Chemical Process Industry, Liquid Storage Tanks, Inorganic Chemical Industry, Food and Agricultural Industries, Wood Products Industry, Mineral Products Industry, Metallurgical Industry, Miscellaneous Sources, Greenhouse Gas Biogenic Sources, and Ordnance Detonation. Chapter 11, Mineral Products Industry, includes HMA plants (EPA 2004).</u>

HMA plant emissions result from both controlled (i.e., ducted) and uncontrolled sources. Emissions are estimated for materials handling (fugitive emissions), generators (primarily diesel that are used at mobile plants for electricity), storage tanks, and process emissions (EPA 2004).

EPA defines an emissions factor as "a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant." Emissions factors are usually expressed as the weight of pollutant divided by a unit weight, volume, distance, or duration of the activity emitting the pollutant (e.g., kilograms of particulate emitted per megagram of coal burned). Such factors facilitate estimation of emissions from various sources of air pollution. In most cases, these factors are simply averages of all available data of acceptable quality, and are generally assumed to be representative of <u>long-term averages</u> for all facilities in the source category (i.e., a population average) (EPA 2004).

The general equation for emissions estimation is:

 $E = A \times EF \times (1 - ER/100)$

where: E = emissions; A = activity rate; EF = emission factor, and ER =overall emission reduction efficiency, % (EPA 2004 found online at http://www.epa.gov/ttn/chief/ap42/index.html)

Compounds Potentially Emitted From HMA Plants

AP42 predicts that HMA plants could emit as many as 159 compounds. Most of the predicted 159 compounds emitted from HMA plants do not warrant further assessment for community exposure because they are insignificant from the standpoint of toxicity, quantity emitted, or odor. To narrow the list that required an in-depth evaluation, ATSDR initially sorted compounds into the following groups:

| Compounds of Interest | Factors |
|------------------------------|------------------------------------|
| Emitted in Large Quantities | Emission Factor (EF) |
| Possible Effects | EF and Threshold Limit Value (TLV) |
| Potential Risk | EF and Hazard Index or Risk |
| Odor Warning Properties | Odor Threshold (OT) and TLV |
| Significant/Sustained Odor | EF and OT |

1. Asphalt-related Compounds Emitted in Large Quantities

We examined the list of compounds associated with HMA Plant Emissions and sorted them by relative quantity. We ranked the "highly emitted" compounds based on **Emission Factor (EF)** data. Table B1 lists the top 10 Emissions Factors compiled from AP-42 for compounds potentially released from HMA plants. The entries are sorted by the relative predicted quantity of emissions. These predictions are based on data for all types of HMA plants (batch, counterflow, parallel flow) using all types of fuels (e.g., natural gas, #2 fuel oil, waste oil, etc.) and pollution control devices (e.g., cyclones, scrubbers, filters, etc.). Compounds predicted to be emitted by HMAs in the greatest quantity are at the top of this list.

| Table B1. Emissions Factor Table | | | | | |
|---|------------|----------|----------|----------|--|
| Chemical | CASRN | Max EF | MW | TLV ppm | |
| Carbon Dioxide | 124-38-9 | 3.30E+01 | 4.40E+01 | 5.00E+03 | |
| Total PM (particulate) or TSP | 7601-54-9 | 3.20E+01 | 1.64E+02 | N/A | |
| PM10 (particulate matter <10m) | | 6.50E+00 | N/A | N/A | |
| Particulate PM-2.5 | | 1.50E+00 | N/A | N/A | |
| Nitrogen Oxide (NOx) | 11104-93-1 | 5.50E-01 | 3.00E+01 | 2.50E+01 | |
| Carbon Monoxide | 630-08-0 | 1.30E-01 | 2.80E+01 | 2.50E+01 | |
| Organic PM (particulate matter) | | 5.80E-02 | N/A | N/A | |
| Sulfur Dioxide | 7446-09-5 | 5.80E-02 | 6.41E+01 | 2.00E+00 | |
| TOC as propane (or total VOC) | 74-98-6 | 4.40E-02 | 4.41E+01 | 1.00E+03 | |
| Methane | 74-82-8 | 1.20E-02 | 1.60E+01 | 1.00E+03 | |
| CASRN-Chemical Abstract Registry Number Max EF- Maximum Emissions Factor MW- Molecular Weight TLV- Threshold Limit Value | | | | | |

2. Compounds with Possible Health Effects based on Quantity and Toxicity

ATSDR examined the list of compounds that were released in the highest quantities, but had low Threshold Limit Values (TLVs). More toxic substances have lower TLVs. The **ratio of EF/TLV** represented compounds with possible health effects. *Those compounds that ranked higher on this list are those that are released in the highest quantities and also have a low threshold limit value (TLV)*. Table B2 shows the top 10 list of possible compounds released from HMA plants sorted by the relative quantity predicted to be emitted (from all types of HMA plants) divided by the TLV.

| Table B2. EF/TLV ppm | | | | | |
|----------------------|------------|----------|----------|----------------------|--|
| Chemical | CASRN | Max EF | TLV ppm | EF/TLV | |
| Sulfur Dioxide | 7446-09-5 | 5.80E-02 | 2.00E+00 | 0.028999999165535 | |
| Nitrogen Oxide (NOx) | 11104-93-1 | 5.50E-01 | 2.50E+01 | 2.19999998807907E-02 | |
| Lead | 7439-92-1 | 5.40E-04 | 5.00E-02 | 1.07999993488193E-02 | |
| Manganese | 7439-96-5 | 6.50E-04 | 8.90E-02 | 7.30286259204149E-03 | |
| Carbon Dioxide | 124-38-9 | 3.30E+01 | 5.00E+03 | 6.59999996423721E-03 | |
| Carbon Monoxide | 630-08-0 | 1.30E-01 | 2.50E+01 | 5.200000141561E-03 | |
| Formaldehyde | 50-00-0 | 3.10E-03 | 1.00E+00 | 3.1000008903444E-03 | |
| Barium | 7440-39-3 | 2.50E-04 | 8.90E-02 | 2.80777108855546E-03 | |
| Quinone | 106-51-4 | 2.70E-04 | 1.00E-01 | 2.69999983720481E-03 | |
| Copper | 7440-50-8 | 1.70E-04 | 7.69E-02 | 2.20930459909141E-03 | |

3. Compounds with Greatest Health Risk Based on Quantity Released and Hazard Index or Cancer Risk

We looked at the compounds emitted in high quantities that had either a **high Hazard Index (HI) or high cancer risk (CR) level**. This Emission Risk Index sort was ranked according to EF divided by CV (either an HI or CR). Table B3 lists the top 10 results. Since a *higher risk is indicated by a lower* the risk value, the *compounds at the top of the list are those released in higher quantity and also have a relatively high hazard index or cancer risk*.

Note: Safety factors will impact the actual effect levels on which the Reference Doses (RfDs) and risk levels are based. As a result, the ratios (EF/HI and EF/"risk") will be a ranking of <u>chemicals</u> by RfD-associated or CSF-implied <u>safety factors</u>, rather than by relative <u>hazard</u>. (For example, PCDDs, PCDFs, PCBs, and PAHs would rank well above metals on such a list, even though metals would likely pose the more realistic hazard potential for exposed populations.)

The risk levels noted in Table B3 are based on EPA ambient air reports from Regions 3 and 9.

| Table B3. Emission Factor/ Hazard Index or Risk | | | | | | |
|--|---|----------|------------|----------------|----------------------|--|
| Chemical | CASRN | Max EF | CV (ug/m3) | CV Ref (E=EPA) | EF/CV | |
| Nickel | 7440-02-0 | 1.30E-03 | 8.00E-03 | CA@E-6R (E3) | 0.162499994039536 | |
| Manganese | 7439-96-5 | 6.50E-04 | 5.10E-02 | N=0.1HI (E3) | 1.27450982108712E-02 | |
| Benzene | 71-43-2 | 3.90E-04 | 2.30E-01 | CA@E-6R (E3) | 1.69565214309841E-03 | |
| Acetaldehyde | 75-07-0 | 1.30E-03 | 8.70E-01 | CA@E-6R (E3) | 1.49425282143056E-03 | |
| Barium | 7440-39-3 | 2.50E-04 | 5.20E-01 | N=0.1HI (E3) | 4.80769260320812E-04 | |
| Carbon Monoxide | 630-08-0 | 1.30E-01 | 1.00E+04 | NAAQS (E) | 1.29999998534913E-05 | |
| Toluene | 108-88-3 | 2.90E-03 | 4.00E+02 | N=0.1HI (E3) | 7.24999972590012E-06 | |
| Hexane | 110-54-3 | 9.20E-04 | 2.10E+02 | N=0.1HI (E3) | 4.38095230492763E-06 | |
| Xylene (m-/p-) | 1330-20-7 | 2.70E-03 | 7.30E+02 | N=0.1HI (E3) | 3.69863028026884E-06 | |
| Acetone | 67-64-1 | 8.30E-04 | 3.70E+02 | N=0.1HI (E3) | 2.24324321607128E-06 | |
| CA@e-6R = 10 to E3 = EPA Region | N = non-cancer risk # which is 10% of the EPA hazard index CA@e-6R = 10 to the minus 6 cancer risk E3 = EPA Region 3 derived CV E9 = EPA Region 9 derived CV | | | | | |

4. Compounds with Low Odor Warning Properties

ATSDR examined each chemical based on whether it is odorous at levels above the TLV. *Those compounds with odor thresholds above the TLV provide little or no warning of exposure. We ranked these compounds according to* **Odor Threshold (OT)/Threshold Limit Value (TLV)**. Table B4 ranks the top 10 chemicals in *descending* order of their warning odor effectiveness. The ranking is a ratio of Toxicity to Odor, so that the greater the toxicity, relative to the degree of odor, the *higher* it will rank. The smellier the chemical, relative to its potential toxicity, the *lower* it will rank. However, the available *numerical surrogates* for Odor and Toxicity, i.e., the odor threshold (or mean OT) and the Threshold Limit Value (TLV), are actually *inverse indicators* of odor and toxicity. The *stronger* the odor of the substance (smellier), the *lower* the odor threshold (OT). Similarly, the *more toxic* the substance, then the *lower* the threshold limit value (TLV) (generally). In order to express the desired ratio Toxicity/Odor *using the OTs and TLVs*, the ratio must be written as "OT/TLV".

OT/TLV = (1/ ODOR)/(1/ TOXICITY) = TOXICITY/ODOR

In a list of chemicals ranked in *descending* order of OT/TLV ratios, those chemicals with the <u>least</u> effective warning odors will rank *highest* (i.e., have the <u>highest</u> OT/TLV ratios), while those with the <u>most</u> effective warning odors will rank <u>lowest</u> (i.e., have the <u>lowest</u> OT/TLV ratios).

Where possible, ATSDR used the geometric mean odor detection threshold (see list of odor references below). Where a mean was not available, we used the minimum odor detection threshold.

| Table B4. Geometric Mean Odor Threshold of Detection/TLV | | | | | |
|--|-----------|------------|----------|-------------------|--|
| Chemical | CASRN | GM_OTd_ppm | TLV ppm | OTd/TLV | |
| Carbon Tetrachloride | 56-23-5 | 252 | 5.00E+00 | 50.4000015258789 | |
| Acrolein | 107-02-8 | 1.8 | 1.00E-01 | 18 | |
| Benzene | 71-43-2 | 61 | 1.00E+01 | 6.09999990463257 | |
| Sulfur Dioxide | 7446-09-5 | 2.7 | 2.00E+00 | 1.35000002384186 | |
| 1,1,1-Trichloroethane | 71-55-6 | 390 | 3.50E+02 | 1.11428570747375 | |
| Methyl chloroform | 71-55-6 | 390 | 3.50E+02 | 1.11428570747375 | |
| Xylene (m-/p-) | 1330-20-7 | 20 | 2.00E+01 | 1 | |
| Xylene (o-) | 95-47-6 | 20 | 2.00E+01 | 0.998143136501312 | |
| Tetrachloroethene | 127-18-4 | 47 | 5.00E+01 | 0.939999997615814 | |
| Ammonia | 7664-41-7 | 17 | 2.50E+01 | 0.680000007152557 | |

5. Compounds With a High Degree of Odor

ATSDR sorted the list of potentially emitted compounds based on the "Degree of Odor" using **Emission Factor (EF)/OT**. Substances which have low odor (detection) threshold and are emitted from HMA plants at higher concentrations will be at the top of this table. In Table B5, ATSDR ranks the top 10 chemicals in *descending* order based on those which are emitted at greater quantities and can only be detected (via odor) at higher concentrations.

| Table B5. Maximum EF/Geometric Mean Odor Detection Threshold | | | | | |
|--|-----------|----------|------------|----------------------|--|
| Chemical | CASRN | Max EF | GM_OTd_ppm | EF/OT | |
| Sulfur Dioxide | 7446-09-5 | 5.80E-02 | 2.7 | 2.14814804494381E-02 | |
| Acetaldehyde | 75-07-0 | 1.30E-03 | 0.067 | 1.94029845297337E-02 | |
| Naphthalene | 91-20-3 | 6.50E-04 | 0.038 | 1.71052645891905E-02 | |
| Toluene | 108-88-3 | 2.90E-03 | 1.6 | 1.81249994784594E-03 | |
| Crotonaldehyde | 4170-30-3 | 8.60E-05 | 0.11 | 7.81818176619709E-04 | |
| Xylene (m-/p-) | 1330-20-7 | 2.70E-03 | 20 | 1.3500009322539E-04 | |
| Heptane | 142-82-5 | 9.40E-03 | 230 | 4.08695632359013E-05 | |
| Ethylene | 74-85-1 | 7.00E-03 | 270 | 2.59259268204914E-05 | |
| Acrolein | 107-02-8 | 2.60E-05 | 1.8 | 1.4444447869319E-05 | |
| Acetone | 67-64-1 | 8.30E-04 | 62 | 1.33870962599758E-05 | |

How Did ATSDR Choose Odor Thresholds?

To find information on odors and odor responses for the 159 AP-42 chemicals, ATSDR used the following publications in this order:

1. Odor Thresholds for Chemicals with Established Occupational Health Standards 1997, AIHA Review Subcommittee, The American Industrial Hygiene Association;

ATSDR chose this publication first because the AIHA did an extensive literature review and rejected numerous studies based on a rigorous list of criteria. Studies accepted were then ranked by the panel size, panel odor sensitivity, panel calibration, and several other factors. Most of the chosen and rejected thresholds were compiled from reference #2.

2. Compilations of odor threshold values in air, water and media 2003, L.J. Van Gemert, Boelens Aroma Chemical Information Service (BACIS)

3. TLVs and BEIs Based on the Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices 2004, The American Conference of Governmental Industrial Hygienist.

Additional odor threshold information was acquired by researching different electronic databases. The electronic databases used included ISI Web of Science, PubMed, ProQuest and Micromedex (which provides information from Medtext, Hazardtext, CHRIS (Chemical Hazard Response Information System), HSDB (Hazardous Substance Data Bank), IRIS (Integrated Risk Information System), LOLI, NIOSH Pocket Guide, OHM/TADS (Oil and Hazardous Materials/Technical Assistance Data System), RTECS (Registry of Toxic Effects of Chemical Substances), Reprotext, Reprotox and Poisindex-Toxicology Management).

The odor thresholds and other relevant information from the electronic databases and literature was stored in a database.

How Did ATSDR Use These Tables?

The EF, OT/TLV, and EF/[HI or CR] tables were used in conjunction with TLV and selected Lowest Observable Adverse Effect Levels (LOAELs) to make decisions on which chemicals to investigate further in a toxicological evaluation.

The OT/TLV and EF/OT tables are useful for selecting chemicals for further literature searches on response and adverse response levels. ATSDR and others can use this information for making nuisance odor level recommendations.

Note on ATSDR site-specific sampling: When predicting community exposures, ATSDR generally uses worst case scenarios. Although we believe that most of the 159 compounds will not be detected in nearby communities due to low concentrations or, in the case of particulates, they usually fallout before they could reach a community, we still consider them and in many instances include them in our sampling and analytical methods

Top Compounds by Category from the AP-42 HMA Plant Emissions Factors Evaluation

Of the top 10 compounds from each of the previously discussed tables, *the most toxicologically significant substances were found to be sulfur dioxide, nitrogen dioxide, carbon monoxide, aldehydes (such as acrolein), some metals, and particulates (such as quartz, dust).*

The other chemicals represented in the tables are not likely to be toxic (at the concentrations found in the atmosphere) or are likely to be found in the air at extremely low concentrations, which are not significant enough to pose concern to the area's surrounding HMA plants. However, chemicals such as sulfur dioxide and the aldehydes are highly reactive and may cause irritation to the eyes and upper respiratory system. Further, particulates (such as quartz) which are released by HMA plants are comprised of substances which accumulate in the lungs and effect lung functions once inhaled (HSDB).

Top Ten List of Substances for which ATSDR Conducted Further Toxicological Evaluations

| Compounds of Interest | Factors |
|------------------------------|------------------------------------|
| Emitted in Large Quantities | Emission Factor (EF) |
| Possible Effects | EF and Threshold Limit Value (TLV) |
| Potential Risk | EF and Hazard Index or Risk |
| Odor Warning Properties | Odor Threshold (OT) and TLV |
| Significant/Sustained Odor | EF and OT |

•

•

•

Emission Factor (EF) - Asphalt-related Compounds Emitted in Large Quantities

- Carbon Dioxide
- Carbon Monoxide
- Total PM (Particulate) TSP •
- PM (Particulate matter $<10m \bullet$
- Particulate PM -2.5
- Nitrogen Oxide (NOx) •
- Organic PM (Particulate Matter)
- Sulfur Dioxide
- TOC as propane (or total VOC)
- Methane

<u>EF/Threshold Limit Value (TLV)</u> - Compounds with Possible Health Effects based on Quantity and Toxicity

- Sulfur Dioxide
- Nitrogen Oxide (NOx)
- Lead
- Manganese
- Carbon Dioxide
- Carbon Monoxide
- Formaldehyde
- Barium
- Quinone
- Copper

EF/Hazard Index or Risk - Compounds with Greatest Health Risk Based on Quantity Released and Hazard Index or Cancer Risk

- Nickel •
- Manganese
- Benzene •
- Acetaldehyde •
- Barium

- Carbon Monoxide
- Toluene
- Hexane
- Xylene (m-/p-)
- Acetone

Top Ten List of Substances which are Nuisance Odor Evaluation Indicators

Odor Threshold (OT)/TLV - Compounds with Low Odor Warning Properties

- Carbon Tetrachloride Π
- Acrolein •
- Benzene •
- Sulfur Dioxide •
- 1,1,1-Trichloroethane
- EF/OT Compounds with a High Degree of Odor*
 - Sulfur Dioxide
 - Acetaldehyde •
 - Naphthalene •
 - Toluene •
 - Crotonaldehyde •

*Note: Although H₂S did not rank high on this list because it did not have a significant emissions factor, it does have a low odor detection threshold of around 8 ppb (11 ug/m^3) in the general population and should be considered for sampling.

What AP-42 compounds were not sampled for by ATSDR in communities?

Sampling in the seven communities did not include metals, SO₂, NOx, and aldehydes and there was limited sampling for carbon monoxide. Additionally, we may need to consider how the mixture of chemicals may react to form other hazards such as acid gases. pH measurements may also be needed.

Headaches have been reported as a symptom in many of the communities tested. At what level do the COx compounds produce headaches?

CO and CO_2 are highly emitted from HMA plants. CO produces headaches at 200 ppm (over a 2-3 hour period) and 400 ppm (over a 1-2 hour period (See CO Reference Section).

- Methyl chloroform • Xylene (m-/p-) •
- Xylene (o-) •
- Tetrachloroethene •
- Ammonia •
- Xylene (m-/p-)
- Heptane
- Ethylene •
- Acrolein •
- Acetone
- •

 CO_2 produces headaches at 2000-5000 ppm (See CO_2 Reference Section). The typical level found in occupied spaces with good air exchange is 350 - 1,000 ppm. The levels associated with complaints of drowsiness and poor air are 1,000 - 2,000 ppm.

Using the emissions factors, a typical batch HMA plant produces 6.5 ton/yr CO and 1,650 ton/yr CO₂. A typical drum mix plant produces 13 ton/yr CO and 3,300 ton/yr CO₂. Using those output rates and modeling worst case conditions with SCREEN3¹, it is possible that people may experience headaches from CO for a little more than $\frac{1}{2}$ mile from a facility and from CO₂ up to 4 miles of a facility. However, ATSDR sampling for CO at one site showed a very low downwind concentration of just over 1 ppm. At future asphalt facilities where an ATSDR evaluation is requested, we will include sampling for carbon oxides (CO, CO₂).

Overall Conclusions

As a result of this emission factors evaluation, ATSDR's future sampling at asphalt facilities will also include sulfur dioxide (SO₂), nitrogen dioxides (NOx), carbon oxides (CO, CO₂), and some metals as well as continued sampling for particulates, hydrogen sulfide, VOCs, and PAHs.

We will also include sampling for compounds with the highest degree of significant/sustained odor such as acetaldehyde, naphthalene, toluene, crotonaldehyde, xylene (m-/p-), heptane, ethylene, acrolein, and acetone.

Since chemical mixtures may react and form other hazards such as acid gases, we will include pH measurements where applicable.

¹ SCREEN3 – is a single source Gaussian plume model which provides maximum ground-level concentrations for point, area, flare, and volume sources, as well as concentrations in the cavity zone, and concentrations due to inversion break-up and shoreline fumigation. SCREEN3 is a screening version of the ISC3 model. <u>http://www.epa.gov/scram001/dispersion_screening.htm#screen3</u>

CO References:

Annual Review of Pharmacology Vol. 15: 409-423 (Volume publication date April 1975) (doi:10.1146/annurev.pa.15.040175.002205) The Effect of Carbon Monoxide on Humans R D Stewart Title: Warehouse workers' headache. Source: Journal of occupational medicine [0096-1736] Fleming yr:1992 vol:34 iss:9 pg:872 -872 http://www.ccohs.ca/oshanswers/chemicals/chem profiles/carbon dioxide/health cd.htm http://www.dhfs.state.wi.us/eh/ChemFS/fs/CarbonDioxide.htm http://www.aerias.org/DesktopModules/ArticleDetail.aspx?articleId=138&spaceid=2&su bid=13 http://www.intox.org/databank/documents/chemical/carbdiox/cie747.htm http://www.intox.org/databank/documents/chemical/carbmono/cie57.htm www.ohsonline.com/Stevens/OHSPub.nsf/Articles2/8B509CAEB2CBF8B88625719A00 5DA18B? http://www.osha.gov/dts/sltc/methods/inorganic/id172/id172.html#ref86 http://www.osha.gov/dts/sltc/methods/inorganic/id209/id209.html

CO₂ References:

http://dhfs.wisconsin.gov/eh/ChemFS/fs/CarbonDioxide.htm www.abe.iastate.edu/human_house/aen125.asp www.airproducts.com/nr/rdonlyres/ 6582611c-16c6-4660-8584c172182fb0c2/0/safety18.pdf www.deh.gov.au/atmosphere/airquality/ publications/sok/profiles/**carbon**monoxide.html www.epa.gov/Ozone/snap/fire/co2/appendixb.pdf

Appendix C. Odors Discussion

In general, people have become more intolerant of environmental odors while at the same time, air quality has improved. As "background" odor levels are decreasing, people have become more sensitive and able to detect very low, transient environmental levels.

"Unpleasant odors have long been recognized as warning signs of potential risks to human health. We now know that odors from environmental sources might indeed *cause* health symptoms depending on the individual and the environmental factors" (Schiffman *et al*, 2005). Odor-related mechanisms that may result in symptoms include innate odor aversion, stress-induced illness, aversive conditioning phenomena, and aggravation of existing medical conditions, such as bronchial asthma (Shusterman 1992). After exposure to environmental odors, these processes may occur in some individuals and not in others. Smokers and the elderly may be less aware of odors and therefore at risk for prolonged exposure. In general, women are more sensitive to environmental odors than men are.

Odor-related aversive conditioning may occur when a person experiences low-level odors after an initial traumatic exposure. A common response is hyperventilation with a fast heart rate, dizziness, nausea, sweating, and anxiety. Stress-related health effects may, to some extent, be related to the degree to which an individual believes an odor is causing risk. The symptom-causing odor thresholds of some contaminants may be below levels thought to be hazardous, thus defying classic toxicological explanations. These odor-related mechanisms would help to explain why health complaints expressed by some communities often occur when contaminants are detected below levels associated with known adverse health effects (Shusterman *et al*, 1991).

References

- Schiffman S, Williams, C.M. 2005. Science of Odors as a Potential Health Issue. J Environmental Quality 34:129-138
- Shusterman D, Lipscomb J, Satin K, Neutra R. 1991. Symptom prevalence and odorworry interaction near hazardous waste sites. Environ Health Perspect 94:25-30.
- Shusterman D. 1992. Critical Review: The health significance of environmental odor pollution. Arch Environ Health 47:76-91.

Appendix D. Explanation of Comparison Values

AHERA – Asbestos Hazard Emergency Response Act signed by EPA

CR- Cancer Risk

c-EMEG – ATSDR's Environmental Media Evaluation Guide based on chronic exposure (>365 days)

i-EMEG – ATSDR's Environmental Media Evaluation Guide based on intermediate exposure (15-364 days)

EPA PM10 & EPA PM2.5 – PM 10 is measure of particles in the atmosphere with a diameter of less than ten or equal to a nominal 10 micrometers. PM-2.5 is a measure of smaller particles in the air. PM-10 has been the pollutant particulate level standard against which EPA has been measuring Clean Air Act compliance. On the basis of newer scientific findings, EPA is considering regulations that will make PM-2.5 the new "standard".

HI – Hazard Index

i-MRL- An ATSDR estimate of daily human exposure to a hazardous substance at or below which that substance is unlikely to pose a measurable risk of harmful (adverse), noncancerous effects. MRLs are calculated for a route of exposure (inhalation or oral) over a specified time period (acute, intermediate, or chronic). MRLs should not be used as predictors of harmful (adverse) health effects. (i stands for intermediate and represents between 15 and 364 days of exposure.)

NAAQS – National Ambient Air Quality Standards: Standards established by EPA that apply for outdoor air throughout the country.

NIOSH – National Institute for Occupational Safety and Health (NIOSH)

OSHA PEL – OSHA (Occupational Safety & Health Administration) sets permissible exposure limits (PELs) to protect workers against the health effects of exposure to hazardous substances. PELs are regulatory limits on the amount or concentration of a substance in the air. They may also contain a skin designation. PELs are enforceable. OSHA PELs are based on an 8-hour time weighted average (TWA) exposure.

RBC – The Risk Based Concentration (RBC) Table contains Reference Doses (RfDs) and Cancer Slope Factors (CSFs) for about 400 chemicals. These toxicity factors have been combined with "standard" exposure scenarios to calculate RBCs--chemical concentrations corresponding to fixed levels of risk (i.e., a Hazard Quotient (HQ) of 1, or lifetime cancer risk of 1E-6, whichever occurs at a lower concentration) in water, air, fish tissue, and soil. They can be found at the following website. <u>http://www.epa.gov/reg3hwmd/risk/human/index.htm</u> TLV – Threshold Limit Values (TLVs) are not standards. They are guidelines designed for use by industrial hygienists in making decisions regarding safe levels of exposure to various chemical substances and physical agents found in the workplace. In using these guidelines, industrial hygienists are cautioned that the TLVs are only one of multiple factors to be considered in evaluating specific workplace situations and conditions.

TLVs are determinations made by a voluntary body of independent knowledgeable individuals. They represent the opinion of the scientific community that has reviewed the data described in the Documentation, that exposure at or below the level of the TLV does not create an unreasonable risk of disease or injury.

TLVs are health-based values established by committees that review existing published and peerreviewed literature in various scientific disciplines (e.g., industrial hygiene, toxicology, occupational medicine, and epidemiology). Since TLVs are based solely on health factors, there is no consideration given to economic or technical feasibility. (<u>http://www.acgih.org/TLV/</u>)