AP42 Section: 11.1

Reference Number: 357

Title: Written communication from R. Nadkarni to Chief, Emission Factor and Methodologies Section, USEPA, Research Triangle Park, NC,

November 7, 1994.

HOT MIX INC.
P.O. BOX 154
Center Rutland VT 05736
Ph: 802-293-5243 / 802-438-5454

-Sold To-
Wilk Paving

-Ship To-
T OF FAIRHAVEN

T # 3321

Date 10/25/05

Time 13:19:15

Type Batched

P. O. #	
Truck ID	W134
Job ID	95119
Customer ID	WILK
Material ID	806

Pounds	-	Tons
36211	Gross	18.10
0	Tare	0.00
36211	Net	18.10

Loads & Tons Today	Loads & Tons To Date
19 345.82 806	240 4313.80 206
	1 18.25 103
	19 345.82 806

Unit $

Net $
Local $
State $
Haul $ 0.00

Total $

Original Ticket

Arrive: ________ Weigh
Depart: ________ Master: TODD WIGGL

Recv.
By: ____________________

HOT MIX INC.
P.O. BOX 154
Center Rutland VT 05736
Ph: 802-293-5243 / 802-438-5454

-Sold To-
Wilk Paving

-Ship To-
T OF FAIRHAVEN

3320

Date 10/25/95

Time 13:25:49

Type Batched

P.O. #	
Truck ID	W77
Job ID	95119
Customer ID	WILK
Material ID	806

Pounds		Tons
35880	Gross	17.94
0	Tare	0.00
35880	Net	17.94

Loads & Tons Today	Loads & Tons To Date
20 363.76 806	240 4213.60 206
	1 18.05 103
	10 152.71 806

Unit $	
Net $	
Local $	
State $	
Haul $	0.00
Total $	

Original Ticket

Arrived: ______ Weigh
Depart: ______ Master: [illegible]

Recv.
By: ____________________

HOT MIX INC.
P.O. BOX 154
Center Rutland VT 05736

Ph: 802-293-5243 / 802-438-5454

Bill To	Ship To	
WILK HAULING	T OF FAIRHAVEN	T # 3323
		Date 10/25/05
		Time 13:39:13
		Type Batched

P. O. #	
Truck ID	#189
Job ID	95119
Customer ID	WILK
Material ID	006

Pounds	-	Tons
36186	Gross	18.09
0	Tare	0.00
36186	Net	18.09

Loads & Tons Today	Loads & Tons To Date
21 381.55 006	240 4313.60 006
	1 18.05 103
	21 381.55 006

Unit $	
Net $	
Local $	
State $	
Haul $	2.00
Total $	

Original Ticket

Arrival: ______ Weigh
Depart: ______ Master: TODD WIDLI

Rec'd
By ______

HOT MIX INC.
P.O. BOX 154
Center Rutland VT 05736
Ph: 802-293-5243 / 802-438-5454

-Sold To-	-Ship To-	
Wilk Paving	T OF FAIRHAVEN	O # 3264
		Date 10/25/95
		Time 13:44:28
		Type Batched

P. O. #	
Truck ID	W131
Job ID	95119
Customer ID	WILK
Material ID	806

Pounds	-	Tons
43846	Gross	21.92
0	Tare	0.00
43846	Net	21.92

Loads & Tons . Today	Loads & Tons To Date
22 402.77 806	240 4313.50 206
	1 18.25 123
	22 402.77 806

Unit $	
Net $	
Local $	
State $	
Haul $	0.00
Total $	

Original Flower

Driver: ______ Weigh
Depart: ______ Master: TODD WILC(

Rec'd
By: ______

HOT MIX INC.
P.O. BOX 154
Center Rutland VT 05736
Ph: 802-293-5243 / 802-430-5454

END RUN 2

Sold To
Wilk Paving

Ship To
HOT MIX INC

No. 3028

Date 10/25/92

Time 10:50 AM

Type Batched

P.O. #	
Truck ID	W1-I
Job ID	10000
Customer ID	WILK
Material ID	806

Pounds		Tons
35580	Gross	17.79
0	Tare	0.00
35580	Net	17.79

Loads & Tons Today	Loads & Tons To Date
1 17.79 806	4 82.48 103
	1 17.79 806

Unit $	
Net $	
Local $	
State $	
Haul $	0.00
Total $	

Original Ticket

Hauled ___ Weigh
Operator: ___ Master: TODD NICKL

Rec'd
By:___

HOT MIX INC.
P.O. BOX 154
Center Rutland VT 05736
Ph: 802-293-5243 / 802-438-5454

START
RUN3

-Sold To-
Wilk Paving

-Ship To-
T OF FAIRHAVEN

Q # 3020

Date 10/25/95

Time 15:54:56

Type Batched

P. O. #	
Truck ID	W152
Job ID	95119
Customer ID	WILK
Material ID	806

Pounds		Tons
36061	Gross	18.03
0	Tare	0.00
36061	Net	18.03

Loads & Tons Today	Loads & Tons To Date
24 433.73 806	240 4312.80 206
	1 18.05 103
	24 433.73 806

Unit $	
Net $	
Local $	
State $	
Haul $	0.00
Total $	

Original Ticket

Driver ______ Weigh
Deputy ______ Master: TODD WIDLI

Rec'd.
By: ______

HOT MIX INC.
P.O. BOX 154
Center Rutland VT 05736
Ph: 802-293-5243 / 802-438-5454

-Sold To-	-Ship To-	
Wilk Paving	T OF FAIRHAVEN	T # 3020
		Date 10/25/95
		Time 16:01:10
		Type Batched

L. O. W	
Truck ID	W118
Job ID	95119
Customer ID	WILK
Material ID	806

Pounds		Tons
35978	Gross	17.99
0	Tare	0.00
35978	Net	17.99

Loads & Tons Today	Loads & Tons To Date
25 457.77 806	240 4313.60 806
	1 19.05 103
	25 457.77 806

Unit $	
Net $	
Local $	
State $	
Haul $	0.00
Total $	

Original Ticket

Arrived: ______ Weigh.
Depart: ______ Master: TODD WIDLI

Rec'd.
By: ______

Sec. 11.1
Ref. 357

November 7, 1994

Chief, Emission Factor and Methodologies Section
MD-14
USEPA
Research Triangle Park, NC 27711

Dear Sir/Madam:

I am writing this letter in accordance to the draft Public Participation Procedures for EPA's Emissions Estimation Guidance Materials. This Draft, dated 5/9/94, was provided by Mr. Bob McConnell of EPA Region I. I have formatted the information below in accordance with the instructions in Appendix A of that document.

1. **Submitter's Name, Mailing Address and Phone:**

Ravindra M. Nadkarni
340, Franklin Street
Wrentham MA 03093

Work (AM) (508) 699-8800 x 200
Home (PM) (508) 384-7889

2. **Contact Name, Address and Phone:**

Same as above

3. **AP-42 Section, Guidance Document or Database affected:**

This information will supplement material already in Chapter 11 of the latest version of AP-42.

4. **Description of emission source affected:**

These calculations quantify fugitive emissions from asphalt-concrete hot mix plants. These emissions, which are indicated qualitatively in Figures 11.1 - 1 through 11.1 - 3 in EPA's latest version of AP-42, Chapter 11, are quantified in this calculation. The estimate of fugitive VOCs covers two steps: a) fugitive VOCs that are emitted during the loading of the truck and b) fugitive VOCs that are emitted as the truck drives around the plant before it is covered. While the base calculations are for a batch plant, where the truck waits at the loadout station for several batches before it is full, the calculation has also been modified to fit other plants where the loadout is faster because of the use of insulated hot silos to store the hot mix.

SIC Code is SIC 2951, **Asphalt paving and roofing materials and blocks.**

5. **Estimated number of facilities affected:**

Based on AP-42, approximately 3,600 facilities will be affected. Of these, about 2,300 are batch plants (the source of the highest fugitive emissions), 1,000 are parallel flow plants (most with hot storage silos) and about 300 are counter-flow drum mix plants (also with hot storage silos).

6. **Estimated total emissions affected:**

For a batch plant, the calculated emission factor is .8854 lb VOC/ton of product. If the average annual output of a batch plant is 670,000 tons, the annual emissions are 593 tons.

For a plant with a hot storage silo, where loadout is more rapid, the calculated emission factor is .3795 lb VOC/ton of product. If the average annual output of the plant is 900,000 tons a year, the annual emissions would be 342 tons.

7. **Description of proposed addition:**

This is an *estimation technique* for a source that has been flagged as a source of fugitives by the EPA in AP-42, but has not been quantified as yet. As the enclosed photographs (Exhibit B) show, the loadout of the hot mix into a waiting truck emits copious quantities of VOCs. My visual observation was that these emissions appeared to exceed the stack emissions, which were controlled with a fabric filter. The Massachusetts Department of Environmental Protection appeared to focus strictly on stack emissions for air permitting and was ignoring the fugitive emissions even after the enclosed photographs were submitted to them.

8. **New or marked-up text of proposed revision to AP-42:**

Enclosed as Exhibit D.

9. **Brief description of the type and source of data or analysis request:**

The uncontrolled fugitive emissions of VOC have been estimated using mass transfer equations for the flow of air past a plate (upper surface of a loaded truck). The key numbers which affect the results are a) the vapor pressure of material sold as asphalt to a hot mix plant, b) the loadout temperature, c) the period of time that the hot mix is sitting uncovered in the truck.

This is not a revision to an existing factor but the quantification of emissions that are known to the EPA but have not been, to the best of my knowledge, estimated thus far.

10. **Estimate of the range of uncertainty of the estimation technique:**

The range of uncertainty is about ± 30%.

11. **Effect of the proposed change on your facility:**

I am not an operator of a hot mix asphalt plant but am a technically trained person who has been studying emissions from such plants for about 6 months. The proposed change in emissions factors will require the industry to control this major VOC source. Equipment for such control is available, and is not prohibitively expensive. At the state level, because these fugitives are not quantified, they are ignored. In Massachusetts, the DEP has accepted a) a zero value for fugitive VOCs in one application and b) a figure of 1 ton/year for fugitives (estimated as 10% of VOCs in the stack) in another application. The BACT analyses associated with both these applications were inconsistent. EPA's adoption of these factors will force states to pay attention to these large emissions and require control whenever appropriate.

My qualifications for performing calculations presented here are in Exhibit C. Also included are comments of two reviewers, who provided a peer review of these calculations.

12. **Any significant issues associated with the request:**

none

13. **All data and analyses necessary to support the request:**

These are presented in the attached Exhibit A.

14. **Test data:**

No test data are available. Some field sampling would be very helpful in narrowing the range of uncertainty. Field sampling of fugitive is always tricky, because of the problem of sampling in an open air space. In this case, given the variable nature of asphalt, with different amounts of light ends blended in at a terminal, one would have to be even more careful to make sure that the measurements are representative of actual asphalt that is shipped by a terminal operator and not the asphalt that is a true vacuum bottoms that might be produced by a large integrated refinery.

Please call me if you have any questions.

Sincerely,

RMNadkarni

Ravindra M. Nadkarni, P.E.

cc: Bob McConnell, EPA Region I

Exhibit A

Fugitive VOC emissions from hot asphalt

1. Calculation of fugitive emissions of VOC

Visual observation of a truck being loaded at any asphalt plant indicates that there is a large cloud of polynuclear aromatic hydrocarbons (PAHs) released as the hot asphalt is dropped into a truck. (See enclosed photos in Exhibit B taken in mid-August 1994 at a Massachusetts batch plant). At a batch plant, a truck requires more than one dump until it is full. Typically, each batch takes a minute and the truck waits under the hopper until it is full. At a plant with hot storage silos, the filling of a truck is more rapid but the other factors are the same. The hot asphalt in the truck continues to emit visible VOCs, which are mainly polynuclear aromatic hydrocarbons (PAHs), as the truck moves towards the weighing station. The truck is covered with a tarpaulin after it has been weighed and after the driver has completed the paperwork. The tarpaulin cover reduces the PAH emissions, but does not eliminate them. Visual observations indicate that the cloud of vapors released during hot asphalt loading is larger than the cloud released from the truck. This is because there is a more intimate mixing of the air and the loose hot asphalt as it drops through the air into the truck. However, this calculation only attempts to directly quantify the latter by assuming that the top surface of the hot asphalt on a truck is a simple rectangular plate of hot asphalt, and by using standard mass transfer equations applicable for this case. The emissions during loadout have been estimated by using a "correction factor" which is greater than 1 to adjust for the higher emissions rate as the asphalt is falling into the truck.

Trucks used in this service would have an active length of 35 ft or 1,067 cm. and width of 8.5 ft. Assume that the relative velocity between the wind and the truck (caused by truck motion and/or movement of the wind) is 5 mph or 224 cm/sec.

We use equations for mass transfer from a flat plate (the top of the loaded truck) as a fluid (air) flows over it in a direction parallel to the plate, with a negligible pressure gradient. These conditions would be satisfied when a truck moves forward after it is loaded. The book **Mass Transfer**[1] suggests the use of the following equation for calculating the average mass transfer coefficient:

$$[(k_c)_{av} X_T/D] = .037\mathrm{Sc}^{1/3}[\mathrm{Re}_T{}^{0.8} - 15,500] \qquad (1)$$

where:

---

[1] Sherwood, Pigford, Wilke, **Mass Transfer**, McGraw Hill, 1975.

$(k_c)_{av}$ = average mass transfer coefficient = $N/(c_T - c_0)$
X_T = total length of the plate in cm. = 1067 cm.
D = diffusion coefficient in cm^2/sec = .093 (air - hexane)
Sc = Schmidt number: $\mu/\rho D$ = 1.81
Re_T = Reynolds number based on length of plate: $U_0 X_T \rho/\mu = 1.4\ 10^6$
μ = viscosity of air in poise = $1.9 10^{-4}$ poise
U_0 = velocity of air flowing past the plate in cm/sec = 224 cm/sec
ρ = density of air in g/cc = 0.00113 g/cc
N = flux density - g-moles/sec-cm^2
c_T = concentration of "VOC" species in g moles/cc = $^p/RT$
R = gas constant = 82.07
T = air temperature in degrees K
^{p} = partial pressure of volatiles in atm = 30/760 = 0.04
c_0 = concentration at leading edge = 0

Substituting the appropriate values in equation 1 gives the average mass transfer coefficient to be 0.27. Since the mass transfer coefficient equals $N/(c_T - c_0)$, the flux is c_T times the average mass transfer coefficient. This concentration is $1.6\ 10^{-6}$, resulting in a flux of $4.3\ 10^{-7}$ g moles/sec-cm^2. Since the truck is 8.5 ft wide, the total area is $2.76\ 10^5$ sq cm. If the molecular weight of the volatiles is assumed to be based on anthracene, $C_{14}H_{10}$, the grams of volatiles emitted per second are 21.1 grams per sec.

At the peak capacity of 400 tons per hour of asphalt, there will be over 18 trucks loaded during each hour. If each loaded truck is uncovered for 3 minutes, the emissions per hour are 252.8 lb. This number is more representative of plants with hot storage silos.

For batch plants, the loading of a truck takes longer since the truck has to wait for about a minute for the mixing of each batch. The emissions are correspondingly higher.

2. Discussion

Photographs (see Exhibit B) and visual observation at any asphalt plant show that there will be dense clouds of VOCs during truck load-out and from truck movements within the plant boundaries. This happens while the stack (which emits dryer exhaust after dust removal in a baghouse) is clear. This photographic evidence clearly indicates that fugitive emissions exceed stack emissions.

A. Estimation of vapor pressure: The key number in equation 1 is the vapor pressure of asphalt at the operating temperature of around 300 degrees F. Since actual emission measurements are not available, these emissions have to be estimated from other information.

I have used four approaches for estimating vapor pressures or emissions. These four approaches give reasonably consistent results.

1. Model compounds: The first approach was to use model compounds as proxies for the species present in the vapor to estimate the vapor pressure. Since asphalt is a mixture of various hydrocarbon compounds, such model compounds should either have the same range of initial melting points and boiling points as asphalt and/or be known to be present in asphalt. Typical model compounds might include the light aromatic compounds such as benzene, toluene, and xylene as well as complex polynuclear aromatics such as anthracene, methyl benzene, phenanthrene, naphthalene, triethyl benzene and methyl anthracene. These compounds have boiling points in the correct range and are either expected to be present or have been found in on a list of asphalt plant emissions such as the list from Environmental Research Foundation, in EPA's AP-42 or in research papers on volatiles in asphalt. Since asphalt is kept hot, it is also possible that some cracking takes place increasing the concentration (and subsequent release) of the light ends.

Based on the Clausius-Clayperon equation, we would expect a straight line relationship between log(vapor pressure) and 1/T where T is the absolute temperature. This is plotted in the attached Figure 1 for several compounds, based on data on pages 6-69 to 6-87 of the Handbook of Chemistry and Physics, 74th Edition, CRC Press, 1993.

The figure indicates that at 190 degrees C, the vapor pressure of asphalt will be in the range of 20 to 40 mm of mercury. If the loadout temperature is lower, for example around 150 to 160 degrees C, the vapor pressure would be lower. We have used the value of 30 mm. mercury for the vapor pressure. (This value is supported by method 2).

According to Raoult's Law, vapor pressure should be proportional to the mole fraction of the substance. Since the molecular weight of the light material is at least one order of magnitude lower than that of the heavy fraction, the mole fraction of the light end should be high, close to 1. Thus, the Raoult's law effect can be ignored.

2. Extrapolation of Room Temperature Information in Material Safety Data Sheets: The second approach was to use the limited data in Material Safety Data Sheets to corroborate the estimates based on model compounds. There is information in Material Safety Data Sheets from two refiners which gives a vapor pressure limit at room temperature. Figures 2a and 2b say that the vapor pressure is "<.0001 mm. Hg @ 20 deg C"or at 15 deg C..

An engineer at one of the large integrated oil refineries was kind enough to send me a graph from the American Petroleum Institute's "Technical Data Book" - Petroleum Refining, Vol 1, Fifth Edition, May 1992. I have used the room temperature vapor pressure in the MSDS (Figure 2) and the graph from API (Figure 3) to estimate the vapor pressure at 300 degrees F. Using the vapor pressure at room temperature as a data point, I have drawn three lines A, B, C on the graph of Figure 3 to find the vapor pressure at 300^0 F. These three lines were drawn parallel to the lines for different possible boiling points of the liquid and correspond to boiling points of 700 F, 800 F and 900 F. The MSDS information indicates that initial boiling point for asphalt is 900 F (Figure 2a) or above 800 F (Figure 2b). While the intersection of lines A, B and C with the 300 degree F line is from an extrapolated section of the graph, such extrapolation is justified since the graph contains straight lines on the semi-log scale. Since the vertical scale of the graph is in atmospheres, the results have to be converted into mm. Hg.

The results show that the vapor pressure at 300 F will be in the range from **14 mm Hg.** (for the 700 F line) **to 180 mm.** Hg (for the 900 F line). **The mid-point result for a boiling point of 800 deg F is 50 mm. Hg.** These results are about the same, or somewhat higher, than those produced by the earlier calculation, which gave a mid-point value of 30 mm. Hg for a slightly higher temperature.

The fact that these two methods (model compound method and the extrapolation of room temperature data to 300 F) end up with vapor pressures in the same range supports the earlier comment that Raoult's law effects can be ignored.

3. The use of lower explosive limit data: The Handbook of Chemistry and Physics, 74th Edition, CRC Press, 1993, presents data on the lower explosive limit for a wide variety of hydrocarbons on page 15-43. It indicates that this lower explosive limit is at 1% by volume for typical hydrocarbons. This table also gives the flash points for the same hydrocarbons. Since the flash point is the lowest temperature at which the vapors will sustain a flame or explode, it is reasonable to assume that when the hydrocarbon reaches the temperature of the flash point, its vapor pressure equals the lower explosive limit. This hypothesis can be tested for several pure compounds such as benzene where data on the variation in vapor pressure with temperature and the flash point temperature is available. (pages 6-69 to 6-87.). These tests show that the hypothesis is reasonable. (The fit might have been better if the lower explosive limit had been measured and published more precisely to the second significant figure). This method would indicate a vapor pressure of asphalt to be 7.6 mm. mercury at 450 degrees F, the flash point according to Figure 2a.

The result above is at the lower limit of the range indicated by more direct methods. However, this finding is also explained by the discussion in the MSDS attached as Figure 4. Under "HOT ASPHALT FLASH WARNING" it states that "Such vapors may exhibit flammability characteristics of a significantly lower flash product than would be indicated by the open cup flash test." This means that the Cleveland Open Cup (COC) test overstates the flash point temperature. If the flash point is adjusted downwards by 50 to 75 degrees F, that data is also reconciled with the vapor pressure results calculated by more direct methods. Such an adjustment would be consistent with the warning in the MSDS of Figure 4.

I was also able to get an explanation for this phenomenon from an oil company engineer who spoke only on the promise of anonymity. He stated that while the MSDS data might be based on an "ideal" product from the refinery, actual asphalt that is shipped will be blended with kerosene or naphtha to control viscosity and other physical characteristics at the terminal. This means that the vapor pressure of these blends is higher. This explains both the high vapor emissions observed at the asphalt plants as well as the warning in the MSDS.

Finally, it has to be remembered that asphalt is a product of vacuum distillation. The refining industry uses vacuum distillation in order to lower the boiling point of the liquid so that the various fractions can be separated with minimum thermal cracking. When hot asphalt is stored for a long time under atmospheric pressure or when it is sprayed on hot aggregate, chances are high that this thermal cracking takes place, releasing the volatile light ends as a byproduct. Thus, thermal cracking will also increase vapor pressure.

4. Direct estimation of emissions based on volume of vapor: It is possible to estimate the emissions directly based on the volume of vapor. The abstract of a paper by E.S. Hansen[2] indicates that when worker exposure to asphalt fumes was measured with personal samplers, the values ranged from 0.5 to 260 mg/m^3. We can use the figure of 260 mg/m^3 for fume concentration and use photographs of asphalt plant emissions to estimate the volume of the VOC cloud. The photos show that the volume of the cloud is about 510 m^3 so that the emissions for each loadout are 133 grams or 0.3 lb. This number has to be increased to account for the emissions during truck travel and during the period while the truck is waiting for additional loads. We will use a factor of 2.5 for this purpose. Therefore, the total emissions are .75 lb per 5 ton load. With an annual output of 670,000 tons, this results in emissions of slightly over 50 tons per year. This number is at the lower limit of the range estimated by equation 1. It is possible that when the fumes were very dense, the workers stepped away from the cloud so that the personal sampler measurements have a low bias.

To conclude, the various techniques used to estimate vapor pressure fully support the use of value of 30 mm. Hg that was used in equation 1 to estimate fugitive emissions.

Sensitivity Analysis

The total tons of VOCs emitted per year from the asphalt plant are proportional to several factors used in the mass transfer calculations. Specifically, the emissions are proportional to vapor pressure (itself a function of temperature), and the time that is spent from the load-out of the asphalt until the truck is weighed and covered.

> Cycle time: The base calculation assumed that the truck was uncovered for 3 minutes. The sensitivity analysis covers the range from 5 to 11 minutes.
>
> For a plant with hot silos, a cycle time of 3 minutes was used to calculate the emission factor. For a batch plant, a cycle time of 7 minutes was used to calculate the emission factor.

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[2] E.S. Hansen, "Cancer Incidence in an Occupational Cohort Exposed to Bitumen Fumes", **Scandinavian Journal of Work, Environment and Health**, Vol 15, No 2, (1989) pp 101 - 105.

Vapor Pressure: Since the MSDS uses the "<" symbol, one can consider that the value in the MSDS is a "not to exceed" value. In that case, we can assume that the vapor pressure could be even lower by one order of magnitude, i.e. 3 mm. of Hg. (The discussion in the previous section indicates that this is more of a theoretical issue since the blending of light ends such as kerosene and naphtha and/or cracking will increase vapor pressure, not lower it.)

Correction for emissions during load-out vs. emissions during truck travel: Visual observations show that the emissions during loadout are much higher than they are during the period that the truck is moving towards the weigh station. The mass transfer equation estimates the emissions only during the latter process. An easy way to correct for this is to use a correction factor, based on visual observation, to estimate the extra emissions during loadout. In the sensitivity analysis, this correction factor has been varied from 1 (no correction) to 2.

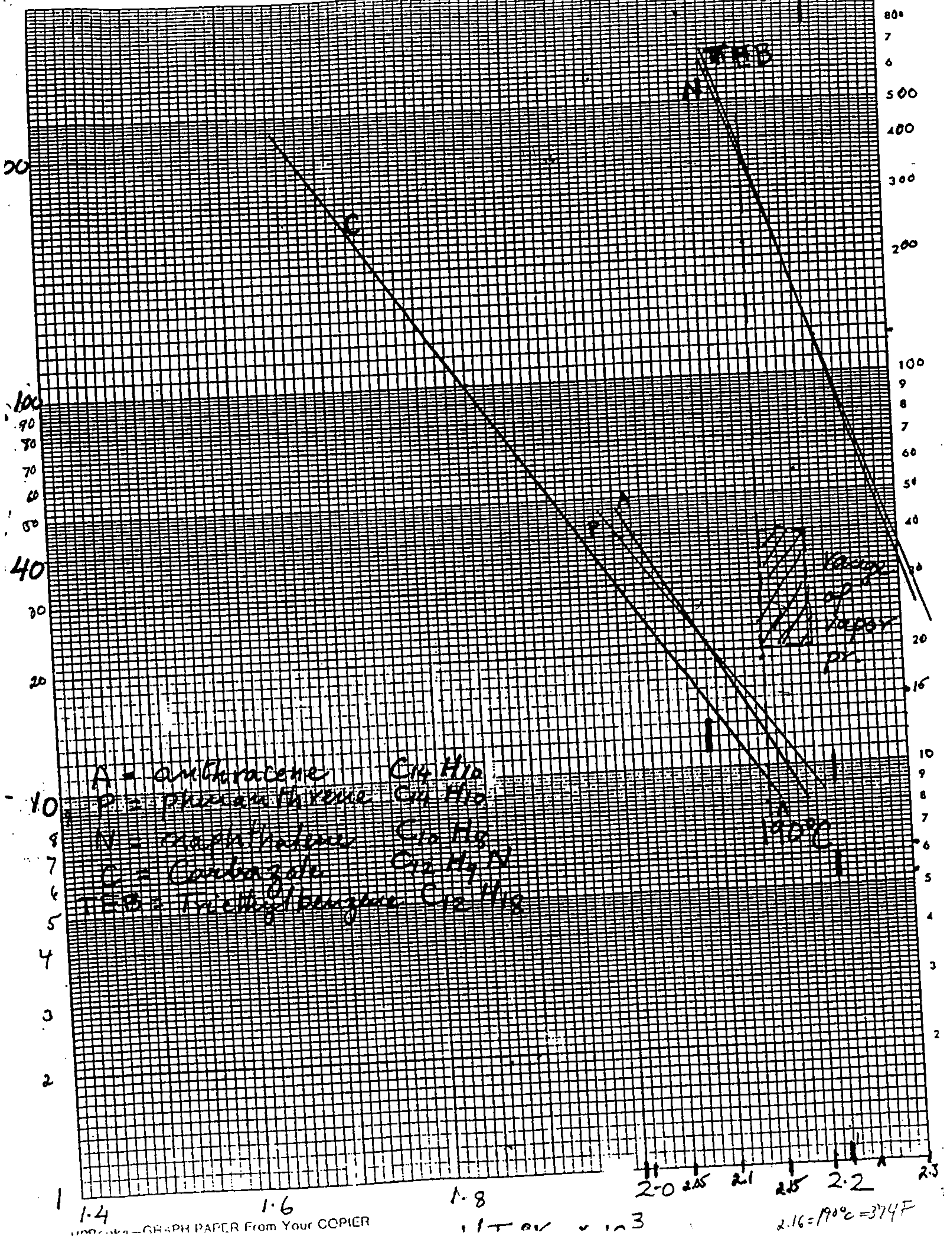
The results of the sensitivity analysis are shown in the Table 1. The sensitivity analysis shows that the range of these ground level emissions is of the order of 100 to 600 tons. While these appear to be enormous numbers, they should be compared to the plant throughput. With a plant output of 670,000 tons, and with the asphalt being about 8% of this amount, the annual throughput of asphalt is about 54,000 tons. This means that these emissions are 0.2 to 1.1% of the total asphalt that is used each year. The boiling off of this small quantity of light ends from a mixture is not unreasonable from a process standpoint. The issue is the environmental impacts of these emissions.

Table 1: ***Sensitivity Analysis***

Type of Option	Vapor pressure (mm. Hg)	Time for load out (minutes)	Time correction factor	Annual emissions (tons)
Base case: hot silo loadout	30	3	1	127
Fast loadout in a batch plant	30	5	1.5	318
Slow loadout in a batch plant	30	11	1.5	699
No time correction factor	30	6	1	254
High time correction factor	30	6	2	508
low vapor pressure (a)	4	6	1.5	68
low vapor pressure (b)	3	6	1.5	38

90 Divisions (2 millimeters) 5th, 10th Accent by 3 Cycle Semi-Log

Figure 1



GRAPH PAPER From Your COPIER

Figure 2a

2.0 Physical Data

Physical Hazard Classification (Per 29 CFR Part 1910.1200)

No	Combustible	No	Flammable	No	Pyrophoric
No	Compressed Gas	No	Organic Peroxide	No	Reactivity
No	Explosive	No	Oxidizer	Yes	Stable

Boiling Point, 760 mmHg, °C(°F): 482 (900) *
Specific Gravity (60/60°F) (H_2O=1): 1.0-1.2
Vapor Density (Air=1): >1
% Volatiles by Volume: None
Melting Point, °C(°F): ND
Vapor Pressure, mmHg (15°C): <0.0001
Solubility in H_2O, % by Weight: Insoluble
Evaporation Rate (Butyl Acetate=1): NA
pH of Undiluted Product: NA
Molecular Wt.: >2000 *
Appearance and Odor: Black solid or viscous liquid; tar-like or heavy hydrocarbon odor

3.0 Fire and Explosion Data

Flash Point, COC, °C(°F)	>232 (>450)
Flash Point, PM, °C(°F)	ND
Fire Point, COC, °C(°F)	ND
NFPA Rating[2]	Health: 1 Flammability: 1 Reactivity: 0
Flammable Limits (% by volume in air)	Lower: NA Upper: NA
Extinguishing Media	CO_2, dry chemical.
Special Fire Fighting Procedure	Wear self-contained breathing apparatus when in a confined area. Avoid inhalation of fumes. Water or foam may cause frothing.
Unusual Fire or Explosion Hazard	Under some conditions, sulfur compounds in hot asphalt may evolve hydrogen sulfide. This is a colorless gas. At low air concentrations the odor resembles decaying eggs. At higher concentrations, odor fatigue may occur, resulting in life-threatening inhalation hazard.

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[2] Hazard Rating: least-0; slight-1; moderate-2; high-3; extreme-4
CITGO assignment based on our evaluation per NFPA guidelines.

Figure 26 (cont.)

EXPOSURE CONTROL / PERSONAL PROTECTION

CONSULT WITH A HEALTH/SAFETY PROFESSIONAL FOR SPECIFIC SELECTION.

VENTILATION

USE ONLY WITH ADEQUATE VENTILATION. VENTILATE AS NEEDED TO COMPLY WITH EXPOSURE LIMIT. MECHANICAL VENTILATION RECOMMENDED. SEE SECTION 16 FOR ADDITIONAL INFORMATION.

PERSONAL PROTECTIVE EQUIPMENT

EYE

SPLASH PROOF CHEMICAL GOGGLES OR FULL FACE SHIELD RECOMMENDED TO PROTECT AGAINST SPLASH OF HOT PRODUCT. SEE SECTION 16 FOR ADDITIONAL INFORMATION.

GLOVES

PROTECTIVE GLOVES RECOMMENDED TO PROTECT AGAINST CONTACT WITH HOT PRODUCT. THE FOLLOWING GLOVE MATERIALS ARE ACCEPTABLE: INSULATED POLYVINYL CHLORIDE; INSULATED NITRILE;

RESPIRATOR

CONCENTRATION-IN-AIR DETERMINES PROTECTION NEEDED. USE ONLY NIOSH CERTIFIED RESPIRATORY PROTECTION. RESPIRATORY PROTECTION USUALLY NOT NEEDED UNLESS PRODUCT IS HEATED OR MISTED. IF HYDROGEN SULFIDE IS PRESENT FULL-FACE SUPPLIED AIR RESPIRATOR WITH ESCAPE BOTTLE OR SCBA IS REQUIRED. HALF-MASK AIR PURIFYING RESPIRATOR WITH ORGANIC VAPOR CARTRIDGES IS ACCEPTABLE TO 10 TIMES THE EXPOSURE LIMIT. FULL-FACE AIR PURIFYING RESPIRATOR WITH ORGANIC VAPOR CARTRIDGES IS ACCEPTABLE TO 50 TIMES THE EXPOSURE LIMIT NOT TO EXCEED THE CARTRIDGE LIMIT OF 1000 PPM. PROTECTION BY AIR PURIFYING RESPIRATORS IS LIMITED. USE A POSITIVE PRESSURE-DEMAND FULL-FACE SUPPLIED AIR RESPIRATOR OR SCBA FOR EXPOSURES ABOVE 50X THE EXPOSURE LIMIT. IF EXPOSURE IS ABOVE IDLH(IMMEDIATELY DANGEROUS TO LIFE & HEALTH) OR THERE IS THE POSSIBILITY OF AN UNCONTROLLED RELEASE OR EXPOSURE LEVELS ARE UNKNOWN THEN USE A POSITIVE PRESSURE-DEMAND FULL-FACE SUPPLIED AIR RESPIRATOR WITH ESCAPE BOTTLE OR SCBA. SEE SECTION 16 FOR ADDITIONAL INFORMATION.

OTHER

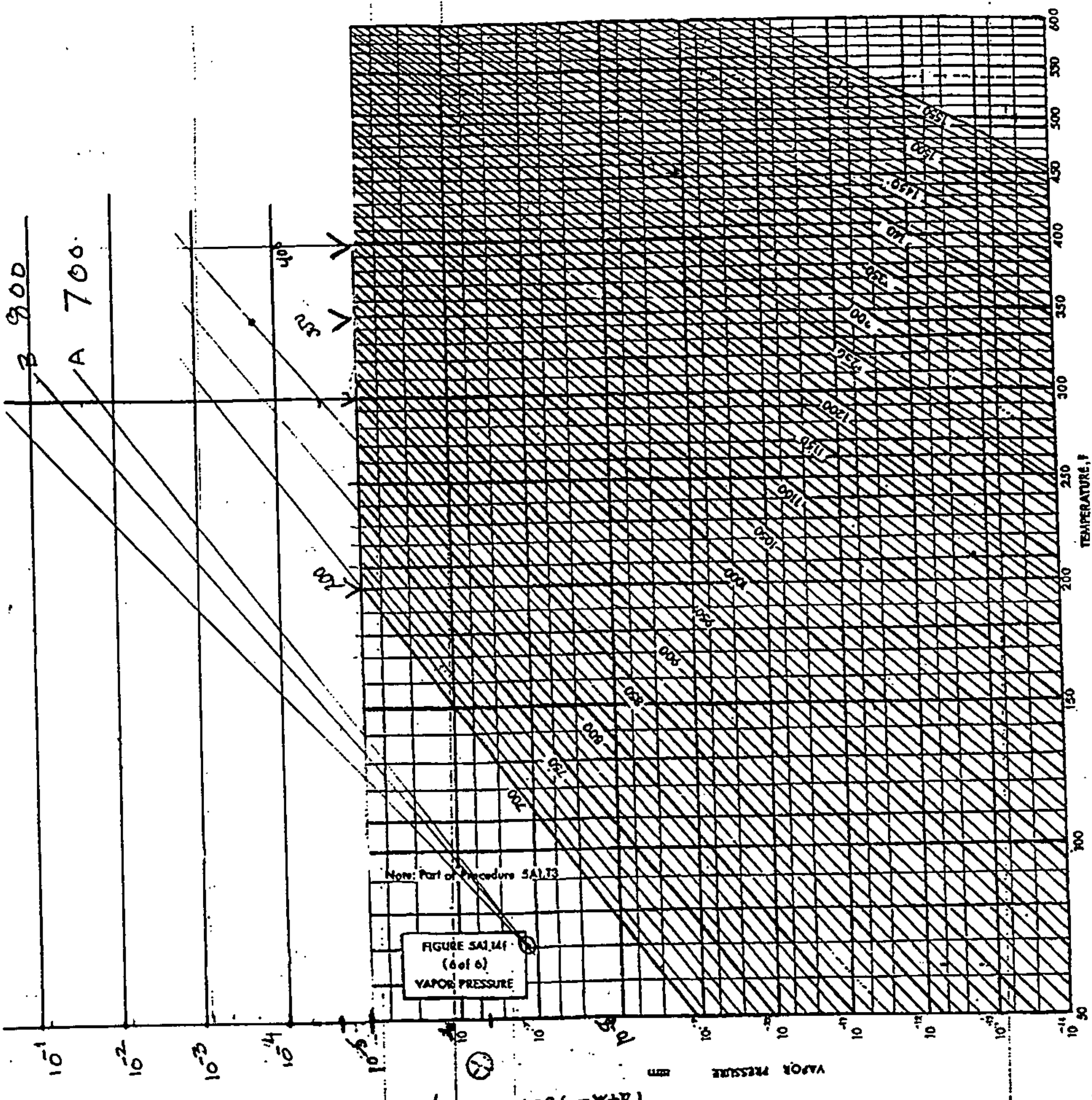
AVOID ALL SKIN CONTACT. AS NEEDED TO PROTECT AGAINST SPLASH OF HOT PRODUCT. THE FOLLOWING MATERIALS ARE ACCEPTABLE AS PROTECTIVE CLOTHING MATERIALS: POLYVINYL ALCOHOL(PVA); POLYVINYL CHLORIDE(PVC); NEOPRENE; NITRILE; VITON; POLYURETHANE; SAFETY SHOWER AND EYE WASH AVAILABILITY RECOMMENDED. LAUNDER SOILED CLOTHES. FOR NON-FIRE EMERGENCIES, POSITIVE PRESSURE SELF-CONTAINED BREATHING APPARATUS (SCBA) & STRUCTURAL FIREFIGHTERS' PROTECTIVE CLOTHING WILL PROVIDE LIMITED PROTECTION. SEE SECTION 16 FOR ADDITIONAL INFORMATION.

PHYSICAL AND CHEMICAL PROPERTIES

BOILING POINT.......: > 800 (DEG. F) ____ > 426 (DEG. C)
MELTING POINT.......: 125 - 150 (DEG. F) ____ 52 - 66 (DEG. C)
SPECIFIC GRAVITY....: 1.04 (WATER=1)
PACKING DENSITY.....: 1000 (KG/M3)
VAPOR PRESSURE......: < 0.0001 (MM HG @ 20 DEG C)
VAPOR DENSITY.......: 10+ (AIR=1)
SOLUBILITY IN WATER.: NIL (% BY VOLUME)
PH INFORMATION......: N/A AT CONC. N.D. G/L H2O
% VOLATILES BY VOL..: NIL
EVAPORATION RATE....: NIL (ETHYL ETHER=1)
OCTANOL/WATER COEFF.: N.D.
APPEARANCE..........: BLACK SEMI-SOLID
ODOR................: ASPHALT-LIKE ODOR
ODOR THRESHOLD......: N.D. (PPM)
VISCOSITY...........: N.D. SUS @ N.D DEG F ... N.D. CST @ N.D DEG C
MOLECULAR WEIGHT....: N.D. (G/MOLE)

= NOT APPLICABLE N.D. = NO DATA / NOT DETERMINED

Figure 3



Note: Part of Procedure 5A1.13

FIGURE 5A1.14f
(6 of 6)
VAPOR PRESSURE

Figure 4

f skin is contacted with hot asphalt, thermal burns will result. In this case, the contaminated rea should be treated similarly to other thermal burns by cooling the affected area immediately ith coolest available water. It is not usually advisable to immediately remove the asphalt aterial. Natural separation will occur in 48-72 hours. Removal should be attempted only under he direction of a physician. If removal is attempted, mineral oil (not mineral spirits) or ineral oil ointment may be applied to soften the asphalt to facilitate removal.

HALATION
f overcome by H2S, immediately remove to fresh air and call a physician. If breathing is rregular or has stopped, start resuscitation, administer oxygen, if available.

GESTION
If ingested, DO NOT induce vomiting; call a physician immediately.

D. FIRE AND EXPLOSION HAZARD INFORMATION

LASH POINT (MINIMUM)	AUTOIGNITION TEMPERATURE
232°C (450°F) ASTM D 92, Cleveland Open Cup	Greater than 260°C (500°F)

ATIONAL FIRE PROTECTION ASSOCIATION (NFPA) - HAZARD IDENTIFICATION

Health	Flammability	Reactivity	BASIS
0	1	0	Recommended by the National Fire Protection Association

ANDLING PRECAUTIONS
Use product with caution around heat, sparks, pilot lights, static electricity, and open flame.

LAMMABLE OR EXPLOSIVE LIMITS (APPROXIMATE PERCENT BY VOLUME IN AIR)
Estimated values: Lower Flammable Limit 0.9% Upper Flammable Limit 7%

OT ASPHALT FLASH WARNING
Studies have shown that relatively low flash point substances, such as hydrogen sulfide and low-boiling hydrocarbons, may accumulate in the vapor space of hot asphalt tanks and bulk transport compartments. Such vapors may exhibit flammability characteristics of a significantly lower flash product than would be indicated by the open cup flash test. As a precaution, keep ignition sources away from vents and openings, including prevention of accumulation of pyrophoric iron sulfide. Asphalt Institute Publication IS-180 and American Petroleum Institute Publication 852-20230 contain further information and guidance on the safe storage and handling of hot asphalt.

EXTINGUISHING MEDIA AND FIRE FIGHTING PROCEDURES
Foam, water spray (fog), dry chemical, carbon dioxide and vaporizing liquid type extinguishing agents may all be suitable for extinguishing fires involving this type of product, depending on size or potential size of fire and circumstances related to the situation. Plan fire protection and response strategy through consultation with local fire protection authorities or appropriate specialtists.

The following procedures for this type of product are based on the recommendations in the National Fire Protection Association's "Fire Protection Guide on Hazardous Materials", Eighth Edition (1984):

Use water spray, dry chemical, foam, or carbon dioxide to extinguish the fire. Water or foam may cause frothing. Use water to keep fire-exposed containers cool. Water spray may be used to flush spills away from exposures. Minimize breathing of gases, vapor, fumes or decomposition products. Use supplied-air breathing equipment for enclosed or confined spaces or as otherwise needed.

DECOMPOSITION PRODUCTS UNDER FIRE CONDITIONS
Fumes, smoke, carbon monoxide, hydrogen sulfide, sulfur oxides, aldehydes and other decomposition products, in the case of incomplete combustion.

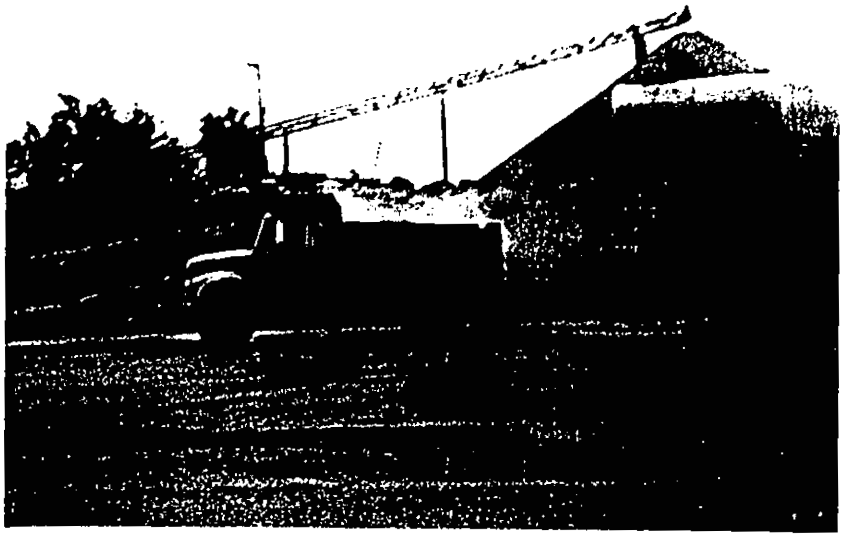
"EMPTY" CONTAINER WARNING
"Empty" containers retain residue (liquid and/or vapor) and can be dangerous. DO NOT PRESSURIZE, CUT, WELD, BRAZE, SOLDER, DRILL, GRIND OR EXPOSE SUCH CONTAINERS TO HEAT, FLAME, SPARKS, STATIC ELECTRICITY, OR OTHER SOURCES OF IGNITION; THEY MAY EXPLODE AND CAUSE INJURY OR DEATH. Do not attempt to clean since residue is difficult to remove. "Empty" drums should be completely drained, properly bunged and promptly returned to a drum reconditioner. All other containers should be disposed of in an environmentally safe manner and in accordance with governmental regulations. For work on tanks refer to Occupational Safety and Health Administration regulations, ANSI Z49.1, and other governmental and industrial references pertaining to cleaning, repairing, welding, or other contemplated

Exhibit 13

Photograph 1 shows a truck receiving its first load of asphalt from the batching tower. (Time zero). You can notice the copious emissions of carcinogenic VOC's. This plant takes about 1 minute to mix a batch so that even a small truck, after receiving the first load, waits under the tower for a minute until the next load is dumped. A small truck like the one in the photograph (6-wheeler) is filled with just 2 dumps. A larger truck, a 10-wheeler or an 18-wheeler, would hold more dumps and would have to wait longer under the batch tower, emitting carcinogenic VOCs during that time.

Photograph 2 shows the truck during this waiting period where the first load continues to emit VOCs. (Elapsed time is about 30 seconds).

Photograph 3 shows the truck just after the second load is dumped. The fumes are very thick again. (Elapsed time is 1 minute to 1 minute 5 seconds).



Photograph 4 shows the truck moving towards the weigh station. The photo shows that the fumes are still coming off the truck but are not as dense as before because the truck is moving and the air is dispersing these VOCs.

The truck then drives to the weigh station and the driver goes inside to complete the paperwork. After he comes out, he covers the loaded truck and drives off. Photograph 5 shows the driver in the process of covering up the loaded truck. There are still significant emissions off the truck. (Total elapsed time 5 to 5.5 minutes).

Photograph 6 shows two important points. In the background, you can see the entire plant. THE PLANT STACK IS CLEAR. Unless you know the plant design, you would not be able to locate the stack based on this picture. YET, THE MASS DEPT. OF ENVIRONMENTAL PROTECTION (DEP) ACCEPTS-- THAT THE VISIBLE FUMES ARE 10% OF THE INVISIBLE STACK EMISSIONS.

In the foreground, the photograph shows a water truck spraying the roadways for dust control.

Exhibit C

Ravi Nadkarni

Dr. Nadkarni has a Ph. D. in Metallurgy with a minor in Ceramic Engineering from the University of Utah. From 1967 to 1983, he was with Arthur D. Little, the well-known international research and consulting firm. During that time, he was involved in a wide spectrum of assignments for private and governmental clients in this country and abroad. His assignments included process development in the chemical and metallurgical industries, technical/economic evaluations in mineral processing, ferrous and non-ferrous metallurgy, market studies for new technology, pollution control, environmental policy, econometric modelling, conversion of coal and biomass to alternate fuel forms and resource recovery from solid wastes. In 1980, he was made Vice President for Energy Technology. From 1981 to 1983, as Vice President, Chemical and Metallurgical Engineering, he managed the technical activities within the company for the process industries, involving a group of about 45 professionals.

In 1983, he joined the Leach & Garner Company as Corporate Vice President for Technology and established a new division for multidisciplinary research in new materials and new processes for the precious metals industry. Subsequently, he was the Vice President and General Manager for Leach & Garner Refining, a major refiner of precious metals, which became Metalor USA Refining Corporation in 1989. He stepped down as General Manager in 1994 but is still associated with Metalor.

Over the years, Dr. Nadkarni has authored/coauthored about 70 professional papers or presentations. These have included subjects such as economic impact of pollution control regulations (work which directly resulted in Section 119 of the Clean Air Act), production of conventional and non-conventional fuels (such as coal liquefaction and ethanol from biomass), statistical process control in chemical analysis, slurry transportation, precious metals processing, strategic materials, metal recycling, resource recovery and so on. He has edited two books and contributed a section on pollution reduction to a handbook on petroleum refining. He holds several patents in the chemical processing and pollution control fields.

Dr. Nadkarni has won several awards for his contributions. These include the Best Paper Award of the Metallurgical Society of AIME and the Application to Practice Award which is given "to recognize outstanding achievement in the transfer of research results or findings in the metallurgical or materials science fields into commercial production and practical use".

Dr. Nadkarni is a member of the Metallurgical Society of AIME, the American Institute of Chemical Engineers, Indian Institute for Metals, Providence Jewelers Club, the Gold Institute, International Precious Metals Institute and the Wrentham Environmental Coalition. He is a Registered Professional Engineer in Massachusetts. He is active as a member of the Board of Directors of the International Precious Metals Institute and serves on two committees on improving science education in the schools.

September 11, 1994

To Whom It May Concern:

I am employed as an environmental chemist at Camp Dresser and McKee Inc. (CDM) in Cambridge, MA. I have a Ph.D. in physical chemistry from Cornell University. Prior to joining CDM, I conducted postdoctoral research in the fields of flue gas control at the U.S. Department of Energy and bioremediation at Cornell University. Two years ago I was involved in a citizen review of a proposed asphalt plant in my neighborhood. Through this review, I have become familiar with the chemistry of asphalt and its production.

I have reviewed the letter dated August 29, 1994 by Ravindra M. Nadkarni, P.E. to Ms. Nancy Baker of the Executive Office of Environmental Affairs concerning Mr. Nadkarni's calculations of ground-level fugitive VOC emissions during truck loading at an asphalt plant. I have also reviewed all attached data and calculations.

Given the paucity of chemical composition and physical chemical data on asphalt, it is very difficult to formulate calculations concerning asphalt production. Nevertheless, I have found Mr. Nadkarni's assumptions and emissions calculations to be well conceived and technically sound. His work is entirely consistent with the small amount of available asphalt data. In particular:

- It is reasonable to expect benzene, toluene, and xylene in hot asphalt.
- The use of model compounds is the only way I know to estimate vapor pressures. The model compounds used are the best choice given what we do know about the hydrocarbon molecular weight range in asphalt.
- The graphical estimation of vapor pressure is technically sound.

If you have any questions on my review comments, please feel free to contact me at (617) 252-8822.

Sincerely,

Michael E. Miller

Michael E. Miller, Ph.D.
Environmental Chemist

DAVID J. KINNEBERG
8 CLAIRE DRIVE
ATTLEBORO, MA 02703

September 13, 1994

To Whom It May Concern:

I have reviewed the calculations of Dr. R.M. Nadkarni, entitled "Exhibit E - Estimation of Fugitive VOC Emissions from Hot Asphalt [Revised August 26, 1994]."

Without question, Dr. Nadkarni is attempting to describe a complicated physico-chemical phenomena - the evaporation of volatile species from a mixture of organic substances during the loading of a haulage truck. To do so, he must resort to simplifying assumptions, particularly regarding the geometry of the system. He chose to assume a flat plate analog for a loaded truck. This assumption, while underestimating overall area available for mass transport and thus underestimating VOC emissions, allows a standard mass transfer correlation to serve as the basis for calculation. His equation E-1 is a well-known and commonly applied correlation of mass transfer coefficients with physical properties. Correlations of this type have been applied with great success for decades in the chemical industry.

Having accepted his approach, the next issue concerns data. In order for Equation E-1 to predict VOC losses, it must be parameterized with the appropriate data. In this regard, Dr. Nadkarni has made conservative choices when data are not available in the open literature. For example, the diffusion coefficient he used applies to room temperature and not the elevated temperatures of hot asphalt. His estimate of the vapor pressure, a difficult parameter to estimate because of the complex nature of asphalt, is best reviewed by a physical chemist familiar with asphalt chemistry.

Inserting the various parameters into Equation E-1 results in an estimate of VOC emissions of about 20 grams per second from a truck 8.5 feet wide by 35 feet long. This can be easily converted into total emissions per year if one knows the average time a truck remains uncovered and the number of truck loads per year.

In conclusion, I concur with Dr. Nadkarni's approach to estimating VOC emissions from hot asphalt. It is a standard technique used with great success by the chemical industry. While I cannot confirm all the parameters used in the mass transfer correlation, his values do not appear unreasonable and in most cases seem conservative.

DAVID J. KINNEBERG
8 CLAIRE DRIVE
ATTLEBORO, MA 02703

Concerning my qualifications for such a review, I hold B.S., M.S. and Ph.D degrees in Metallurgical Engineering from the University of Utah. At the University, I specialized in the mathematical modeling of rate processes and both my Master's thesis and Ph.D. dissertation involved descriptions of kinetic phenomena. I also took several courses specifically dealing with mass transport phenomena and was the teaching assistant for one such course. For the last ten years, I have served in various engineering capacities (most recently as Director of Research and Development) in an industry where estimations of emission rates are critical in complying with State and Federal regulations.

Respectfully,

David J. Kinneberg, Ph.D.

Exhibit D

Table 11.1-5 (English Units).
EMISSION FACTORS FOR DRUM MIX HOT MIX ASPHALT PLANTS[a]

EMISSION FACTOR RATING: D

Process	Filterable PM		Condensible PM			Total PM[b]	
	PM	PM-10[c]	Inorganic	Organic	Total	PM	PM-10
Dryer (gas-fired) (SCC 3-05-002-05)							
Uncontrolled	19[d]	4.3	0.027[e]	0.054[f]	0.081	19	4.4
Venturi scrubber	0.033[g]	ND	ND	0.020[f]	ND	ND	ND
Fabric filter	0.014[h]	0.0045	ND	ND	0.0037[j]	0.018	0.0082
Dryer (oil-fired) (SCC 3-05-002-05)							
Uncontrolled	19[d]	4.3	0.023[e]	0.0026[e]	0.026[e]	19	4.3
Venturi scrubber	0.033[g]	ND	ND	ND	ND	ND	ND
Fabric filter	0.014[h]	0.0045	0.023[k]	0.0026[k]	0.026[k]	0.040	0.031

[a] Tests included dryers that were processing reclaimed asphalt pavement (RAP). Because of the limited data available, the effect of RAP processing on emissions could not be determined. Filterable PM emission factors were developed from tests on dryers firing several different fuels. ND = no data available. All emission factors in lb/ton of product. SCC = Source Classification Code.

[b] Total PM emission factors are the sum of the filterable PM and total condensible PM emission factors. Total PM-10 emission factors are the sum of the filterable PM-10 and total condensible PM emission factors.

[c] Particle size data from Reference 23 were used in conjunction with the filterable PM emission factors shown.

[d] References 31, 36-38.

[e] Although no emission test data are available for uncontrolled condensible PM, values are assumed to be equal to the maximum controlled value measured.

[f] References 36-37.

[g] References 29, 32, 36, 37, 40.

[h] References 25-28, 31, 33, 40. EMISSION FACTOR RATING: C.

[j] Reference 39.

[k] Reference 25, 39.

Total VOC

0.3795 lb/Ton

Process

loadout from hot silo

This SECTION is Final Except for Tech Edit

Table 11.1-2 (English Units).

EMISSION FACTORS FOR BATCH MIX HOT MIX ASPHALT PLANTS[a]

Process	Filterable PM				Condensible PM						Total PM			
	PM	EMISSION FACTOR RATING	PM-10[b]	EMISSION FACTOR RATING	Inorganic	EMISSION FACTOR RATING	Organic	EMISSION FACTOR RATING	Total	EMISSION FACTOR RATING	PM	EMISSION FACTOR RATING	PM-10	EMISSION FACTOR RATING
Dryer (gas-fired) (SCC 3-05-002-01)														
Uncontrolled	32[e]	E	4.5	E	0.0033[d]	D	0.00078[d]	D	0.0041	D	32	E	4.5	B
Low-energy scrubber[c]	0.077	D	ND		0.0033	D	ND		ND		ND		ND	
Venturi scrubber[c]	0.052	E	ND		ND		ND		ND		ND		ND	
Fabric filter	0.040[f]	D	0.016	D	0.0027[g]	D	0.00078[j]	D	0.0035[h]	D	0.044[j]	D	0.020	D
Dryer (oil-fired) (SCC 3-05-002-01)														
Uncontrolled	32[e]	E	4.5	E	0.017[d]	E	ND		0.045[d]	D	32	E	4.5	E
Venturi scrubber[c]	0.052	E	ND		0.017	E	ND		ND		ND		ND	
Fabric filter	0.040[e]	D	0.016	D	ND		ND		0.045[k]	D	0.085[m]	D	0.061	D

[a] Filterable PM emission factors were developed from tests on dryers fired with several different fuels. ND = no data available. All emission factors in lb/ton of product. SCC = Source Classification Code.

[b] Particle size data from Reference 23 were used in conjunction with the filterable PM emission factors shown.

~~[c] Reference 5.~~

[d] Although no emission test data are available for uncontrolled condensible PM, values are assumed to be equal to the maximum controlled value measured.

[e] Reference 15.

[f] References 15, 24, 40-41.

[g] Reference 24.

[h] References 24, 39.

[j] References ~~15, 24, 39,~~ 40-41.

[k] Reference 39.

[m] Reference 40.

VOC

Total

.8854 lb/T

Process

batch loadout

Ron Ryan

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

SEP 5 1995

Dr. Ravinda M. Nadkarni, P.E.
340 Franklin Street
Wrentham, Massachusetts 03093

Dear Dr. Nadkarni:

Thank you for your November 7, 1994 submittal of a proposed method for estimating fugitive air emissions from the loading of hot mix asphalt into trucks. I apologize for the delay in providing you with our comments and questions.

Our Public Participation Procedures for Emission Estimation Methodologies are not intended to be used to resolve individual regulatory disputes, which are best handled at a local level. While we recognize an element of this in your particular interest at this time, we also recognize that these emissions may be significant on a national level, yet they have never been quantified. While we cannot commit any Agency resources to the measurement of these emissions at this time, we would like to help facilitate a resolution to the emissions estimate question.

Be advised that we are currently reviewing the hot mix asphalt section of our AP-42 document for possible revision, but we have not found any emissions test data for the truck loading operations. Also, the Emissions Inventory Improvement Program (EIIP), a joint Federal and State venture also open to public participation will be releasing a draft document on how to inventory emissions from hot mix plants within the next month. However, we do not expect that this document will have any additional information on fugitive emissions from truck loading.

My comments on the proposed estimation method are enclosed. In summary, I think that the significant uncertainties associated with some of the assumptions warrants a more direct approach to quantifying the vapor pressure, concentration, or the emissions. If you would like to submit a revised method or otherwise respond to these comments, I would like to make the material available for public review and comment via our electronic bulletin board system. Please submit any materials that you can in some electronic form in order to expedite the process. Thank you for your efforts to help improve emission estimates for this source category.

Sincerely,

Rebecca Lee Tooly for
Ronald B. Ryan, P.E.
Environmental Engineer
Emission Factor and Inventory Group

3 Enclosures

cc: James E. Belsky, MA DEP
John Courcier, Region I
Lloyd Fillion, CAAP
David Mobley, EMAD (MD-14
John Seitz, OAQPS (MD-10)
EFIG Emission Factor Team

U.S. ENVIRONMENTAL PROTECTION AGENCY
COMMENTS (August 30, 1995)

FUGITIVE VOC EMISSIONS FROM HOT ASPHALT

submitted by Ravinda M. Nadkarni
*dated No*vember 7, 1994

1. SELECTION OF MASS TRANSFER EQUATION

I have not evaluated the applicability of the flat plate to fluid mass transfer equation as a model for the surface of the loaded asphalt truck. However, one question which immediately comes to mind is whether the rate-determining step of the process is the transfer from the asphalt surface to the air or the migration of the volatiles through the depth of the loaded asphalt to the surface. The proposed model relies on the fact that the supply of volatile materials to the surface is constant enough to maintain a vapor pressure of 30 mmHg. This would not be true if the volatiles could not readily move through the solid, or if the amount of volatiles initially present was less than the lb/ton emission factors derived by assuming a steady off-gassing.

2. ESTIMATE OF VAPOR PRESSURE

I agree that the key variable in the method as proposed is the vapor pressure of asphalt. However, if a direct measure of the concentration C_T were available, the vapor pressure would not be needed. The submittal does not clearly specify what C_T represents, but it appears to be the equilibrium concentration of organics above a liquid asphalt surface (at 300 F?). If this is correct, can a value for C_T be obtained from data for the vapor phase composition of a heated asphalt tank? I am enclosing copies of two reports done by EPA's Control Technology Center which may shed some light on the magnitude of C_T. Direct measurements above the blended asphalt may be the best solution.

I did not receive any of the five figures cited in the four alternative methods of estimating the vapor pressure, but I have several questions based on the text submitted.

Model Compounds. My understanding of using model compounds to estimate the vapor pressure of a mixture requires the assignment of liquid mole fractions to the model compounds and the assumption that the mixture is ideal, and thus that Raoult's law is applicable. Assuming that asphalt or asphalt blended with lighter material is an ideal mixture is very speculative.

Although the light aromatic compounds cited have been found in the emissions streams from asphalt plants, and they have significant vapor pressures as pure compounds, some data is needed to show that they are a measurable fraction of the liquid, and thus contribute any measurable amount to the total mixture vapor pressure. What fractions for what compounds did you assume in preparing Figure 1? The last paragraph under Model Compounds, referring to Raoult's Law, is unclear. The mole fraction of the lighter materials in the vapor phase should be close to 1, even though their liquid phase mole fraction would be close to 0, due to their much higher vapor pressures. What effect is being referred to?

Extrapolation from MSDS. I do not know what the information referred to as Figure 3 could be, but it presumably provides a set of parallel lines for vapor pressure versus temperature for liquids boiling at various temperatures. The one data point used for the extrapolation is a vapor pressure maximum (<0.0001 mmHg) at 20 C. The combination of this point with the uncertainty of the initial boiling point of asphalt (cited as 900 F or > 800 F) makes this method very speculative. Note that asphalt does not boil at 1000 F in a vacuum distillation column, and that the vapor pressure of anthracene is two orders of magnitude less than the maximum given on the MSDS (1.3 E-6 mmHg at 25 C). Also, the text cites vapor pressures at 300 F ranging from 14 mmHg for the 700 F line to 180 mmHg for the 900 F line. The vapor pressures seem to be reversed for the different boiling points.

Lower Explosive Limit Data. I am not familiar with this method, but I expect significant uncertainty could be introduced by the possibility that small amounts of much more volatile material may be present in the mixture. However, I note that it indicates a vapor pressure of 7.6 mmHg at 450 F. Using this data point and two others cited in your method 2 (<0.0001 at 20 C and 760 mmHg at 900 F), I have very roughly plotted a straight line of the log of vapor pressure versus 1/T (in Kelvin). This line indicates a vapor pressure of about 0.2 mmHg at 300 F.

3. RELEASE OF LIGHT ENDS

In addition to the two reports done by the CTC, I am enclosing a copy of our latest version of AP-42, Section 11.1. This version contains some emission factors for organic compounds passing through the particulate control devices on the dryers at drum mix plants and on the pug mill at batch mix plants. We are not certain of the amount of contact of the hot asphalt cement with the air flowing from the dryers in drum mix plants. But for batch mix plants it seems reasonable to expect that much of any light ends material would be volatilized in the pug mill. The data do not appear to show that these emissions are as large as you have estimated for the next process step downstream, the loadout operation. Have you noticed any fugitive emissions from the loading of hot mix into the storage silo?

4. MINOR COMMENTS

What is the asphalt temperature for which a vapor pressure is needed? The derivation of a value for C_T (1.6E-6 g-mol/cc) is based on a partial pressure (0.04 atm) figured at 300 F (423 K), but the temperature used in the derivation is 298 K. Figure 1 refers to a vapor pressure at 190 C (374 F).

The diffusion coefficient cited (0.093) appears to be for heptane, rather than hexane. The value for hexane is 0.2, but values for much heavier molecular weight materials may be more appropriate. The value for anthracene is 0.0324.

It is not clear how the batch versus continuous loadout emissions factors are calculated. What is the magnitude of the additional "correction factor" that is used? Note that the value of 252.8 lbs/hr at the end of section 1 of the submittal should be 151 lbs/hr.

Under Model Compounds, methyl benzene and triethyl benzene are not complex polynuclear aromatics. Also, methyl benzene is toluene, previously cited under light aromatics.

5. SUMMARY

While I have not visited a hot mix asphalt plant, it is obvious from observing a road paving operation that something continues to be released from the material even after it leaves the plant site. The odor and the fact that emissions can be seen would indicate the presence of particulate or condensible organics rather than lighter molecular weight organics, although some amount of the lighter material is undoubtedly present. It is not clear that the flat plate diffusion model selected is appropriate for the lighter weight materials, much less for the heavier vapors or particulates. Some of the data contained in the enclosures may provide insights to develop a more direct method of estimation.

October 26, 1995

Ronald B. Ryan, P.E.
Environmental Engineer
Emission Factor and Inventory Group
Office of Air Quality Planning and Standards
United States Environmental Protection Agency
Research Triangle Park NC 27711

Dear Mr. Ryan:

I apologize for the delay in answering your letter of September 5, 1995. I retired at the end of September and the transitional issues have kept me very busy until now.

In order to speed up the writing of this response and in keeping with the format you adopted in your letter, I will answer your letter in two parts; the first non-technical and the second technical. This letter will be non-technical and the second letter, to follow in about two weeks, will be technical. I hope you don't mind.

You do me great injustice when you open your letter with the comment: "Our Public Participation Procedures for Emission Estimation Methodologies are not intended to be used to resolve individual regulatory disputes, which are best handled at the local level". The local dispute in Wrentham was formally over on November 1, 1994, when the local builder, IBPC, surrendered their Air Permit to Mass DEP. This resolution was not a surprise to our group since we had been contemplating an arbitration procedure for 2 months before that. My letter to you was dated November 7, 1995. I had waited until the local issue was closed so that it would not affect EPA's consideration of the problem of fugitive emissions during truck loading and truck transport. This issue is national in its scope since the U.S. has about 3,600 hot mix plants. In addition, in order that this national nature of the problem be understood, I went to the trouble of first obtaining the format for such submittals from EPA Region I and adhered to it. There were no references to any local issue in my communications to you. I wish you had called me directly on this rather than checking with third parties who obviously misled you.

Wrentham is "blessed" with four hot mix asphalt plants in two locations along its borders with adjoining towns. These plants are on public roads so that it is easy to park across the street and observe the operations. I have taken full advantage of the proximity and the ease of access to these plants and observed their operations on hot days and cold, in good weather and bad.

As a process engineer, I was trained to ignore anything that is labelled "fugitive". This ignoring of fugitives is an almost subliminal process; akin to ignoring the "insect parts and rodent hair" which are allowed in small quantities in peanut butter by the USDA. We know they are there when we force ourselves to think about them, but it normally does not affect our consumption of peanut butter. The same phenomenon can be observed in the EPA publication, AP-42, which is issued by your office. It correctly catalogs all the emissions from a hot mix plant. The fugitive emissions are properly catalogued, but they are not quantified. Before my first visit to

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a hot mix plant, I was also fully prepared to ignore these fugitive emissions. However, as I sat across the street from these plants and observed the emissions, I realized that the bulk of the emissions to the environment were fugitive and came from a) the dumping of the hot mix from the storage silo into a truck waiting below, b) from the truck as it travelled uncovered from the storage silo to the weigh station, and c) from the stationary truck at the weigh station until the hot mix was covered with a tarp. Since all plants, old and new, have the same design for truck loading, these emissions were not a function of plant design. At some of the plants, there were also significant visible emissions from the top of the storage silos. These emissions appear to be a function of plant design. I observed that stack emissions in each case, downstream of the baghouse, were quite minor. Unfortunately, AP-42 and other EPA publications only quantify these minor stack emissions.

In your letter, you mentioned that you have never visited an asphalt plant. I suggest that you visit at least one and observe the emissions. With my November 7, 1994, letter, I had enclosed color photographs that showed these emissions, because I felt that these photos would be much more instructive than any calculation. Since you did not mention these photos in your comments, and you also said that some of the figures were also missing, I presume that they were lost at the EPA before the letter reached your desk. Please let me know if they are lost. I am sure I can dig up another set or take additional photos.

I don't mean to appear immodest but as the former head of the Chemical and Metallurgical Engineering Section of Arthur D. Little and as a winner of the "Application to Practice" Award of The Metallurgical Society for translation of research results into industrial practice, I bring considerable technical skills to the observation of emissions. In the case of hot mix plants, opacity is a good measure of hydrocarbon emissions because a) polycyclic aromatic hydrocarbons are vaporizing at around 300 degrees F, and are condensing in the colder ambient air, and b) all of the ingredients are dry (since moisture contained in the aggregate is going up the dryer stack) so that condensed water vapor is not contributing to opacity. These hydrocarbon emissions take on a characteristic blue tinge and, unlike water vapor emissions, they don't disappear suddenly through evaporation.

At each plant you will observe the same thing:

1. A large cloud of hydrocarbons is released as the hot mix is dumped into a truck from a storage silo. This loadout area is always in the open and its design has not changed in over 20 years in essential aspects, whether for a batch or a drum plant. In either case, hot mix drops through the air from a height of about 10 to 15 feet. At one plant where the load out area was surrounded by a shed, open on both ends like a tunnel, the emissions of blue smoke were just as bad as they would have been if the shed had not been there.

2. As the hot mix sits in the truck and as the truck moves around the yard, the hot mix continues to emit these hydrocarbons. Visually, the emission rate of the hydrocarbons does not decrease, indicating that the hot mix is porous enough to allow the light volatile fraction to move

through the solid and evaporate at a constant rate from the surface.

3. Overall, the visible emissions during step 2 are at a lower rate than the emissions during step 1. This is to be expected since the relative velocity of the hot mix and air should be much greater in step 1 than in step 2.

4. The emissions attenuate after the hot mix is covered with a tarp. However, the tarp does not provide a hermetic seal and you will continue to smell the hydrocarbons if you were to follow the truck in your car, even with your windows closed.

5. During this entire period, there will be no visible emissions from the stack, which is the focus of the EPA's emissions regulatory effort. On just one occasion, on a cold and damp day, I observed some water vapor emissions from the stack. All of the plants use a fabric filter/ baghouse for dust control. Enclosed parts of the plant which might also emit hydrocarbon vapor are also vented to this baghouse. It is not difficult to picture the fine dust acting as nuclei around which the hydrocarbons can condense and be trapped in the baghouse.

It was because of these observations that I searched for techniques for quantifying these emissions. I ended up with several techniques which gave similar results and also explained anomalies in the Material Safety Data Sheets published by the manufacturers of asphalt. The least non-technical of these methods was presented under Section 4 on page A-5 of my letter of November 7, 1994. This method relied on two measured values. The first was a published, experimentally measured value for concentration of hydrocarbons in asphalt fume, (expressed in mg of pollutant / cubic meter). This value had been obtained with personal monitors worn by asphalt workers. The second value was for the volume of the cloud as measured off the photograph that I sent you. The photo was taken at the end of the first minute after hot mix was dumped on the truck. Thus, the volume of the cloud accounted for the hydrocarbons emitted during the first minute. The truck was open for 5 minutes and, in order to be conservative and to account for a lower relative velocity between air and asphalt as the hot mix sat in the open truck, I increased the total mass emitted during these five minutes by a factor of only 2.5 rather than by 5. This simple calculation also gave us numbers that were also the same order of magnitude as the other, more complex calculations. This simple calculation indicated that the emissions would be about 50 tons of carcinogenic hydrocarbons per year; which means that nationally, about 180,000 tons of this material are being emitted without any control by the EPA or by local authorities who rely on EPA's guidance. If I had used a factor of 5, this number would have been doubled. In contrast, emissions from the stack are of the order of 5 tons per year or less. I notice that you did not comment on this method at all in your detailed response.

My point, very simply, is this: There is something terribly wrong with a set of regulations which completely ignores a major portion of emissions but puts considerable efforts in quantifying minor emissions. You seem to realize this when you state "we also recognize that these emissions may be significant on a national level, yet they have never been quantified."

I suggest that a reallocation of effort is in order since your efforts, unfortunately, have been misdirected at minor emissions. (I don't mean to be too critical. Such "Monday morning quarterbacking" on my part occurred only after spending many hours observing asphalt plants and after my calculations were complete. Again, the calculations were aimed at quantifying my observations; nothing more. If you had visited a few plants and seen the visible emissions, I am confident that you too would have reached the same conclusion.)

You also state that you cannot commit any Agency resources to the measurement of these emissions at this time. All I am asking is that you first establish for yourself that fugitive emissions are much more significant than stack emissions at hot mix plants by visiting and observing these emissions. It is then up to you to either use my estimates as an interim estimate or use totally different methods, theoretical or experimental, that quantify these observations. I understand the Agency faces budget constraints, but the evidence here calls for a reallocation of effort not supplemental effort. I hope you also realize that I, as a retired person, don't have the resources to undertake experimental work for "a more direct approach to quantifying vapor pressure, concentration, or the emissions" as you suggest. At this stage, based on the visual and photographic evidence alone, you should be focussing the Agency's resources on quantifying these emissions and not put the burden of proof on me.

Sincerely,

RMNadkarni

Ravi Nadkarni, P.E.

cc: J. David Mobley EPA EMAD (MD-10)
John Seitz, OAQPS (MD-14)
John DeVillars EPA Region I
Senator Edward Kennedy
Senator John Kerry
Rep. Joseph Moakley
Rep. Joseph Kennedy
Rep. Peter Blute
James E. Belsky MA DEP
Lloyd Fillion

November 16, 1995

Ronald B. Ryan, P.E.
Environmental Engineer
Emission Factor and Inventory Group
Office of Air Quality Planning and Standards
United States Environmental Protection Agency
Research Triangle Park NC 27711

Dear Mr. Ryan:

As promised in my letter of October 26, I am sending this more technical letter which addresses your questions and comments dated August 30, 1995 which accompanied your letter of September 5, 1995. I will respond to the questions raised in the same order as that in your letter with one exception: I will deal with the comments in **Section 5. Summary** first, because it indicates to me that you and I are using somewhat different terminology. Clearing up these differences will make the rest of my comments below a little easier to follow.

Summary

You state, "The odor and the fact that emissions can be seen would indicate the presence of particulate or condensible organics rather than lighter molecular weight organics, although some amount of the lighter material is undoubtedly present. It is not clear that the flat plate diffusion model selected is appropriate for the lighter weight materials, much less for the heavier vapors or particulates." [Emphasis added.] In these statements, you are differentiating between three types of materials: "lighter molecular weight organics", "heavier vapors" or "condensible organics" and "particulates". Since all of my efforts were triggered by visual observations, I never tried to make this fine a differentiation. My technical training told me that "particulates" i.e. dust particles from crushed rock, would be trapped in the bag house and would not be a part of the fugitive emissions from the hot mix during truck loading. Thus, I have always considered the totality of all organic compounds which would evaporate from the hot mix at temperatures between 300 and 350 F and then condense in the ambient air at around 70 degrees F. These would include compounds that are gases at ambient temperature as well as compounds that are condensed submicron particulates. From the viewpoint of health impacts, the submicron condensates, rich in polynuclear aromatic compounds, might well be the more dangerous component of the two.

Asphalt is a very complex mixture of hydrocarbons. It is typically hydrogenated after vacuum distillation so that it is stable during storage and transport. In addition, it contains light ends (naphtha) which are added at the terminal to control its viscosity. The limited available data on asphalt, available in Material Safety Data Sheets, appears to be based on material shipped from a refinery rather than the material that is delivered to a user by a terminal. Visual observations show that some of these organics vaporize during loadout. These organics have to meet only two conditions to be visible: a) They have to have a boiling point above 70° F (in order that they condense and form a visible fog). b) They have a boiling point below about 300° to 450° F.

The first condition is absolute since the fog would not be visible without condensation. The second condition is not absolute since all substances have significant vapor pressure at temperatures near but below their boiling point; hence the range of temperatures. Much of your criticism is based on a differentiation between lights and heavies. Such differentiation is not necessary since I can now show that the results predicted by the mass transfer model match very closely the actual measurements in EPA reports which you kindly sent me.

1. Selection of Mass Transfer Equation

As mentioned in my letter of October 26, 1995, any observer of an asphalt plant will notice that there are two "regimes" for volatile hydrocarbon emissions while trucks are being loaded. The first regime or the first stage occurs when hot mix drops through the air from a height of about 5 to 15 feet on to the bed of the truck. During this stage, the loose hot mix is falling through the air with a significant relative velocity between the hot mix and the air. Thus, a large amount of hydrocarbon fume is generated. The second regime occurs when the loose mix is sitting uncovered on the bed of the truck. Because the hot mix is loose, it contains a lot of air in the interstices. Because it is hot, the loose pile will "breathe", i.e. hot air, with vaporized organic compounds, will rise from the top of the pile and be replaced by colder air. [There is extensive literature on this "breathing" phenomenon since it can lead to fires in loose, combustible materials stored in the open.] Hydrocarbon emissions will continue as the truck either sits in the yard in a queue to be weighed or is driven to the weigh station for weighing and for the completion of paperwork. I have observed that the truck driver will weigh the truck, complete the paper work, level off the load with a shovel if necessary and then cover the load with a tarp; all of which takes 5 to 10 minutes. Visual observations show that the hydrocarbon emissions from the truck bed during the second stage are less copious than during the first stage, but they continue at this lower but constant rate over that period. This is to be expected since the relative velocity between air and the hot mix is less in the second stage.

You have asked whether the volatiles continue to diffuse through the loose asphalt in a truck and feed the top surface to maintain a constant vapor pressure. Your question is very reasonable and correct. My repeated observations indicate that the emission rate from the top of the truck does not attenuate over the first 5 to 10 minutes, therefore this condition is met. The reason for this constant rate of emissions is the "breathing" phenomenon mentioned earlier. In other words, visual observation would suggest that the rate-determining step is the transfer of organic compounds from most of the surface of the hot mix pile to the air and not the migration of the volatiles through the thickness of the hot mix to the surface. In my search of the literature for an appropriate mass transfer equation, I found the flat plate equation. I used it because it seemed to support all of my observations including the fact that the vapor emissions rate was constant from the top surface, indicating that the conditions for the derivation of that equation were being met in the field. The top surface is not perfectly flat or smooth; an assumption in the flat plate equation. Since the relative air/truck motion is in the turbulent flow regime, the lack of a smooth surface is less important than it would have been had the flow been laminar. Also, the lack of smoothness means that results predicted by the mass transfer equation are based on a lower Reynold's number and have a low bias. You might ask which is the appropriate area to use in the flat plate equation. There are two relevant areas: The first is the area of the loose mass of the hot mix (including the internal area) which feeds the vaporized organics to the surface. This feeding of the top layer of the hot mix justifies the use of the flat plate equation. The second area is the surface area of the top of the truck, the "flat plate" of the equation, where the relative motion takes place between the truck and air.

2. Estimation of Vapor Pressure

We both agree that the actual vapor pressure of asphalt is a key input variable for the mass transfer calculations. [Since you say that you did not receive the figures attached to my letter of November 7, 1994, I am attaching another complete copy of that letter - I had several extras in my file. This letter also contains color xerox copies of the photos which, while not as good as the original color photos I had sent before, are sufficiently detailed to show the clouds. I am assuming that the original photos and figures were separated from my letter as it moved through various EPA offices to your desk. I am also enclosing color xerox copies for all the other addressees of this letter so that they can also get a visual impression of the magnitude of this problem.]

You are correct in assuming that C_T represents the concentration of vapor over the asphalt at 300 F. I agree that a direct measurement of vapor pressure would be the best way to obtain a value of C_T. However, I would measure vapor pressure rather than vapor phase composition, since it is a more direct way and is likely to be less expensive. Measuring the vapor pressure in the free space above a hot asphalt storage tank would be a good way. Better yet and more controllable would a laboratory measurement using the Langmuir or the Knudsen methods. In any event, such measurements are less important now since EPA data support the results of the mass transfer calculation, as discussed below.

I have reviewed the two publications that you sent. While they don't measure equilibrium vapor pressures, they contain enough data to **fully support** my calculations. Both reports evaluate emissions from hot mix or from heated liquid asphalts at elevated temperatures. In the first report, "EVALUATION OF EMISSIONS FROM PAVING ASPHALTS" prepared by Accurex Environmental Corporation, emissions from a hot, compacted sheet of hot mix were measured using various sampling trains and a gas chromatograph/ mass spectrometer (GC/MS) for analysis. The results of this study are less applicable to the situation at hand for two reasons: First, the hot mix was compacted by hand on a heated "table" before air sampling was initiated. This compacting took two people 5 to 15 minutes. The test was therefore measuring emissions from a simulated hot, but compacted road surface. (I am sure that the rate determining step for the transfer of the volatiles in this case would be migration through the compacted mass and the rate would fall off with time.) In contrast, my entire focus has been on loose, uncompacted hot mix with significant interstitial volume full of air. The second reason for not using the results in this first report relates to the way in which air was entering the sampling chamber (the "burn hut") and the way in which it was picking up the asphalt vapors. Figure 3 in the report suggests that some of the incoming air would have bypassed the vapor emitted by the compacted asphalt. A few qualitative tests with incense or titanium tetrachloride would reveal the streamlines and would show that this is probably the case. Thus, the numbers collected in this report should have a low bias. Also, with such bypassing, it would be impossible to model the fluid flow pattern and use the data in any mass transfer equation.

The second report, "EVALUATION OF VOC EMISSIONS FROM HEATED ROOFING ASPHALT" by the same contractor, dated November 1991, is more useful for our purposes. In this case, three grades of roofing asphalt were held in a heated kettle and the vapor emissions were sampled at three different temperatures. Figure 1 and Figure 2 of this report show the air flow across the heated kettle. While the air flow in this case might not be ideal either, bypassing is not obvious. Second, because the report used liquid asphalt, the situation is much closer to using loose, uncompacted asphalt from the viewpoint of mass transfer, i.e. the surface was being continuously supplied with the volatiles. Finally, the report does provide information that can be used directly, although the numbers probably have a low bias for total hydrocarbon emissions since baffles were used to deflect volatilized, condensed liquid droplets from the sampling tube.

In this report, emissions were measured at three temperatures: The lowest was the temperature at which the asphalts were just molten. The second temperature was when the asphalt viscosity had decreased sufficiently such that it would have been used to mop a roof. The third temperature was 66 degrees C higher than the second temperature, which is a typical superheat temperature for delivering hot asphalt to a roof. Table 1 below shows data from this report for the middle temperature, which is closest to the loadout temperature for hot mix plants. The first column is the type of asphalt used. The second column is the actual temperature at which the emissions were measured. The third column is the VOC emissions, measured as weight loss over the duration of the experiment of about 4 hours. The final column is this VOC emission/weight loss, normalized to weight loss per hour per square meter of area based on information in the report.

Table 1: Measured Emissions from Roofing Asphalt

Asphalt Type	Temperature °C/(° F)	VOC emissions/ Weight loss kg	Normalized weight loss g/hr - m^2
Type 1	163 (325)	0.002	3.61
Type 2	170 (338)	0.014	25.26
Type 3	218 (424)	0.013	23.26

Source: "EVALUATION OF VOC EMISSIONS FROM HEATED ROOFING ASPHALT" Table 15 for weight loss; p. 31 for time and area data

Of the results in Table 1, the operating temperature for Type 3 asphalt is too high and these numbers are not appropriate for our purpose of estimating vaporized organic emissions from loose hot mix. As discussed on page A-6 of my letter of November 7, 1994, the mass transfer equation gave emission numbers that ranged from **0.2% to 1.1% by weight of the asphalt used.** Even at 0.2%, the emissions exceed 100 tons per year and the plant is a major source of pollution as defined in the Clean Air Act Amendments. In other words, if the weight loss data in Table 1 can be suitably applied to the hot mix example and it shows the same degree of weight loss/vaporized organic emissions, the case is proved since we would have arrived at the same result without using any estimate for the vapor pressure of asphalt.

There are just three factors that are needed to apply the EPA-determined normalized weight loss to the case of hot mix in a truck: the time for evaporation of asphalt; the surface area of asphalt and the relative air flow conditions for the two cases: EPA experiment vs. truck movement.

a) Time: Further observations over the past year indicate to me that the best range of times to use is from 5 to 10 minutes for each truck. The most representative time is perhaps 7.5 minutes on average. This covers the time from the loading of the truck until it is covered with a tarp and is driven off the premises, which is generally 4 to five minutes. It includes an allowance of an additional 3.5 to 3.5 minutes to cover the more rapid fume evolution during truck filling compared to truck movement. But, careful examination of photos 1 to 3 compared to photo 4 suggests that this is a conservative allowance and could easily be doubled.

b) Surface area: In the case of loose hot mix, where crushed stone is coated with a thin layer of hot asphalt, the relevant evaporating surface is the entire surface area of the loose hot mix, which is close to the surface area of the crushed stone. There will be some agglomeration, making the total crushed stone area an estimate with a high bias, but it is a good starting point. In the calculation to follow, this is accommodated by assuming that the particle size of the slightly agglomerated hot mix is larger than the particle size of the crushed stone.

c) Flow conditions: The air flow across the asphalt was very slow during the EPA experiment compared to the air flow over a truck in the open. The plate Reynold's number for the truck was 1,400,000 at a wind speed of 5 mph (see page A-2 of the November 7, 1994 letter) while the Reynold's number for the EPA measurement, based on room dimensions of 2.4x2.4x2.4 meters (p. 4) and kettle area of 0.138 m^2. (p. 31) is 2,258. Since the mass transfer coefficient varies in proportion to Reynold's number raised to 0.8 power, we need to correct the emissions from the lab experiment by this factor.

Tables 2 and 3 show these calculations for various sizes of crushed stone. While a 1/2" size is probably representative of crushed stone used in the hot mix, the larger sizes represent some agglomeration of the hot mix. The time has been varied between 5 and 10 minutes. The results in Table 2 are for a normalized weight loss (vaporized organic compound emissions) of 3.61 g/hr-m^2 while Table 3 presents the same data for a normalized weight loss (vaporized organic compound emissions) of 25.26 g/hr-m^2; both of which are figures from the EPA data presented in Table 1.

Table 2: Percent VOC emissions with normalized wt. loss of 3.61 g/hr-m^2

Particle diameter inches	Time of 5 minutes	Time of 10 minutes
.50	1.07%	2.14%
2.00	0.27%	0.53%
5.00	0.11%	0.21%

Table 3: Percent VOC emissions with normalized wt. loss of 25.26 g/hr-m^2

Particle diameter inches	Time of 5 minutes	Time of 10 minutes
.50	7.48%	14.96%
2.00	1.87%	3.74%
5.00	0.75%	1.50%

Tables 2 and 3 show that the values derived from the experimental data are very similar to those predicted by the mass transfer equation. This indicates that there is some agglomeration of the hot mix, but the results match remarkably well.

I have to bring up one caveat, however, with respect to the data in this report. There are some differences between roofing asphalt and asphalt cement relating to the use of air oxidation for the former. I don't think it applies to Type 1 and Type 2 asphalt but I am not sure.

Please note that the results in Table 1 are similar to results reported by other investigators. For example, the paper by Oestman, et al. ("A laboratory method for the assessment of polycyclic aromatic compound emission from heated bitumen", Fuel, Vol. 66, December 1987, pp. 1720 - 1726) shows weight losses in the range of .05 - 6.7%. Because these are dynamic tests and not equilibrium tests, the rate of weight loss depends on many experimental parameters. Oestman shows that the rate of weight loss, after an initial high rate, was constant, indicating that the asphalt was not depleted of the volatiles. The only reason for quoting this paper is to show that the results in Table 1 are not unexpected.

Model Compounds: You are challenging the use of Raoult's Law and the parallel assumption that the mixture is ideal. For the past 100 years, all types of calculations involving solutions and mixtures have relied on Raoult's Law in the absence of experimental data. I would also argue that for a material with a high mole fraction, the use of Raoult's law is not a "stretch". The crushed stone is an inert material and a second phase. It is not involved in any way. However, I would be the first to abandon this approach should any good equilibrium data be available. In the absence of such data, I don't know of any other way to quantify these emissions. Do you have an alternate suggestion?

You agree that a) light compounds have been found in emissions from asphalt plants, and b) they have significant vapor pressures as pure compounds. You would like to be shown that a) they are a measurable fraction of the liquid and b) they therefore contribute a measurable amount to the total vapor pressure. Through qualitative reasoning I will attempt to answer these two questions. Visual observations indicate that enough vaporized organics come off heated asphalt to form dense clouds. EPA measurements support this as discussed above. My point is that you don't need to have a large weight percent of these light ends for this to happen. Asphalt is a mixture of very high molecular weight hydrocarbons (with molecular weight from 3,000 to over 5,000, according to manufacturers' MSDS) and light hydrocarbons with molecular weight of under 200 or 300. Under these conditions, a small fraction by weight of the light fraction means many molecules of this material. In contrast, a large weight fraction of the heavy material still leads to a small number of heavy molecules. This means that the mole fraction of the light fraction is considerable, even when its weight fraction is not. Thus, you don't need a high concentration by weight of the light fraction for it to evaporate and form dense fumes. Note that the Oestman paper indicates that the asphalt condensates are fairly rich in 3-ring compounds with a molecular weight under 300.

I will not critique your comments under "Extrapolation from MSDS or Lower Explosive Limit Data. You did not have the attachments, and it is unfair to deal with your comments when you were unable to read and fully understand these parts of the package. In any event, they are less important now.

3. Release of Light Ends

I had previously studied the emission factors for organic compounds that pass through the bag house, published in AP-42. I was not surprised that these emissions are low. I expect that the bulk of the unburnt vapors from the drum or from the pug mill and the vapors from the inclined conveyor, all of which are vented to the bag house, condense around the fine particles and are captured in the bag house dust.

In terms of other fugitive emissions, I have noticed fugitive emissions from the top of the storage silo in some cases, but not in all cases. The inclined conveyor which takes the hot mix to the top of the silo is normally open at the top but is under a draft induced by the baghouse fan. If this draft is not adequate, there will be significant visible fugitive emissions from the top of the silo. These emissions occur most often when pressure balancing is poor and there is inadequate draft. In one case, the plant added an electrostatic precipitator with an additional induced draft (ID) fan just after the electrostatic precipitator but ahead of the bag house. I expect that this was done to control the draft at the top of the silo and also to reduce the volatiles entering the bag house, which might have affected bag life. This booster ID fan was good enough to prevent emissions from the top of the silo. Unfortunately, this additional ID fan is the exception, not the rule.

4. Minor Comments

The mass transfer equation requires the asphalt vapor pressure at the temperature of the hot mix at load out, i.e. 300 to 325 degrees F. The temperature used in the mass transfer equation is the ambient temperature since it is the temperature of the air that will flow past the asphalt hot mix at 300 degrees F.

You have commented that the diffusion coefficient I used appears to be for heptane rather than hexane. I think I took it from the Sherwood, et al. **Mass Transfer** book, which I no longer have and am unable to check it. In any event the value used was a low number.

I calculated different factors for batch vs. continuous loadout based by applying different loadout times for the two cases. As you know, a drum plant loads from an insulated silo at a much faster rate than a batch plant. At the latter, the truck has to wait while two or three batches are mixed and loaded on the truck, one after the other, with a waiting time of a minute or more between the batches. [See photos 1 to 3.]

In your summary, you state that "it is not clear that the flat plate diffusion model selected is appropriate ....". I am not sure that I understand the reasoning behind this comment. It seems to me that the model would be inappropriate if the rate determining step were the transfer of vaporized organics from the bulk of the loose asphalt to the surface, which is not the case. We can both argue about the value of vapor pressure used by me in the model; but this disagreement is best addressed by using alternate values of vapor pressure in the model rather than by rejecting the model itself. This is a minor quibble on my part. Overall, I was very pleased to see that you had done a very careful and professional job of giving my work an appropriate "peer review".

No additional response is necessary on the other minor comments since, as noted above, the EPA report appears to support the conclusions reached through the mass transfer modeling.

Summary

I have attempted to use a mass transfer equation to model and quantify the emissions I observed. The technique that I used is not unique and there are probably other better, independent ways to estimate these emissions. Also, I focussed on total vaporized organics since hydrocarbons are criteria pollutants and are important to us since Massachusetts is a non-attainment region. Again, I feel confident that you will agree with the magnitude of the problem once you have visited a few plants and observed these clouds of organics in person.

Now that EPA data also support these calculations, I would like to suggest that we continue this dialog on how best to deal with the implication of this finding. This finding shows that there are about 3,600 asphalt plants around the U.S. which are major emission sources, as defined in the Clean Air Act since they emit over 100 tons per year of vaporized hydrocarbons. Until now, these plants have escaped regulatory scrutiny because these emissions were considered fugitive and not quantified.

Sincerely,

Ravi Nadkarni

Ravi Nadkarni, P.E.

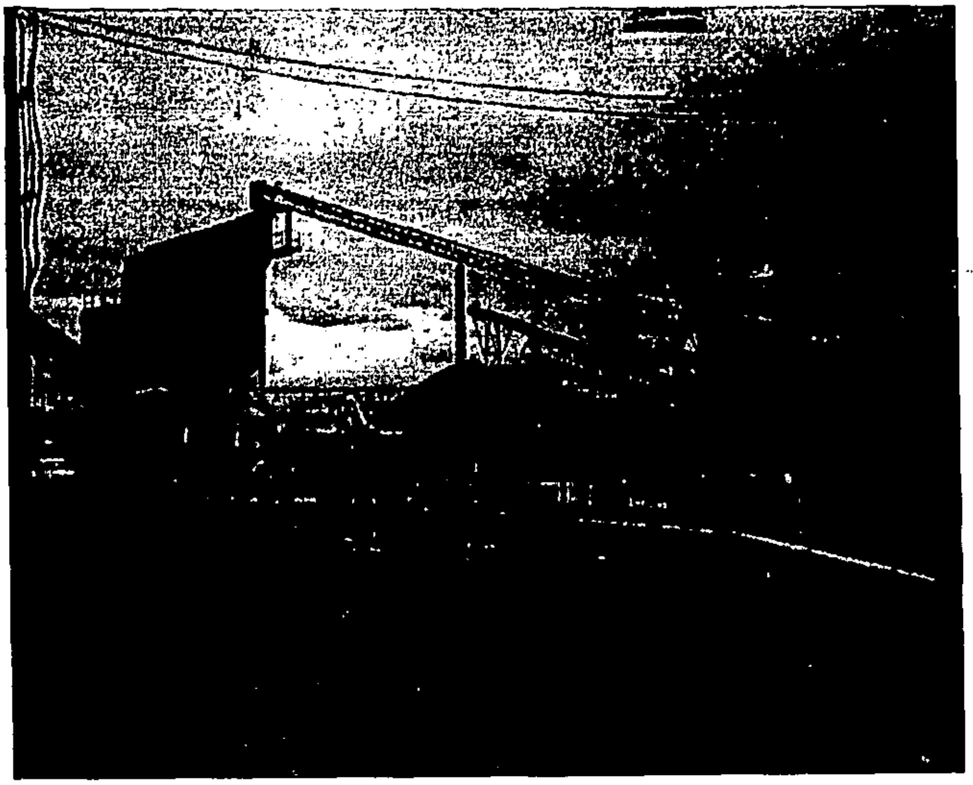
cc:
J. David Mobley EPA EMAD (MD-10)
John DeVillars EPA Region I
Senator John Kerry
Rep. Joseph Kennedy
James E. Belsky MA DEP
John Seitz, OAQPS (MD-14)
Senator Edward Kennedy
Rep. Joseph Moakley
Rep. Peter Blute
Lloyd Fillion

Photograph 1 shows a truck receiving its first load of asphalt from the batching tower. (Time zero). You can notice the copious emissions of carcinogenic VOC's. This plant takes about 1 minute to mix a batch so that even a small truck, after receiving the first load, waits under the tower for a minute until the next load is dumped. A small truck like the one in the photograph (6-wheeler) is filled with just 2 dumps. A larger truck, a 10-wheeler or an 18-wheeler, would hold more dumps and would have to wait longer under the batch tower, emitting carcinogenic VOCs during that time.

Photograph 2 shows the truck during this waiting period where the first load continues to emit VOCs. (Elapsed time is about 30 seconds).

Photograph 3 shows the truck just after the second load is dumped. The fumes are very thick again. (Elapsed time is 1 minute to 1 minute 5 seconds).

Photograph 4 shows the truck moving towards the weigh station. The photo shows that the fumes are still coming off the truck but are not as dense as before because the truck is moving and the air is dispersing these VOCs.



The truck then drives to the weigh station and the driver goes inside to complete the paperwork. After he comes out, he covers the loaded truck and drives off. Photograph 5 shows the driver in the process of covering up the loaded truck. There are still significant emissions off the truck. (Total elapsed time 5 to 5.5 minutes).

Photograph 6 shows two important points. In the background, you can see the entire plant. THE PLANT STACK IS CLEAR. Unless you know the plant design, you would not be able to locate the stack based on this picture. YET, THE MASS DEPT. OF ENVIRONMENTAL PROTECTION (DEP) ACCEPTS THAT THE VISIBLE FUMES ARE 10% OF THE INVISIBLE STACK EMISSIONS.

In the foreground, the photograph shows a water truck spraying the roadways for dust control.

July 5, 1996

Mr. J. David Mobley, Leader
Emission Factor and Inventory Group
United States Environmental Protection Agency
Research Triangle Park NC 27711

Dear Mr. Mobley:

I am writing this letter in response to the four comment letters that you sent Lloyd Fillion and me with your letter of April 16, 1996. I had been waiting for EPA's response to my two letters of October 25, 1995 and November 16, 1995 to Ronald Ryan. Since it appears that there will be no technical response from the EPA to these letters, I will comment on the other letters and on other data uncovered in the interim.

Overall, I am disappointed that neither the EPA nor any other commentator has responded to my two letters mentioned above and their technical content; particularly because they showed that my **original calculations of emissions of polynuclear aromatic hydrocarbons (PAH) were supported by data collected in EPA labs.** In addition, I have uncovered information from the National Asphalt Pavement Association (NAPA) and their affiliates which also supports these emission numbers. This new information will be presented here in section A. The information in these various sources leads to the same conclusion, i.e. a) the vapor pressure of asphalt is significant and b) the industry has avoided regulatory scrutiny by not reporting these fugitive emissions. I am particularly concerned that EPA appears to be headed in the direction of having NAPA measure these fugitive emissions. Since NAPA has considerable self-interest in the outcome of these tests, it is very important that these tests be designed with citizen input. The actual full-scale tests should be preceded by smaller-scale, laboratory tests where more control and better sampling is possible. Also, the full-scale tests and sampling should require appropriate EPA and third party supervision.

The format of this letter will be to discuss this new data first and then discuss the four letters you received, one by one.

A. New data supports vapor pressure used for original calculation of PAH emissions

We have found a letter written on August 11, 1994 by Thomas E. Brumagin of NAPA on the subject of vapor pressure of asphalt. (Exhibit A). The scientific basis for the assertions in this letter is extremely weak and is contradicted by the information attached to the letter. In fact, it proves my point that the vapor pressure is at least 30 mm of Hg.

The first two paragraphs are incorrect. While Mr. Brumagin is correct that the Reid vapor pressure method, a rapid measurement technique, is not applicable for the measurement of asphalt vapor pressure, his conclusion that "there is no current test method to determine the vapor pressure of asphalt materials" is wrong. Vapor pressure is a thermodynamic property and techniques for the measurements of these properties over a very wide range are available in any standard book on thermodynamic measurements. For example, the Langmuir or Knudsen methods can be used as suggested in my letter to Ron Ryan of November 16, 1995 on page 3, paragraph 3.

In the third paragraph of his letter, Mr. Brumagin states:

> "I have attached a figure from Petroleum Refinery Engineering which can be utilized to extrapolate a vapor pressure for asphalt cement at a temperature of 300° F. I have connected the material's temperature of 300° F to an initial boiling point for asphalt of 750° F. The nomograph yields a vapor pressure of less than 0.5 mm of mercury, or less than 0.01 psi."

In the Supplemental Draft Environmental Impact Statement (SDEIR) on Todesca's proposed plant in Boston, this basic information was amplified by Tech Environmental to read as follows:

> "research data collected by the National Asphalt Pavement Association reveals this assumption (that the vapor pressure was 30 mm. of mercury) to be in error".

No such research data was ever presented by Tech Environmental, unless information from a book labeled "Esso Research and Engineering Company" (see page 206 in Exhibit A) has become "research data collected by NAPA"; which appears to be the case.

The SDEIR (see relevant pages in Exhibit B) goes on to state:

> "Figures from *Petroleum Refinery Engineering* can be used to extrapolate a vapor pressure for asphalt cement at a temperature of 300° F. The actual boiling point of asphalt cement is typically between 900° F and 1000° F. Assuming the lower end of the scale to be conservative, the vapor pressure of asphalt cement is actually less than 0.01 mm of mercury, or less than four orders of magnitude than the commenter's assumption."

The second page of Mr. Brumagin's letter, page 206 from "*Petroleum Refinery Engineering*" (author and publisher unknown), provides the diagram which has been used to support both sets of comments. Since the temperature of asphalt in hot mix at load out is at least 300° F, we are looking at different positions along the vertical 300 degree line on page 206. If the reader knows or assumes an *initial* boiling point for the hydrocarbon product under consideration, the vapor pressure can be read on the vertical axis on the left. Mr. Brumagin assumed an initial boiling point for asphalt of 750° F and thereby obtained a vapor pressure of 0.5 mm mercury. Tech Environmental assumed an initial boiling point of over 900° F and thereby stated "the vapor pressure of asphalt cement is actually less than 0.01 mm of mercury". This same figure also reveals that for asphalt to have a vapor pressure of 30 mm of mercury (as I had calculated), the initial boiling point would have to be about 525° F. **Thus, the issue at hand is to determine**

whether asphalt as shipped to a hot mix plant from a terminal contains a blending agent which has an initial boiling point under 525^0 F.

All petroleum products are mixtures of many different types of hydrocarbons. At any particular temperature, the lighter compounds boil over into vapor while the heavier compounds stay in the liquid. This is the reason for considering the initial boiling point as the relevant parameter as was done correctly by Mr. Brumagin, rather than use the average boiling point as was done by Tech Environmental. Exhibit C contains 4 pages from Chemical Engineers' Handbook, 5th Edition, McGraw-Hill, 1973, which succinctly present many details about the entire range of distillate and residual petroleum fuels and products. Residual fuels are discussed in the second paragraph on page 9-10 in the first column. It describes how different grades of residual fuel are produced by blending distillation-tower bottoms with distillates. The same blending occurs at a terminal with respect to asphalt cements. Asphalt cements are sold in various grades with different viscosities; for example, AC-5, AC-10, AC-20 and AC-30, etc where the number is the viscosity in centipoise at a reference temperature of 140^0 F. The various grades are produced at the terminal by blending the appropriate amounts of diesel or No. 2 fuel or lighter distillates such as naphtha with residuum or tower bottoms. The boiling ranges of these blended ingredients are shown in Figure 9-2 on page 9-8. This figure packs a lot of interesting information. It can be seen that the initial boiling point of fuel oils from No. 1 to No. 6 is the same. This initial boiling point is 300^0 F, which is well below the required 525^0 F for the blend to have a vapor pressure of 30 mm of mercury. This commonality exists because all fuel oils use the same grade of distillate (naphtha) for blending, using more of it for No. 1 oil than for No. 6 oil. (Except that the lighter grades do not contain tower bottoms.) Thus, regardless of the specific blending ingredient used, from naphtha to No. 6 fuel oil, the initial boiling point for asphalt will be about 300^0 F, close to the initial boiling point of the light component. Figure 9-4 shows how viscosity of these blends changes with temperature. The vertical axis is kinematic viscosity (viscosity divided by density). The density of asphalt cement is 1.04, and for this reason, the graph can be read directly in viscosity units (centipoise) for asphalt without much loss in accuracy. It can be seen that the viscosity range for No. 6 fuel oils is 6 to 18 centipoise, which basically covers the range of viscosities of commercially available asphalt cements. In other words, there is little essential difference between No. 6 fuel oil and the asphalts sold for hot mix. This shows that the comments of NAPA and Tech Environmental were based on an incorrect reading of the information in the reference. A correct reading of this information would show that a vapor pressure of 30 mm of mercury is correct and may be even a little conservative. This high vapor pressure is, of course, also supported by visual observations of hydrocarbon clouds during load out.

B. Response to comment letters

1. Letters (E-Mail) from Minnesota

I fully agree with comments by Paul Kim. Specifically, I agree that "the fact the VOC emissions may be substantial, but have not been quantified is disturbing. ..... this issue is definitely worth pursuing as a part of future research"

The comments of Mary Jean Fenske include a lot of questions which I will answer here.

1. In comparison to plants in Massachusetts, the average plant size in Minnesota appears to be small. The figure used in my calculations is based on *production* capacity of several plants recently permitted by the State. The hourly capacity is generally around 300 to 400 tons per hour and thus, the maximum potential output is much larger. I have found the proposed batch plants to be somewhat smaller than the proposed drum plants. Thus, it is possible that the plants in Minnesota are predominantly of the batch type. It is also possible that the median plant size in Minnesota is larger than 100,000 tons/year. In a segmented market, the smaller plants often serve the home driveway market, while the larger plants sell the bulk of the hot mix sold in the State and are involved in selling hot mix for repaving of the state and Federal roadways.

2. The ratio of asphalt cement in hot mix that I used was taken from the permits that I have reviewed. I have seen higher numbers; for example, the Todesca plant's permits state that their asphalt cement consumption will be 10%.

3. The calculation shown is correct. However, batch plants tend to emit more hydrocarbons per unit of output because a truck waits uncovered under the mixing tower for a long time as several batches are mixed and dumped into the same truck. In contrast, a drum plant's silos unload continuously and the truck is loaded faster. For a batch plant with 100,000 tpy capacity, I believe that a range of about 40 to 65 tons per year would be an appropriate figure for fugitive emissions from loadout. The only reason why this number is less than that derived by me for Massachusetts is because of the lower average plant capacity in Minnesota.

4. There are two methods available to control these emissions of hydrocarbons. The first is to totally enclose the truck loading area. This can be done through an enclosure that has four sides and a roof. This enclosure is exhausted either to the bag house directly or to the bag house after some of the condensible organics have been removed with an electrostatic precipitator such as the "Smog Hog". This device is specifically sold to the asphalt industry by its equipment suppliers for removing condensible organics that lead to "blue smoke". Obviously, such an approach requires opening and closing of the doors to the enclosure each time a truck is being loaded. This can be avoided using the "air knife" technology that is used in the European mining industry to allow trucks to go in and out of buildings during winter. This approach places a curtain of high velocity recirculating air across the entrance or exit so that outside air does not have free access into the building. In Boston, a particular proponent has proposed an open shed, open in front and back, as an alternative and such a shed has been in operation in their Rochester, MA, plant. Based on visual observations at the Rochester site by several individuals including the staff of the City of Boston Board of Health and Hospitals, this approach does not work.

The second approach has been proposed by David Sprogis of Boston, a person with over 30 years of construction experience. He says that the best approach is to have portable plants that are located at or near the place where the pavement is laid down. This way, a particular neighborhood does not have to endure the fumes all the time. I believe that the State of South Dakota has already embraced this approach.

2. Letter from Wisconsin

The first three paragraphs under "Asphalt Cement" deal with properties of this material. Information presented in Section A of this letter refutes the statements made here.

I find the fourth paragraph confusing. While my letter clearly dealt with fugitive emissions released during truck loading and truck travel, this paragraph deals with what happens inside the drum and with stack emissions. I have never disputed EPA's AP-42 numbers for stack emissions.

Under "Moisture"the contention is that the visible emissions are probably moisture. As stated in my letters, if this were so, one would expect the steam to dissipate with a clean edge and not spread out in a cloud of blue smoke with no distinctive boundaries. I am very familiar with EPA-suggested protocol on observing stack emissions and the Ringelmann technique. The author assumes that the residual moisture evaporates to steam during truck loading. It is more likely taht this would occur when the asphalt is sprayed onto the hot stone and gravel and that this evaporation occurs in the mixing drum and is captured by the control device for the mixing drum. Nevertheless, by using the volume of the cloud created during this step, as measured off photographs, it can be shown that the moisture in the cloud would not reach saturation and therefore would not be visible. This calculation is presented in the response to the Cambridge Environmental letter.

The release agents in use today are mainly water-based, detergent-rich foamy materials. I have never attributed VOC emissions to this source.

I agree with the comment that emissions increase when recycled asphalt pavement is used.

The issue of asphalt content of hot mix has already been addressed.

3. Letter from NAPA

It is interesting that NAPA has already concluded that "We also believe that we are dealing with a relatively minor source of air emissions from the typical asphalt facility". I am also not sure what NAPA means by "avoiding action that might further inflame the local situation in Massachusetts".

These comments lend weight to my concerns that critical tests to measure fugitives are being designed by an industry group with a considerable financial interest in the outcome of the tests.

Overall, I have serious concerns of how the EPA, the regulatory Agency, can allow "the fox to guard the chicken coop".

4. Letter from Cambridge Environmental

This letter was a result of work done by Cambridge Environmental for the Town of Uxbridge, Mass. In a public meeting in Uxbridge, Dr. Zemba, the principal author of the letter, reversed his position and stated that he now believed that the calculations are in the correct range, or only modestly overestimate the actual emissions. Specifically, he said, " When I originally looked at the calculations, I thought that these were grossly overestimated. I can see your point though and they might not be overestimated by as much as I originally thought." He also admitted that he had not studied my two 1995 letters to the EPA until after the report draft had been submitted. Thus, my critique of his work will be relatively short.

His critique of the use of mass transfer equation is that there needs to be adequate internal mixing within the liquid. It can be shown, assuming that molecular mixing, the slowest possible process, is rate controlling, that the flux of molecules of the volatile fraction to the evaporating surface can be sustained.

Before presenting this calculation, I want to reiterate the mechanism of mass transfer.

1. The first step is the diffusion of the light fraction through the bulk of the asphalt liquid to the evaporating surface. The asphalt is hot, at 300 ^{0} F, and has a viscosity of about 2 centipoise at this temperature, very close to that of water. It is present as a coating on the particles of crushed stone and the evaporating surface is the total surface of the stone or a slightly smaller surface area because of agglomeration.

2. The light fraction evaporates from this surface.

3. The vapor is removed from the interstices because of its buoyancy and because of air flow across the top surface of the loose pile of hot mix in the truck, which creates a draft and "pumps" the vapor from the interstices.

The mass transfer equation calculates a mass rate of 21.1 g/s for the third step. (See page A-2 of my letter of November 7, 1994.) Thus the question is whether the first step, molecular diffusion, is capable of supporting this rate of mass transfer.

The integrated form of Fick's law can be used to address this question:

$$\text{mass rate (g/s)} = D*A*M*\Delta C/\Delta x$$

where D = diffusion coefficient

A = area
M = molecular weight of light fraction
ΔC =concentration gradient
Δx = thickness of boundary layer

The diffusion coefficient for water is $2*10^{-5}$ cm^2/s. Assume that the diffusion coefficient for the light ends in hot asphalt is 10^{-7}. Based on data on diffusion in polymers[1], this assumption appears reasonable and conservative since the viscosity of asphalt at this temperature is about the same as that of water.

The area of the evaporating surface, based on an effective diameter of 2" (consistent with Tables 2 and 3 of my letter to Ron Ryan of November 16, 1995) is 10^7 cm^2.

The molecular weight of the light fraction is assumed to be 150.

The concentration gradient is C_{bulk} - $C_{surface}$. Since the material is evaporating at the surface, $C_{surface}$ is zero. C_{bulk} can be estimated at 0.1 g/cm^3. This is probably a low estimate since EPA measurements[2] would indicate that the VOC content of this material would be about 29% or the concentration could be as high as 0.29 g/cm^3.

Finally, the limiting film thickness under agitation, the Nernst layer, has been estimated[3] to be 10^{-3} cm. Since there is little or no agitation in this case, the film thickness can be increased by two orders of magnitude to 0.1 cm.

Based on these parameters, the mass transfer rate is 150 g/s which is more than adequate to sustain the mass transfer in the third step. Also note that in this calculation, every parameter used was valued conservatively and this shows that molecular diffusion is not a slow step under these conditions.

In the second paragraph on page 2, the authors present two footnotes that provide global conclusions, yet the conclusions can't be verified since these are not real references but their opinions. Similarly, in the second half of this paragraph, the authors miss the point that hot mix

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1. Sherwood, Pigford and Wilke, "**Mass Transfer**", McGraw-Hill, 1975, page 46.

2. "EVALUATION OF VOC EMISSIONS FROM HEATED ROOFING ASPHALT" by Accurex Environmental Corporation, EPA-600/2-91-061. November 1991, Tables 3 to 11.

3. G.F. Kortum and J. O'M. Bockris, "**Textbook of Electrochemistry**", Vol. 2, 403 - 405, Elsevier Publishing Co., Amsterdam, 1951.

in a truck is a loose pile which has a large surface. The authors also misstate the viscosity of asphalt. The viscosity of water is 1 centipoise while that of asphalt cement at 140^0 F, depending on the grade, varies from 5 to 30 centipoise, as given in specific Material Safety Data Sheets, and drops rapidly with increasing temperature, so that it is in the range of 2 to 4 centipoise at 300^0 F. Nowhere have I seen it to be 50 centipoise at the operating temperature.

On pages 3 and 4, Cambridge Environmental calculate the cooling of the surface based on heat transfer to the air. These calculations are summarized in Table 1 on page 5. The numbers in the Table show that there is something seriously wrong with their calculations. This problem might be the result of their not understanding the nature of the actual surface at which the light ends evaporate. In Massachusetts, the minimum temperature of hot mix at the delivery point, as defined by Mass Dept of Highways' regulations, is 275 ^{0}F. Colder hot mix is rejected. The table shows that any truck could never leave the plant doors since it would cool down to below this minimum delivery temperature in one minute. In reality, while the total evaporating surface will cool down because of evaporation, heat transfer from the heated stone and gravel to the surface keeps the temperature more or less constant. This is the reason why asphalt trucks can deliver hot mix to a site as far as 50 miles away.

I will not discuss their nitpicks about vapor pressure since this has been dealt with in Section A of this letter.

In the third paragraph on page 7, they discuss the mass balance calculation. I am afraid that the authors make several claims that are incorrect. For example, they state that "the fume concentration .... was taken in a study of asphalt fumes generated at much higher temperatures than those of interest to an HMA asphalt facility". This statement is not quite correct. The Hansen paper[4] only mentions the temperature at which the asphalt mastic is transported in a closed, heated container; not the temperature at which it is applied after it is transferred to the work site in small buckets.

In Hansen's work, the concentration of hydrocarbons was measured as condensed particulates with personal monitors. Even if water vapor were present, it would not have been measured. Thus, they measured only hydrocarbons and not hydrocarbons plus water. Thus, their statement that "a portion (perhaps substantial) of the cloud may be water vapor and not condensing VOCs" is incorrect as is their conclusion.

Finally, it can be shown that the visible emissions are not water, based not only on visual observations of the absence of a disappearing cloud of steam but also on calculations which show

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4. E. S. Hansen, "Cancer Incidence in an Occupational Cohort Exposed to Bitumen Fumes", **Scandinavian Journal of Work, Environment and Health**, Vol 15, No. 2, (1989) pp. 101 - 105.

condensation under conditions when such clouds have been observed. If 10 lb of water are present in 5 tons of hot mix, (page 7, paragraph 3) and the volume of the cloud is 510 cubic meters or 18,000 cubic ft. (see page A-5 of my letter of November 7, 1994), this moisture increases the humidity of ambient air by 0.008 lb. water per lb.of dry air. A review of any psychrometric chart will show that this incremental amount of moisture would not lead to visible condensation of water, except perhaps on a very humid July day. These are not the conditions when such emissions have been observed and photographed.

Finally, the authors quote an EPA emission factor for pug mills in batch plants to attempt to discredit the calculations. They conclude that the EPA emissions factor is "about an order of magnitude smaller than Dr. Nadkarni's estimate for truck loadout", or my calculations are too high by an order of magnitude. The pug mill area in a batch plant is totally enclosed therefore the conditions under which the organics are removed from this enclosure are quite different compared to truck loadout, where there is a high relative velocity between the hot mix and air. Second, my calculation has focused on total organic emissions, not just VOCs. Since EPA analysis of asphalt fume[2] seems to indicate that VOCs are only about 29% of total emissions, it would appear that the EPA emission factor, when adjusted in this fashion for total organics is within a factor of 3 of the numbers calculated in my original paper, even under these poor evaporative conditions.

Please call me if you have any questions.

Sincerely,

Ravi Nadkarni

Ravi Nadkarni

cc:
Ronald Ryan, OAQPS (MD-10)
Senator Edward Kennedy
John DeVillars EPA Region I
Rep. Peter Blute
Lloyd Fillion
Norma Marshall
John Seitz, OAQPS (MD-14)
Senator John Kerry
Rep. Joseph Moakley
Rep. Joseph Kennedy
Konrad Schultz

EXHIBIT A

NAPA
NATIONAL ASPHALT PAVEMENT ASSOCIATION
NAPA Building ■ 5100 Forbes Boulevard ■ Lanham, Maryland 20706-4413 ■ Tel: (301) 731-4748 ■ Fax: (301) 731-4621
Mike Acott, President

VIA FACSIMILE (407) 578-0577

August 11, 1994

Mr. Dave Brashears
Gencor Industries, Inc.
5201 N. Orange Blossom Trail
Orlando, FL 32810

Dear Dave:

As discussed in our phone conversation today, as far as I know there is no current test method to determine the vapor pressure of asphalt materials. The test method used for lighter petroleum products such as gasoline or kerosine is called the "Reid" vapor pressure method. This method requires that the material be poured through a small hole or orifice into the meter. The meter is then shaken to measure the vapor pressure of the material.

This method will not work for asphalt since the asphalt material will plug the opening to the pressure gauge side of the meter. There are also concerns about having to heat the material to get it into the meter's container and whether the test can be performed at an elevated temperature.

Since no direct measure of vapor pressure is available, a calculation of the vapor pressure has been developed. I have attached a figure from Petroleum Refinery Engineering which can be utilized to extrapolate a vapor pressure for asphalt cement at a temperature of 300 °F. I have connected the material's temperature of 300 °F to an initial boiling point for asphalt of 750 °F. The nomograph yields a vapor pressure of less than 0.5 mm of mercury, or less than 0.01 psi.

I would consider this to be a conservative valve since the actual initial boiling point of asphalt cement is normally closer to 1000 °F, which will yield a lower value.

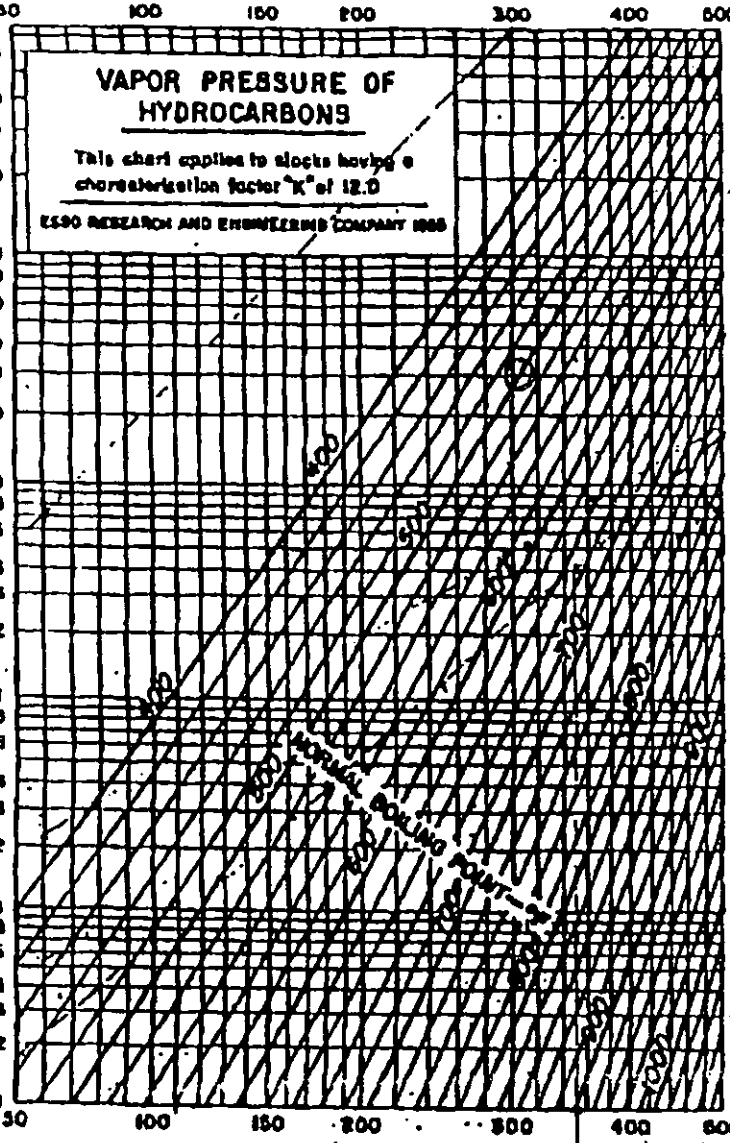
I trust this information will be of assistance. Should you have any questions or if we can be of any further assistance, do not hesitate to contact our office.

Respectfully,

TEB

Thomas E. Brumagin, P.E.
Director of Environmental
and Safety Services

Attachment



5-25. Vapor pressure of hydrocarbon oils (low range). (*Esso Research and Eng.*

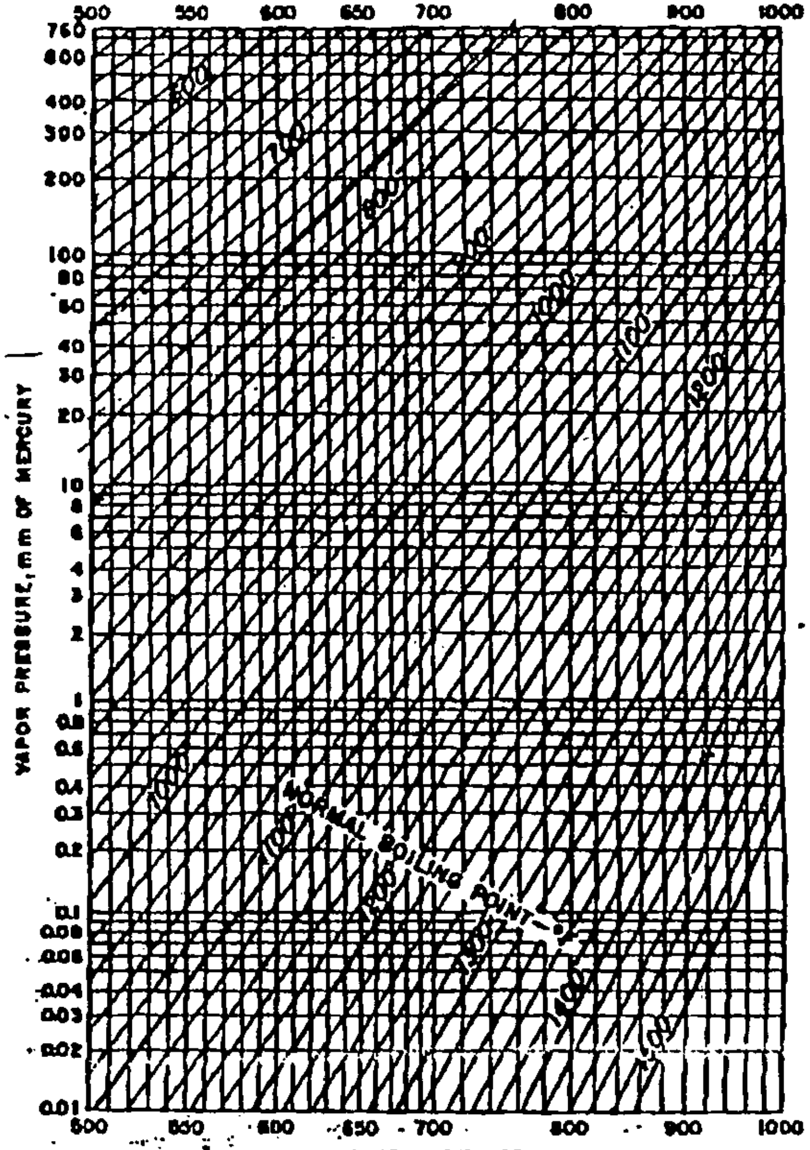


Fig. 5-26. Vapor pressure of hydrocarbon oils (high range). (*Esso Research and Eng. Co.*)

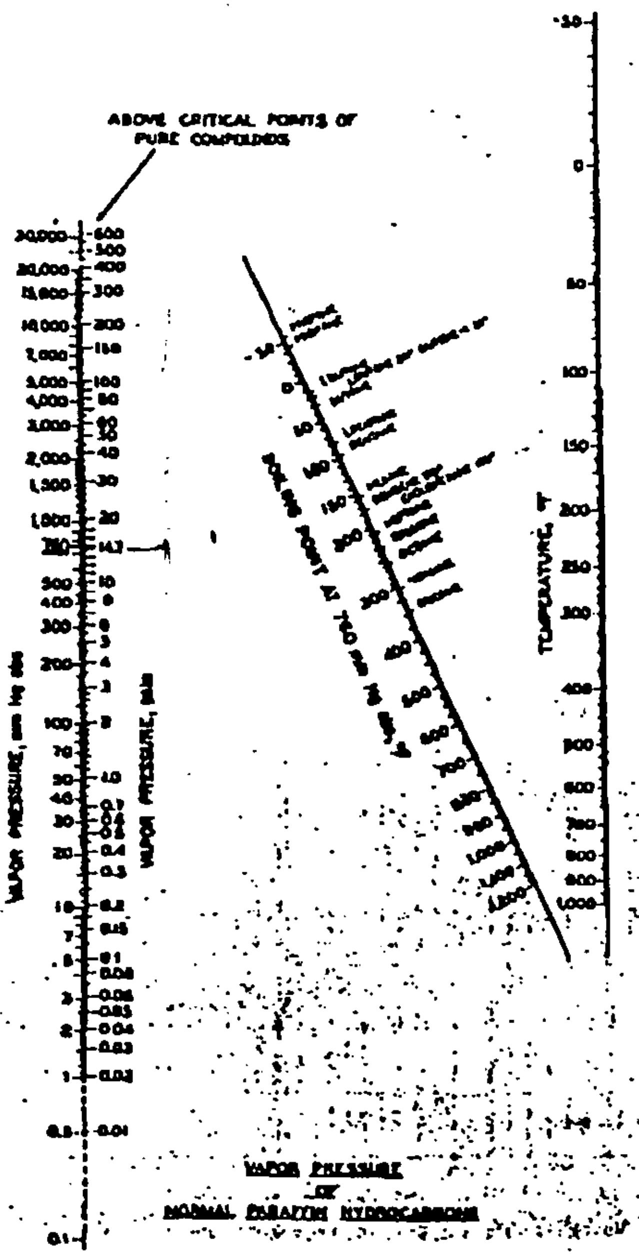


Fig. 5-27. Vapor pressure and boiling-point corrections for normal paraffin hydrocarbons and petroleum fractions.

Width of boiling range as in a petroleum fraction appears to have little effect on the change of boiling point with pressure.[29] Inherently, the *true-boiling-point* type of distillation curve should correlate most exactly because it consists of the boiling points of nearly pure materials as they distill one by one. The equilibrium flash vaporization curves illustrate the other extreme type of distillation curve, and corrections of this curve from one pressure to another should not be exactly the same as the correction for fractionating distillations. Nevertheless, a large difference does not seem to exist between these two extremes of boiling-point corrections, nor does the slope of the distillation curve seem to alter the vapor-pressure or boiling-point corrections to a great extent.

Piromoov and Beiswenger[30] find that the slopes of flash-vaporization curves are practically independent of pressure, so that the correction of the boiling point or flash-vaporization point is a constant number of degrees throughout the entire curve. They suggest that the correction should be determined by correcting the intersection point between the true-boiling-point curve and the flash-vaporization curve by the vapor-pressure data of the paraffin hydrocarbons. The intersection point is used because the true-boiling-point curve and the flash-vaporization curve intersect at approximately the same percentage point regardless of pressure.

Edmister, Reidel, and Mervin[31] have determined flash-vaporization curves on three oils up to pressures of 200 psia. They find that the higher the pressure the flatter the vaporization curve, and hence the curves at high pressures should not be drawn parallel to the atmospheric-pressure curve. Obviously, the flash curve should be horizontal at the critical pressure, and hence the slope of the flash curve will be flatter and flatter as the pressure is increased. They find that the 50 per cent atmospheric boiling point should be corrected to the new pressure by using the vapor-pressure relationship of the paraffin hydrocarbons (Fig. 5-27). In practical design computations it is common practice to convert to the new pressure by using any convenient point on the atmospheric flash-vaporization curve. Refer also to Figs. 4-22 and 15-13.

Compression or Expansion. When gases or vapors are expanded or compressed under adiabatic conditions, the amount of work done and the amount of heat required are dependent upon the ratio of the specific heat at constant pressure to the specific heat at constant volume. The expansion of a gas can always be expressed by an equation of the form

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[29] Nelson and Haltenberger, *Oil Gas J.*, June 11, p. 38, and June 18, p. 40, 1942.

[30] Equilibrium Vaporization of Oils and the Carrying Effects of Light Ends, *API Bull.* 10, no. 2, sec. II, p. 52, 1929.

[31] Equilibrium Flash Vaporization of Three Petroleum Fractions, *Trans. A.I.Ch.E.*, 39, 457 (1943).

EXHIBIT B

7.20 Ravindra M. Nadkarni, P.E.

Received from: Ravindra M. Nadkarni, P.E.

Date: October 20, 1994

7.20.1 Emission Sources

Figure 11, Potential Air Emission Points, is reproduced from the EPA publication AP-42 and indicates all potential emission points at the facility. A complete list of these points, both fuel combustion and process fugitive, is included in Section 5.1.2, Source Emissions and Stack Data.

Quantifying fugitive emissions is difficult, at best, as demonstrated by the lack of estimation techniques published in the Hot Mix Asphalt section of AP-42. Where possible, however, these sources have been estimated (see Section 6.1.3, Fugitive Emission Estimates). More important are the controls to mitigate any effect from these fugitive sources. The proponent has proposed an extensive list of fugitive emission controls in Section 6.1.2 for each possible PM_{10} or VOC fugitive source at the facility.

7.20.2 Fugitive VOCs from Asphalt Trucks

A set of engineering calculations is presented by the commenter which contain many assumptions leading up to the calculation of 38 to 699 tons per year of fugitive emissions for annual production of 670,000 tons of asphalt. Among the many assumptions used to arrive at these numbers is the asphalt vapor pressure at 300°F. The commenter assumed that the vapor pressure was 30 mm of mercury, on average, and would rise at increasing boiling points. However, research data collected by the National Asphalt Pavement Association reveals this assumption to be in error. Since no direct measure of vapor pressure is available, a calculation of vapor pressure has been developed. Figures from *Petroleum Refinery Engineering* can be used to extrapolate a vapor pressure for asphalt cement at a temperature of 300°F. The actual boiling point of asphalt cement is typically between 900°F and 1,000°F. Assuming the lower end of the scale to be conservative, the vapor pressure of asphalt cement is actually less than 0.01 mm of mercury, or four orders of magnitude less than the commenter's assumption. In addition, the light hydrocarbons, such as naphthalene, are present in asphalt cement at very low quantities. The mass transfer analysis that was provided assumes that there is no limitation in the light fractions. Since only the surface of the mix is exposed, only the top surface

temp.

where is it?

WRONG

exposed to the air really has the opportunity to participate in VOC emissions. The analysis done by the commenter assumes there is unlimited supply of these light end VOCs at the interface surface. This is not so.

No emission estimation techniques have been developed by DEP or EPA to quantify the fugitive VOC emissions from asphalt trucks. However, the most recent edition of AP-42 (July 1994) does state "there may be *slight* (emphasis added) fugitive VOC emissions from transport and handling of the hot mix from the drum mixer to the storage silo and also from the load-out operations to the delivery trucks." The evidence does not support any of the rather far-fetched emission guesses put forth by the commenter.

7.20.3 MEPA Review Thresholds

See Response to Comment 7.20.1.

7.20.4 Lowest Achievable Emissions Rate (LAER)

LAER is applicable to new, or modified, major sources of pollution in a non-attainment area. A major source of NO_x or VOC in the Boston area is one with potential emissions greater than 50 tons per year (tpy). Potential emissions of this plant are 6.5 tpy of NO_x and 0.081 tpy of VOC; hence, LAER is not applicable.

7.20.5 Air Toxics

This analysis has been conducted. See Section 5.1.4.4 within the Air Quality Modeling Assessment section.

7.20.6 Emission Sources

Emission rates from a drum mix plant are different than those for a batch plant, as demonstrated in AP-42. The correct emission rates for the site's drum mix plant continue to be used in the SDEIR.

7.20.7 Truck Washing Facility

Truck bodies will be sprayed with an asphalt release agent prior to loading with hot asphalt to prevent bonding of the paving material to the truck body. The release agent will be POLY-SLIP, which is a non-petroleum aqueous-based release agent. There will be no truck washing on-site.

EXHIBIT G

Chemical Engineers' Handbook

McGraw-Hill 1973

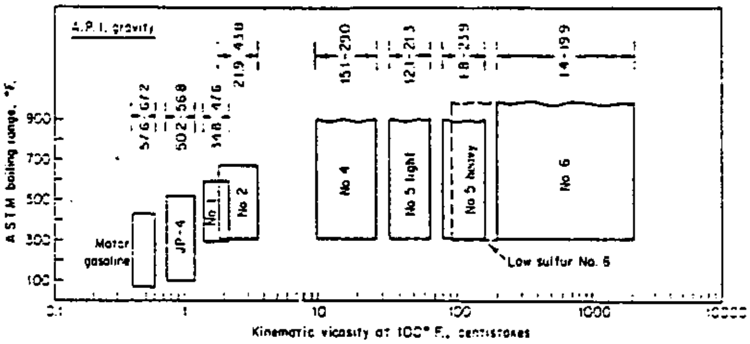

FIG. 9-2. Viscosity, boiling range, and gravity relationships for petroleum fuels.

Table 9-8. Approximate Weights and Heating Values per Cord of Fuel Woods*

Variety of wood	Weight per cord, lb.		Available heat units per cord, million B.t.u.		Equivalent in heat value to tons of coal†	
	Green	Air dry	Green	Air dry	Green	Air dry
Ash, white	4300	3800	19.9	20.5	0.77	0.79
Beech	5000	3900	19.7	20.9	.76	.80
Birch, yellow	5100	4000	19.4	20.9	.75	.80
Chestnut	4900	2700	12.9	15.6	.50	.60
Cottonwood	4200	2500	12.7	15.0	.49	.58
Elm, white	4400	3100	15.8	17.7	.61	.68
Hickory	5700	4600	23.1	24.5	.89	.95
Maple, sugar	5000	3900	20.4	21.5	.78	.84
Maple, red	4700	3200	17.6	19.1	.68	.73
Oak, red	5800	3900	19.6	21.7	.75	.83
Oak, white	5600	4300	22.4	23.9	.86	.92
Pine, yellow	....	....	21.1	22.0	.81	.85
Pine, white	....	....	12.9	14.2	.50	.55
Walnut, black	....	....	18.6	20.8	.72	.80
Willow	4600	2300	10.9	13.5	.42	.52

* The Use of Wood for Fuel. *U.S. Dept. Agr. Bull.* 753.

† Short ton (2000 lb.) of coal having a heating value of 13,000 B.t.u./lb.

LIQUID PETROLEUM FUELS

The principal liquid fuels are made by fractional distillation of petroleum (crude oil), which is a mixture of hydrocarbons and hydrocarbon derivatives ranging in molecular weight from methane to heavy bitumen. As many as half the molecules in crude may contain sulfur atoms; and some contain nitrogen, oxygen, vanadium, nickel, or arsenic, depending on the crude source. Desulfurization, hydrogenation, cracking (to lower molecular weight), and other refining processes may be performed on selected fractions before they are blended and marketed as fuels. Viscosity-gravity-boiling range relationships of the more common fuels are shown in Fig. 9-2.

The highly viscous oil that is solvent-extracted from tar sands on a limited commercial scale is also a grade of crude petroleum. By hydrogenation and subsequent refining, it is converted into conventional petroleum products.

Specifications. Broad specifications developed by the American Society for Testing and Materials are widely used in the United States to classify fuels into types. Table 9-10 shows A.S.T.M. Burner Fuel Specification D 396. Some low-sulfur residual fuels of high wax content do not conform to the A.S.T.M. categories because they require heated storage and handling like No. 6 but, when warm, are in the No. 5 viscosity range. Some industrial fuels fall between No. 2 and No. 4 in gravity and viscosity and are covered by agreements established between seller and purchaser.

Equipment manufacturers and large-volume users (military services, government agencies, airlines, utility companies, corporations) often write their own fuel specifications to suit particular equipment, operating conditions, and economics. Non-standard test procedures and restrictive test limits should be avoided in specifications; they reduce the availability of fuel and increase its cost.

In drawing contracts and making acceptance tests, it is advisable to refer to A.S.T.M. Standards, Parts 17 and 18 (American Society for Testing and Materials, Philadelphia, annual). Part 17 contains most of the pertinent test methods and also contains specifications (classifications) for fuel oil, motor and aviation gasoline, diesel fuel oil, aviation and gas-turbine fuel. Part 18 contains additional procedures, including A.S.T.M. D 270, Method of Sampling Petroleum Products, with detailed sampling procedures for bulk oil in tanks, barges, etc.

Table 9-9. Waste Fuel Analyses*

Type of waste	Heating value, B.t.u./lb.	Percentage composition					Density, lb./cu. ft.
		Volatiles	Moisture	Ash	Sulfur	Dry combustible	
Paper	7,572	84.6	10.2	6.0	0.20		
Wood	8,613	84.9	20.0	1.0	0.05		
Rags	7,652	93.6	10.0	2.5	0.13		
Garbage	8,484	53.3	72.0	16.0	0.52		
Coated fabric—rubber	10,996	81.2	1.04	21.2	0.79	75.60	23.9
Coated felt—vinyl	11,054	80.87	1.50	11.39	0.50	88.61	10.7
Coated fabric—vinyl	8,899	81.06	1.48	6.33	0.02	93.67	10.1
Polyethylene film	19,161	99.02	0.15	1.49	0	98.51	3.7
Foam—scrap	12,283	75.73	9.72	25.30	1.41	74.70	9.1
Tape—resin-covered glass	7,907	15.08	0.51	56.73	0.02	43.27	9.5
Fabric—nylon	13,202	100.00	1.72	0.13	0	99.87	6.4
Vinyl scrap	11,428	75.06	0.56	4.56	0.02	95.44	23.4

* From Hescheles, MECAR Conference on Waste Disposal, New York, 1968, and from "Refuse Collection Practice," 3d ed., American Public Works Association, Chicago, 1966.

Table 9-10. A.S.T.M. Detailed Requirements for Fuel Oils*

Fuel oil grade	Description and requirements for use	Flash point, °F. (°C.)	Pour point, °F. (°C.)	Water and sediment, vol. %	Carbon residue on 10% bottoms, %	Ash, wt. %	Distillation temperature, °F. (°C.)			Saybolt viscosity, sec.				Kinematic viscosity, centistokes				Gravity, °A.P.I.	Copper strip corrosion
							10% point	90% point		Universal at 100°F. (38°C.)		Furol at 122°F. (50°C.)		At 100°F. (38°C.)		At 122°F. (50°C.)			
		Min.	Max.	Max.	Max.	Max.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
No. 1	A distillate oil intended for vaporizing pot-type burners and other burners requiring this grade of fuel	100 or legal (38)	0	Trace	0.15	...	420 (215)	...	550 (288)	...	...	...	...	1.4	2.2	...	...	35	No. 3
No. 2	A distillate oil for general-purpose domestic heating for use in burners not requiring No. 1 fuel oil	100 or legal (38)	20 (−7)	0.10	0.35	...	...	540 (282)	640 (338)	(32.6)	(37.93)	...	...	2.0	3.6	...	...	30	
No. 4	Preheating not usually required for handling or burning	130 or legal (55)	20 (−7)	0.50	...	0.10	...	...	...	45	125	...	...	(5.8)	(26.4)				
No. 5 (light)	Preheating may be required depending on climate and equipment	130 or legal (55)	...	1.00	...	0.10	...	...	...	150	300	...	...	(32)	(65)				
No. 5 (heavy)	Preheating may be required for burning and, in cold climates, may be required for handling	130 or legal (55)	...	1.00	...	0.10	...	...	...	350	750	(23)	(40)	(75)	(162)	(42)	(81)		
No. 6	Preheating required for burning and handling	150 (65)	...	2.00	...	...	...	...	...	(900)	(9000)	45	300	...	...	(92)	(633)		

*A.S.T.M. Burner Fuel Specification D 396.

Table 9-11. Typical Ultimate Analyses of Petroleum Fuels

Composition, %	No. 1 fuel oil (41.5°A.P.I.)	No. 2 fuel oil (33°A.P.I.)	No. 4 fuel oil (23.2°A.P.I.)	Low sulfur, No. 5 F.O. (12.8°A.P.I.)	High sulfur, No. 6 (15.5°A.P.I.)
Carbon	86.4	87.3	86.47	87.26	84.67
Hydrogen	13.6	12.6	11.65	10.49	11.02
Oxygen	0.01	0.04	0.27	0.64	0.38
Nitrogen	0.003	0.006	0.24	0.28	0.18
Sulfur	0.09	0.22	1.35	0.84	3.97
Ash	<0.01	<0.01	0.02	0.04	0.02
C/H Ratio	6.35	6.93	7.42	8.31	7.62

Chemical and Physical Properties. Petroleum fuels consist primarily of paraffins, isoparaffins, aromatics, and naphthenes, plus related hydrocarbon derivatives of sulfur, oxygen, and nitrogen that were not removed by refining. Olefins are absent or negligible except where created by cracking or other severe refining. Vanadium and nickel compounds are low in volatility and do not distill into the No. 1 and No. 2 fuel oil fractions. Vacuum-tower distillates with a final boiling point equivalent to 850 to 1050°F. at atmospheric pressure are occasionally available as fuel not conforming with A.S.T.M. specifications and may contain 0.1 to 0.5 p.p.m. vanadium and nickel.

The black, viscous distillation-tower bottoms (residuum) may be taken directly from the still and burned as industrial fuel without cooling below 450°F., or may be blended into the residual fuels of commerce. Diluted with 5 to 20 per cent distillate this becomes No. 6 fuel oil, or it may be cut back with 20 to 50 per cent distillate to make No. 4 and 5 fuel oils for commercial use, as in schools and apartment houses. Distillate-residual blends are also used as diesel fuel in large stationary and marine engines. However, distillates with inadequate solvent power will precipitate asphaltenes and other high-molecular-weight colloids from "visbroken" (severely heated) residuals. A blotter test, A.S.T.M. D 2781, can be used to detect sludge in pilot blends. Centrifuge tests, filtration tests, and microscopic examination have also been used.

No. 6 fuel oil contains 10 to 500 p.p.m. vanadium and nickel in complex organic molecules, principally porphyrins, which cannot economically be refined out of the oil. Salt, sand, rust, and dirt may also be present, giving No. 6 a typical ash content of 0.01 to 0.5 per cent by weight.

Ultimate analyses of some typical fuels are shown in Table 9-11. Table 9-12 gives analyses of a typical fuel oil ash and the corresponding boiler slag.

Hydrogen content of petroleum fuels correlates approximately with specific gravity and can be calculated from the following formula, which is accurate to within about 1 per cent for petroleum liquids that contain no sulfur, water, or ash:

$$H = 26 - 15s \qquad (9\text{-}8)$$

where H = per cent hydrogen, and s = specific gravity at 60°/60°F. Schmidt ("Fuel Oil Manual," 3d ed., Industrial Press, New York, 1969) improves the precision of the formula by replacing 26 with 24.50 for fuels of 0 to 9°A.P.I. gravity, 25.00 for 10 to 20°A.P.I. gravity, 25.20 for 21 to 30°A.P.I. gravity, and 25.45 for 31 to 45°A.P.I. gravity.

Table 9-12. Typical Slag from Boiler Fired with No. 6 Fuel Oil*

	Oil ash, %	Superheater deposit, %
SiO_2	1.7	7.0
Al_2O_3	0.3	4.1
Fe_2O_3	3.5	5.8
CaO	1.7	4.5
MgO	1.1	2.5
NiO	1.9	1.1
V_2O_5	7.9	0.9
Na_2O	31.5	23.7
SO_3	42.3	46.4

* From McIlroy, Holler, and Lee, A.S.M.E., Paper no. 52-A-160

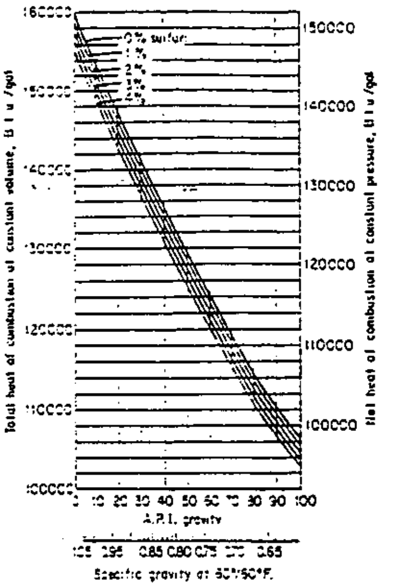

FIG. 9-3. Heat of combustion of petroleum fuels.

Gravity is usually determined at ambient temperature with specialized hydrometers, corrected to 60°F., and expressed in degrees A.P.I., a scale that is related inversely to specific gravity s at 60°/60°F. as follows (see also the abscissa scale of Fig. 9-3):

$$\text{Degrees A.P.I.} = \frac{141.5}{s} - 131.5 \qquad (9\text{-}9)$$

The hydrogen content, heat of combustion, thermal expansion, specific heat, and thermal conductivity data herein were abstracted from *Bur. Standards Misc. Publ.* 97, Thermal Properties of Petroleum Products. These data are widely reproduced and used, although the original bulletin has been out of print more than 30 years, and although newer correlations have appeared, notably that by Linden and Othmer [*Chem. Eng.*, 54(4,5), April and May, 1947].

Heat of combustion also correlates with fuel gravity and can be estimated to within 1 per cent from Fig. 9-3. Corrections for water and sediment must be applied for residual fuels. The corrections are generally insignificant for the distillate fuels because of the low concentration of these impurities.

Viscosity-temperature relationships for typical petroleum fuels are shown in Fig. 9-4. Petroleum fuels between the temperature limits of solidification and vaporization and at pressures of less than 1000 lb./sq. in. are practically newtonian liquids, but at low temperatures where solids begin to separate, petroleum fuels become non-newtonian and the viscosity is dependent on the rate of shear.

Pour point ranges from < −60°F. for some kerosene-type jet fuels to > +115°F. for waxy No. 6 fuel oils, and the viscosity-temperature relationships in Fig. 9-4 are not valid at temperatures near the pour point.

The drop in viscosity with increasing temperature is considerably steeper for some fuels than for others. Generalized viscosity charts become less reliable at temperatures substantially removed from the specification temperatures of 100 or 122°F.

The earlier marine designations of Bunker Fuel Oils are being abandoned in the United States. Bunker C is now considered an alternative name for No. 6. Originally, Bunker C and B were fuels in the upper and lower viscosity ranges, respectively, of the No. 6 classification; and Bunker A was a No. 5 fuel.

Fuel systems for No. 6 fuel oil are usually designed to preheat the fuel to 90 to 120°F. to reduce the viscosity for handling, and

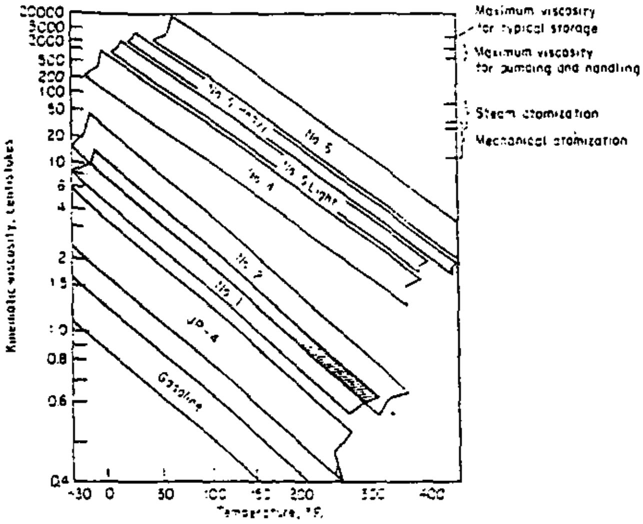

Fig. 9-4. Viscosity-temperature relationships for typical petroleum fuels.

to heat the fuel to 165 to 200°F. to reduce the viscosity further for proper atomization. Steam or electric heating of lines is employed as required by climatic conditions, length of line, and frequency of use. Fuels of No. 2 grade or lighter are not usually preheated; one exception is that industrial gas turbines often require preheating No. 2 fuel oil to a viscosity of 12 centistokes or less for cold starts in winter.

The thermal *expansion of petroleum* fuels can be estimated by the use of the following coefficients, expressed as volume change per unit volume per °F.:

A.P.I. gravity	Coefficient
Below 14.9	0.00035
15.0–34.9	.00040
35.0–50.9	.00050
51.0–63.9	.00060
64.0–78.9	.00070
79.0–88.9	.00080
89.0–93.9	.00085
94.0–100.0	.00090

A.S.T.M.-I.P. Petroleum Measurement Tables (A.S.T.M. D 1250 or I.P. 200), published by American Society for Testing and Materials, should be used for volume corrections in commercial transactions. Pressure relief arrangements may be required on sections of heated pipe lines where fuel could be inadvertently closed between valves. Fuel can expand several *per cent* between 60 and 212°F.

The specific heat of petroleum liquids between 32 and 400°F., having a specific gravity of 0.75 *to 0.96 at 60°/60°F.*, can be calculated within 2 to 4 per cent of the experimental values from the following equation:

$$c = \frac{0.388 + 0.00045t}{s} \qquad (9\text{-}10)$$

where c = specific heat, B.t.u./(lb.)(°F.) or cal./(g.)(°C.); t = temperature, °F.; and s = specific gravity, 60°/60°F. Specific heat varies with temperature, and an arithmetic average *of the specific* heats at the initial and final temperatures can be used for calculations related to the heating or cooling of oil.

The thermal conductivity of liquid petroleum products in B.t.u./(hr.)(sq. ft.)(°F./in.) is given in Table 9-13. Thermal-conductivity coefficients for asphalt and paraffin wax in their solid states are 1.2 and 1.6, respectively, for temperatures above 32°F.

Commercial Considerations. Fuels are sold in gallons, and in multiples of the 42-gal. barrel and, outside the United States, in long tons, metric tons, liters, cubic meters, and Imperial gallons. Transactions exceeding 500 to 10,000 gal. usually involve volume corrections back to 60°F. for accounting purposes.

Fuel passes through an air eliminator and mechanical meter when loaded into or dispensed from trucks. Larger transfers such as pipe-line, barge, or tanker movements are measured by fuel depth in tanks and vessels. After an appropriate settling period, water *in the tank* bottom is measured with a plumb bob or stick smeared with water-detecting paste.

Receipts of tank-car quantities or larger are usually checked for gravity, appearance, and flash point to confirm product identification *and absence* of contamination.

Safety Considerations. Design and location of storage tanks, vents, *piping*, and connections are specified by state fire marshals, Underwriters' Codes, and local ordinances. Liquid petroleum fuels are classified *in the following* categories for safety in transportation and handling:

Flammable *liquid means* any liquid having a flash point below 140°F. and having a vapor pressure not exceeding 40 lb./sq. in. abs. at 100°F. *Flammable liquids* are divided into two classes:

Class I liquids include those having flash points below 100°F. and may be subdivided *as follows:* Class IA includes those having flash points below 73°F. and having a boiling point below 100°F.; Class IB includes those having flash *points below* 73°F. and having a boiling point at or above 100°F.; Class IC includes those having flash points at or above 73°F. and *below 100°F.*

Class II liquids include those having flash points at or above 100°F. and below 140°F.

Combustible liquid means any liquid having a flash point at or above 140°F. and below 200°F. and is *known* as Class III liquid.

When heated to temperatures equal to or higher than their flash points, Class II and III liquids are subject *to the same* handling regulations as flammable liquids (Classes I and II). These regulations may also be applied to liquids with flash points above 200°F. (which are not in Classes I, II and III) when they are so heated.

NON-PETROLEUM LIQUID FUELS

Coal-tar fuels are made from the higher-boiling fractions (over about 450°F.) of the crude tar produced by coke ovens and coal retorts at gas works. The available grades range from liquids of 30 sec. viscosity at 100°F. (Redwood No. 1) to a *pulverizable pitch.* Chemically they are mixtures of hydrocarbons, phenols, and heterocyclic nitrogen, oxygen, and sulfur compounds. They *are much* more aromatic than petroleum fuels and burn with a more luminous flame. Sulfur and ash contents are usually low. The *ash*, unlike petroleum ash, is high in alkaline earth elements and usually free of vanadium. Typical ultimate analyses are shown in Table 9-14. Over the temperature range of 60 to 400°F., thermal properties are: specific heat, 0.35 to 0.40; thermal conductivity, 0.080 *to* 0.085 B.t.u./(sq. ft.)(hr.)(°F./ft.); latent heat of vaporization, 150 B.t.u./lb.; latent heat of fusion, nil. Extensive additional information *is* presented in the monograph edited by W. H. Huxtable, "Coal Tar Fuels" (Association of Tar Distillers, London, 1961).

Newer techniques are being developed to hydrogenate coal into a crude which can be refined into a spectrum of conventional products in a petroleum refinery.

Oil shale contains little extractable oil, but yields an oil high in nitrogen and oxygen when retorted. This has been hydrogenated

Table 9-13. Thermal Conductivity of Liquid Petroleum Products
B.t.u./(hr.)(sq. ft.)(°F./in.)

Temperature, °F.	Degrees A.P.I. 10	20	30	40	50	60
0	0.82	0.88	0.94	1.00	1.05	1.11
200	.77	.83	.88	0.94	0.99	1.05
400	.72	.77	.83	.88	.93	0.98
600	.67	.72	.77	.82		
900	.63	.67	.71			

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

JUL 30 1996

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Dr. Ravinda M. Nadkarni, P.E.
340 Franklin Street
Wrentham, Massachusetts 02093

Dear Dr. Nadkarni:

We have received your letter dated July 5, 1996 regarding the four comment letters which we received on your proposed method of estimating fugitive emissions from loading hot mix asphalt into trucks. We regret that until now we have not sent you a statement of our own position after receiving the comment letters.

We do not have any specific additional technical comments beyond those contained in Mr. Ron Ryan's letter to you of September 5, 1995. However, after reviewing your letters of October 26, 1995, November 16, 1995, and July 5, 1996, and the four comment letters received, we continue to believe that there are significant uncertainties associated with some of the assumptions needed to apply a theoretical approach. Therefore, we feel that some bench-scale or full-scale testing is needed before we can consider endorsing an estimation technique for this source. Mr. Ron Myers of my staff is coordinating with the National Asphalt Paver's Association on this testing and can be reached at (919) 541-5407 should you have any questions or comments. As always, public review and comment is welcome at any stage of the process.

Sincerely,

David Misenheimer

for David Mobley
Leader
Emission Factor and Inventory Group

cc: James E. Belsky, MA DEP
John Courcier, USEPA Region I
Lloyd Fillion, Coalition Against Asphalt Plants in Boston
R. Gary Fore, National Asphalt Pavement Association
Ron Myers, EFIG (MD-14)
Ron Ryan, EFIG (MD-14)
John Seitz, OAQPS (MD-10)
EFIG Emission Factor Team

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

APR 16 1996

Mr. Lloyd Fillion, Chair
Coalition Against the Asphalt Plant
563 Massachusetts Avenue
Boston, Massachusetts 02118

Dear Mr. Fillion:

Enclosed per your telephone request of April 12, 1996 are copies of the four responses we have received from our February 8, 1996 letter requesting comments on Dr. Nadkarni's proposed method for estimating fugitive emissions from the loading of hot mix asphalt into trucks. In addition to comments from the three parties who were originally sent our request, we have also received comments from Mr. Stephen G. Zemba of Cambridge Environmental, Inc., who telephoned us on February 16 to request copies of the materials. Please contact Mr. Ron Myers of my staff at (919) 541-5407 for details on the proposed action plan by the National Asphalt Pavement Association.

Sincerely,

J. David Mobley
Leader
Emission Factor and Inventory Group

4 Enclosures

cc: Dr. Ravinda M. Nadkarni w/Enclosures

OAQPS:EMAD:EFIG:RRYAN(MOBLEY):4330:4201ALEX 4/15/96 ASPH3.RR

CONCURRENCES

SYMBOL	EFIG							
SURNAME	Mobley	Ryan						
DATE	04/16/96	4/16/96						

EPA Form 1320-1A (1/90) *Printed on Recycled Paper* OFFICIAL FILE COPY

NAPA

NATIONAL ASPHALT PAVEMENT ASSOCIATION

NAPA Building ■ 5100 Forbes Boulevard ■ Lanham, Maryland 20706-4413 ■ Tel: (301) 731-4748 ■ Fax: (301) 731-4621
Mike Acott, President

April 1, 1996

Mr. J. David Mobley, Leader
Emission Factor and Inventory Group
United States Environmental Protection Agency
Research Triangle Park, NC 27711

Reference: FEBRUARY 8, 1996, LETTER FROM MOBLEY, U.S. EPA TO FORE, NATIONAL ASPHALT PAVEMENT ASSOCIATION

Dear Mr. Mobley:

The National Asphalt Pavement Association (NAPA) appreciates the opportunity to provide input as requested in your letter of February 8, 1996. Your request and the attached documentation have been reviewed carefully by NAPA's Emissions Task Force. This is the same group which worked with Ron Myers and the Emissions Factor and Inventory Group over the past five or six years. Most recently, this group has worked with Dennis Beauregard and others to effect a credible and effective Emissions Inventory Improvement Guidance Document (EIIP).

NAPA's Emissions Task Force is made up of Hot Mix Asphalt (HMA) contractors, HMA plant manufacturers, and other technical experts in the Industry who are close to the process and have a thorough technical knowledge relating to air emissions.

After considerable discussion, we agree with the EPA that many parameters in the theoretical approach to estimating truck load-out emissions are subject to significant scientific conjecture. We also believe that we are dealing with a relatively minor source of air emissions from the typical asphalt facility. Regardless of these conclusions, NAPA is anxious to cooperate with the U.S. EPA to pursue more credible and cost effective ideas for estimating truck load-out emissions that are grounded in empirical data. This is entirely consistent with our long standing relationship with the U.S. EPA Emissions Factor and Inventory Group. Our goal would be to work with EPA on this project while avoiding actions that might further inflame the local situation in Massachusetts.

As you are probably aware, representatives from NAPA's Emissions Task Force met with members of the Emissions Factor and Inventory Group on March 13, 1996. As a result of that meeting, we have agreed to explore some cost effective ideas for using data based techniques to estimate truck load-out emissions. Our group has a planned meeting on May 2, 1996, at which time we will put our combined talents to the task of generating an action plan. We will stay in touch with the Emissions Factor and Inventory Group staff for purposes of communication and coordination.

Thank you for the opportunity to offer input and to work with EPA on this subject. NAPA values the long-standing partnership with your group and track record of mutual objectives accomplished.

Sincerely,

R Gary Fore

R. Gary Fore
Director of Regulatory Affairs

RGF/gmm

cc: Ronald B. Ryan
Ron Myers
Dennis Beauregard

Cambridge Environmental Inc
58 Charles Street Cambridge, Massachusetts 02141
617-225-0810 FAX: 617-225-0813 E-mail: camenv58@aol.com

March 29, 1996

Ronald B. Ryan, P.E.
Environmental Engineer
Emission Factor and Inventory Group
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dear Mr. Ryan:

Thank you for forwarding the additional materials on Dr. Nadkarni's calculations of volatile organic compound (VOC) emissions from hot mix asphalt (HMA) as it is loaded out onto trucks. We write *per* your invitation to submit comments on Dr. Nadkarni's calculations.

Our comments were developed as part of our work for the Town of Uxbridge, Massachusetts, for which we are serving as a third-party reviewer of a proposed asphalt plant. We initially received Dr. Nadkarni's comments from the Town's Board of Health, who themselves received a copy as part of comments on the proposed asphalt plant. We have considered Dr. Nadkarni's calculations in some detail, and wish to submit these comments for your own consideration of his analysis.

We appreciate Dr. Nadkarni's effort in attempting to derive emission estimates for this process. Based on our analysis, however, we believe that his emission estimates overpredict the actual levels of VOC emissions from HMA loadout (perhaps by a large margin). Both his calculations and our critique, however, are based on a simple analysis of a complex process. Uncertainties in these calculations are substantial. The best way, in our opinion, to quantify VOC emissions from this process would be to measure them in a well-designed field study or experiment.

Please write or call should you have questions on our comments.

Sincerely,

Richard R Lester

Stephen G. Zemba, Ph.D., P.E.
Senior Engineer

Richard R. Lester
Staff Scientist

enc.

Comments on the Estimation of Emission of Volatile Organic Compounds from Hot Mix Asphalt During Loadout onto Trucks

Stephen G. Zemba, Ph.D., P.E., and Richard R. Lester
Cambridge Environmental Inc.

March 29, 1996

Dr. Nadkarni has applied an empirical, but well-tested (in some applications) method to predict the emission rate of volatile organic compounds (VOCs). The equation he employs predicts a mass flux of a contaminant as the product of a mass transfer velocity and a concentration in air (the film-layer concentration) that would be expected to be found just above the surface of the liquid that is evaporating. The key to the calculations lies in estimating representative values for each of these parameters. The typical approach that Dr. Nadkarni follows is to estimate the mass transfer velocity from an empirical correlation that considers (1) the physical/chemical properties of both the contaminant and air, (2) meteorologic conditions, and (3) the size of the source (in this case, a truck bed). Similarly, he uses another typical assumption in which vapor pressure is used as a surrogate for the film-layer concentration.

Dr. Nadkarni's methods have been employed by engineers in a multitude of applications. We have had experience using these equations in attempting to predict the rates at which contaminants evaporate from polluted surface water. The fundamental question, however, is whether the methods are appropriate for predicting VOC emissions from hot mix asphalt during loadout onto trucks.

Based on our experience and review, we believe that Dr. Nadkarni's calculations *overestimate* actual VOC emissions during loadout, at least by a modest, and perhaps by a substantial, degree. The two main reasons that the calculations overestimate are:

- the mass transfer correlation is applied to a physical situation quite different than what it was designed for, and does not account adequately for resistance to evaporation within the liquid phase; and
- the film-layer concentration is likely to be lower than that predicted by Dr. Nadkarni because the surface temperature of the asphalt, which controls the potential vapor pressure above the liquid phase, is likely to be cooler than the bulk (center region) of the asphalt load.

The mass transfer correlation derives from the results of experiments in which volatile compounds were evaporated from liquid pools. The equation assumes that molecules of a contaminant are available to evaporate at the surface of a pool. To provide this condition, an adequate level of internal mixing is needed in the liquid to provide a fresh source of molecules at the surface. In a one component system (*e.g.*, pure liquid water), mixing is not an issue because all of the liquid molecules are the same (and hence some molecules are always available at the surface). The mass transfer equation was designed for such one component (pure substance) liquids.

In other situations, however, the adequate mixing needed to supply molecules at the surface cannot be assumed. As an example, we attempted to apply the same methodology to a surface water impoundment contaminated with methanol, a fairly mobile organic compound.[1] The emission rate predicted by the mass transfer equation was ten times greater than that measured in field tests.[2] The mixing situation is even more difficult in the case of asphalt. HMA is largely solid aggregate material, and while sitting in the truck, only a thin coating of asphalt cement is exposed to air. Wind cannot penetrate the liquid portion of the asphalt to mix it and thereby bring new molecules of volatile organic compounds (VOCs) to the surface. To move from the center or bottom of the asphalt pile to the surface, VOC molecules would have to rely on molecular diffusion, a process that literally requires years. Thus, the bulk of VOCs present in HMA loaded onto trucks is simply not available to evaporate at the surface.

One could counter that there is a sufficient mass of VOCs present solely in the surface layer to account for the evaporation rate predicted by Dr. Nadkarni (0.75 lbs of VOCs for 5 tons of HMA). A second process, however, is likely to limit the mixing required for mass transfer in the surface layer. Specifically, liquid asphalt, even at a temperature of 300°F, has a viscosity roughly 50 times higher than that of room temperature water (HSDB, 1996). This much higher viscosity inhibits the wind-blown mixing needed to bring new VOC molecules to the surface.

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[1] This methodology is in fact the one recommended by the U.S. EPA.

[2] Some of this difference may have been due to differences in meteorologic conditions assumed for the modeling and those present during the field trials, but we believe that at least part of the difference resulted from the fact that liquid-phase resistance (*i.e.*, the mixing necessary to bring contaminant molecules to the surface to evaporate) was not considered in the mass transfer calculations.

Another factor that suggests Dr. Nadkarni's estimates of VOC emissions are too high relates to the thermal properties of HMA. Specifically, HMA is a relatively poor conductor of heat,[3] which has two implications. First, it provides a sufficient amount of time to allow transport of HMA to a job site and application before it cools and hardens. Second, and of importance to mass transfer calculations, the low thermal conductivity induces a significant temperature gradient from the core of the asphalt to its surface. This means that the surface temperature of HMA will cool faster than the internal temperature. A cooler surface temperature implies a lower vapor pressure, and hence a lower emission rate *per* Dr. Nadkarni's calculations.

The temperature of the HMA leaving the batch tower is more or less uniform, so the rate at which the outer surface cools is of importance. Some sense of the rate of cooling can be obtained from basic heat transfer calculations. To do so, we apply the solution of transient conduction in a semi-infinite media. The asphalt is assumed to be at a uniform initial temperature of 300°F, and exposed to surface cooling by wind. A graphical solution to this problem is available from Incropera and DeWitt (Figure 5.16, p. 206). Estimating HMA surface temperatures as a function of time after loading requires (1) properties of asphalt and air and (2) an estimate of the convective heat transfer coefficient. The latter parameter can be estimated from the heat transfer correlation for a flat plate, which is directly analogous to the mass transfer correlation employed by Dr. Nadkarni:

$$\mathrm{Nu} = \frac{h X_T}{k_a} = 0.037\,\mathrm{Pr}^{1/3}\left[\mathrm{Re}_T^{4/5} - 15{,}500\right] \qquad \textbf{(1)}$$

where the terms are:

Nu	Nusselt number (a dimensionless parameter);
h	convective heat transfer coefficient (W/m^2-K);
k_a	thermal conductivity of air (W/m-K);
X_T	total length of the plate (m);
Re_T	Reynolds number based on the length of the plate; and
Pr	Prandtl number of air.

The same values used by Dr. Nadkarni for X_T (10.67 m) and Re_T (1.4×10^6) are assumed. Typical values of Pr and k_a for air are 0.7 and 0.03 W/m-K, respectively (Incropera and DeWitt, 1981). Using these values in Equation (1), a convective heat transfer coefficient h of 6.3 W/m^2-K is found.

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[3] The thermal conductivity of asphalt is listed to be 0.062 W/m-K, which (as examples) can be compared to the conductivities of glass (1.4 W/m-K), brick (1 W/m-K), and water (0.6 W/m-K) (Incropera and DeWitt, 1981).

For the semi-infinite solid solution, the temperature difference between the interior of the asphalt (T_i) and the surface of the asphalt (T_s), divided by the temperature difference between the interior of the asphalt and the ambient air (T_a), is a function of time and properties of the asphalt:

$$\frac{T_i - T_s}{T_i - T_a} = f\left(\frac{h\sqrt{\alpha t}}{k_h}\right)$$

where the undefined terms are:

t	time after HMA loadout onto the truck (s);
α	thermal diffusivity, which is equal to thermal conductivity (k_h) divided by the specific heat (c_p) and density (ρ_h) [$\alpha = k_h/(c_p \rho_h)$] ($m^2/s$);
k_h	thermal conductivity of asphalt (W/m-K);
c_p	specific heat of asphalt (J/kg-K); and
ρ_h	density of asphalt.

Values of 0.062 W/m-K, 920 W/m-K, and 2115 kg/m^3 are obtained from Incropera and DeWitt (1981) for asphalt. These values yield an α value of 3.2×10^{-8} m^2/s.

Table 1 lists asphalt surface temperatures derived from the graphical solution (Incropera and DeWitt, 1981), assuming 300°F and 70°F for temperatures of the internal asphalt and ambient air, respectively, and using the property values above. After a period of 30 seconds after loadout, the surface temperature is predicted to cool 23 degrees F, from the initial temperature of 300°F to 277°F. After three minutes, the surface temperature is predicted to cool to 249°F (a decrease of 51 degrees from the initial temperature). Surface temperatures at additional times are listed in Table 1.

A cooler asphalt surface has important implications to Dr. Nadkarni's calculations, since he assumes that the film-layer concentration (c_T, from his terminology) is equal to the asphalt vapor pressure, and the vapor pressure in turn depends on the surface temperature of the asphalt. Based on the discussion of vapor pressure below, one would expect c_T values at a surface temperature of 300°F to decrease by factors of about 3 and 10 at surface temperatures of 275°F and 250°F, respectively. To calculate the effect of decreasing surface temperatures on Dr. Nadkarni's emission rates, one must consider the integrated effect of surface cooling, since the asphalt surface temperature starts out at 300°F, but continually decreases after it has been loaded on the truck. We estimate (based on such an integral) that consideration of a changing surface temperature would decrease Dr. Nadkarni's estimates by more than a factor of four over the first three minutes after loadout.[4]

Table 1 Estimated surface temperatures of asphalt loaded onto trucks as a function of time after loadout

Time after HMA loadout (min)	$\frac{h\sqrt{\alpha t}}{k_h}$	$\frac{T_i - T_s}{T_i - T_a}$ Estimated from Figure 5.16 of Incropera and DeWitt (1981)	Surface temperature of HMA (F)
0.5	0.099	0.1	277
1	0.14	0.13	270
2	0.20	0.2	254
3	0.24	0.22	249
5	0.31	0.28	236
10	0.44	0.35	220
60	1.1	0.62	157

Comments by the U.S. EPA (Ryan, 1995) have raised a number of questions. Dr. Nadkarni uses a molecular diffusion coefficient of 0.093 cm^2/s in air, which is appropriate for a relatively low molecular weight compound such as heptane. For a higher molecular weight compound such as anthracene, a value of 0.0324 cm^2/s is more appropriate. If one assumes the latter value to be more appropriate for asphalt vapors, Dr. Nadkarni's emission estimate would decrease by a factor of two.

Perhaps an even greater uncertainty is associated estimating the vapor pressure of asphalt. Dr. Nadkarni demonstrates three methods for estimating vapor pressure, and we, like the U.S. EPA

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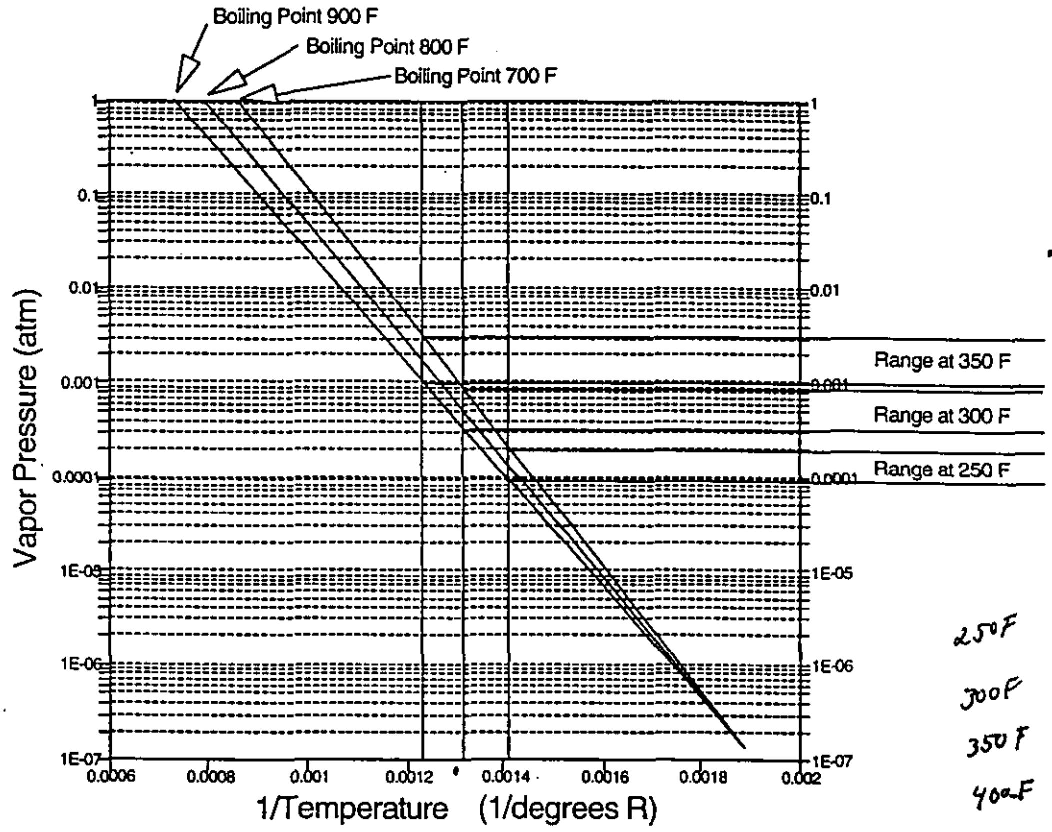
[4] As a quick summary of this calculation, we assume that the vapor pressure is 1/3 its initial value after 30 seconds, and 1/10 its initial value after 3 minutes. If *f* is the fraction of the initial vapor pressure, the time-dependent curve is well described by the equation $f = e^{-\beta\sqrt{t}}$, where β is a value of 0.18, and *t* is in units of seconds. Integrating this equation over a time period from 0 to 180 seconds (3 minutes), an average *f* value of 0.24 is found, which implies a four-fold lower emission rate than that calculated by Dr. Nadkarni.

(Ryan, 1995), have serious concerns over whether the methods are relevant. In particular, Dr. Nadkarni states (p. A-3, 2nd pgh.) that the logarithm of vapor pressure should be proportional to the inverse of absolute temperature. Such a plot is shown in Figure 1. In this figure, the three vapor pressure curves are drawn from the vapor pressure at room temperature (0.0001 mm Hg, or 1.32 × 10^{-7} atm, at 70°F) to the various boiling points considered by Dr. Nadkarni (1 atm [by definition of boiling] at 700, 800, and 900°F). Vertical lines are drawn at temperatures of 350, 300, and 250°F.



250F 1/R = .0014
300F 1/R = .0013
350F 1/R = .00123
400F 1/R = .00116

Figure 1 Asphalt vapor pressure (atm) vs. inverse temperature (1/degrees R).

In Figure 1, the points at which each vertical line intersects the vapor pressure lines represents the range of possible vapor pressures. For 300°F, the typical temperature of HMA, the range is approximately 3 × 10^{-4} to 1 × 10^{-3} atm, which equals 0.2–0.8 mm Hg. This range is considerably lower than the value of 30 mm Hg used by Dr. Nadkarni. As further evidence that Dr. Nadkarni's estimate of vapor pressure may be too high, his own calculations (method 1) assume a temperature of 190°C, or 374°F, which is significantly higher than the typical asphalt temperature of 300°F. Extrapolated downward to 300°F, his own method would yield a vapor pressure on the order of 1 mm Hg.

We suspect that part of the discrepancy between our simple analysis (Figure 1) and Dr. Nadkarni's techniques results from the fact that asphalt is not a single compound, but rather a mixture of compounds that boil over a range of temperatures. To complicate matters, asphaltic concrete varies in composition and grade. Mixtures blended with lighter hydrocarbons may well exhibit vapor pressures on the order of 30 mm Hg. For example, HSDB (1996) provides a reference to a vapor pressure of 19 mm Hg at 300°F. Thus, it is difficult to estimate a vapor pressure appropriate for use in calculations of type made by Dr. Nadkarni.

The final method Dr. Nadkarni uses to support his emission estimate is a simple mass balance calculation based upon an assumed concentration present in vapor clouds that he has observed from above asphalt trucks during loadout. We have two comments regarding this method. First, the upper-end fume concentration of 260 mg/m^3 was taken in a study of asphalt fumes generated at much higher temperatures than those of interest to an HMA paving facility,[5] and thus may grossly overestimate VOC concentrations present in vapor clouds. Second, a portion (perhaps substantial) of the cloud may be water vapor, and not condensing VOCs. The aggregate drying process is not 100% effective. If, for example, a residual water content of 0.1% remained in the HMA, 10 lbs of water would be present in 5 tons of HMA, an amount that can be compared to Dr. Nadkarni's emission estimate of 0.75 lb per 5 tons HMA.

As a whole, we believe that Dr. Nadkarni's calculations overestimate the true levels of VOCs emitted from HMA loaded out onto trucks. As pointed out by the U.S. EPA (Ryan, 1995), if fugitive emissions of VOCs were of the magnitude estimated by Dr. Nadkarni, one would expect to see much higher emission rates of VOCs in batch plants that collect dust and vapors from the pugmill (mixing) area where the asphaltic cement is first introduced. The VOC emission factor listed in U.S. EPA (1994) corresponds to only 0.085 lbs VOCs per 5 tons of asphalt — about an order of magnitude smaller than Dr. Nadkarni's estimate from truck loadout.

All factors considered, we suspect that Dr. Nadkarni's emission estimates are *at least* 10 times greater than actual emissions. There are, however, considerable uncertainties in both his analysis and our critique. The best way to resolve these uncertainties, as noted by Dr. Nadkarni and the U.S. EPA (Ryan, 1995), would be to conduct a direct, well-controlled experimental investigation that takes into account the critical factors related to asphalt loadout (*e.g.*, HMA temperature, drying efficiency, grade of asphaltic cement, *etc.*). We would strongly encourage the U.S. EPA, the National Asphalt Pavement Association, or other national agency to conduct such a study, since its results would be beneficial to all HMA plants.

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[5] The study also involved a different process — indoor use of mastic asphalt.

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WISCONSIN
DEPT. OF NATURAL RESOURCES

State of Wisconsin \ DEPARTMENT OF NATURAL RESOURCES

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March 29, 1996

FILE REF: 4500

Mr. J. David Mobley, Leader
Emission Factor and Inventory Group
Office of Air Quality Planning and Standards
US Environmental Protection Agency
Research Triangle Park, NC 27711

SUBJECT: Comments on Estimation of Fugitive Emissions from Hot Mix Asphalt Paving

Dear Mr. Mobley:

I have been forwarded your request for review of the potential fugitive VOC emissions from the production of hot mix asphalt (HMA). I have dealt with this source category for the previous 7 years involved in a technology transfer team consisting of representatives of the Department of Natural Resources and the industry. I would like to comment on some of the assumptions that Dr. Nadkarni has used to make his calculations.

Asphalt Cement

Formation of asphalt occurs in still bottoms in very high temperatures. These temperatures are not seen in the dryer drum or the pugmill where the asphalt cement is added to the dried aggregate which produces mix at 300 - 325 degrees.

Cracking of the asphalt would be seen in stack emissions tests & blue haze. In other studies on asphalt fumes, the temperature of the material would have to be elevated over 600 degrees to extract any fumes. The contention of loosing 1% of the asphalt cement content to thermal cracking would not likely be acceptable to the design of the mix.

Blending two types of asphalt with different characteristics is common in the industry but the resulting asphalt cement is not blended with light ends such as naptha or kerosene for use at hot-mix plants. This is more likely to occur in the production of cutback asphalts for sealants. These cutback asphalts would not be used in a hot mix plant.

Location of the mixture point may have something to do with emissions of VOC's. A drum mix plant would have the higher emissions as the aggregate & asphalt are being mixed in the drum. Drum mix plants are constructed, however, to have veiling by aggregate rotating through the drum. The introduction of asphalt into the drum is shielded from contact with the flame by a veil of aggregate. If this would cause excessive organic compound emissions, you would see significant "blue smoke" from the stack .

Moisture

Inherent in aggregate, even dried aggreggate, may contain 1-2% moisture. Some of this moisture may be released upon contact of the hot material with the surrounding air.

In air - as hot gasses contact cooler air could cause steam plume (we see more often in the morning when first started up.)

Release agents as a potential source of VOC's

Plants had previously used #1 or #2 diesel oil sprayed into truck boxes (small amount) so that the material would not stick to the truck box. Advances in the state-of-the-art now see other release agents being used such as lime water. More information can be researched on these agents from our Department of Transportation if needed.

Recycled Asphalt Pavement (RAP)

We have seen an increase in the organic compound emissions of HMA plants when processing RAP when there was sealcoating on the old road bed.

Asphalt content of mixes

According to industry representatives, the asphalt content of the mixes in Wisconsin range from 5 - 6.3% rather than the 7-8% used by Dr. Nadkarni.

In summary, based on the physical information of asphalt cement and knowledge of the process, I would believe any significant emissions of VOC's would be seen from the stack. It is hard to determine where 100 + tons of emissions would be created in the process downstream from the dryer drum where this material is colder than when mixed. Quantification of fugitive emissions from the truck loading may be dificult but could be undertaken with monitors placed above the load-in point. Some of the visible emissions witnessed by Dr. Nadkarni may have been water vapor.

Thank you for affording the State of Wisconsin the opportunity of commenting. If you need any further information, I can be reached at (608) 273-5600.

Sincerely,

Lynda M. Wiese
Air Program Supervisor
Wisconsin Department of Natural Resources

cc: AM/7 - Ralph Patterson

Sec. 11.1
Ref. 359

State of North Carolina
Department of Environment,
and Natural Resources

Division of Air Quality
Technical Services Section

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NCDENR

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PAGES including this cover page	10
SUBJECT:	Asphalt

NCDAQ - Liquid Asphalt Terminal Investigation

MEASURED AMBIENT BTEX AT RAILCAR, STORAGE TANK VENT, UPWIND, DOWNWIND, & RESIDENTIAL SITE.
NO RELATION TO PROCESS OPERATIONS
DATA NOT USEFUL FOR EMISSION FACTORS

104952.1.002.06

DIVISION OF AIR QUALITY
TOXICS PROTECTION BRANCH
AIR TOXICS ANALYTICAL SUPPORT TEAM
ANALYTICAL INVESTIGATION OF INMAN ASPHALT TERMINAL
SALISBURY, NORTH CAROLINA, ROWAN COUNTY
Investigation #98015

On April 23, 1998 the Air Toxics Analytical Support Team (ATAST) conducted an investigation of the Inman Asphalt terminal located at 1825 Jake Alexander Boulevard in Salisbury, North Carolina. The investigation was performed upon request by the Mooresville Regional Air Quality Office as the result of odor complaints from a residential area northeast of the facility. The primary objective of this investigation was to assess the ambient impact of BTEX (benzene, toluene, ethyl benzene, and xylene) emitted from the Inman Asphalt terminal. ATAST members Jim Bowyer, Todd Crawford, and William Steinmetz were accompanied by Donna Cook and Debbie Manning of the Mooresville Regional Air Quality Office and Larry Ettel of Inman Asphalt.

REASON FOR INVESTIGATION

The investigation request was submitted to ATAST by Mike Landis, Mooresville Regional Air Quality Supervisor, on March 30, 1998 after several odor complaints were lodged against the Inman facility. Investigational objectives including the sampling itinerary were discussed with the regional office staff in the days prior to the investigation. The facility as well as the complainants were contacted by the Mooresville Regional Air Quality Office prior to our arrival.

INVESTIGATION PROCEDURES

The ATAST, along with Donna Cook and Debbie Manning of the Mooresville Regional Air Quality Office, arrived at the Inman Asphalt terminal about 1030 on April 23, 1998. A brief meeting between DAQ staff and Larry Ettel of Inman Asphalt was conducted upon ATAST's arrival at the facility in order to refine the sampling itinerary. The facility maintained a high level of cooperation during this investigation. The five locations selected for air sampling included an open liquid asphalt railcar hatch, a liquid asphalt storage tank vent during loading, an upwind site, a downwind site, and a residential site. Air sampling through the use of the Organic Vapor Analyzer (OVA), portable GC/MS, and SUMMA canisters was conducted at the selected locations.

INVESTIGATION RESULTS

The following table displays the estimated BTEX concentrations for three of the five SUMMA canister samples collected during this investigation. Quantification of the Railcar Port (Inman02) and the Tank 15 Vent (Inman03) SUMMA canister samples could not be conducted due to volatile organic compound concentrations estimated to be well above the calibration range and the abundance of overlapping pollutant peaks. These samples, delivered to the DAQ Toxics Protection Laboratory under Chain-Of-Custody, were analyzed on April 25, 1998 using the Finnigan Magnum ion trap GC/MS. The GC portion of the Finnigan houses a 60m x 0.32mm ID column with a 3.0 micron thick 100% Dimethylpolysiloxane stationary phase. The oven temperature is ramped from 40°C to 205°C over a 50 minute run time. The detector is configured for full scan mode and quantitation is based on the primary ion using a five point curve covering the range of 0.20 ppbv to 10 ppbv.

SAMPLE NUMBER	DATE	SAMPLE DURATION	LOCATION	POLLUTANTS IDENTIFIED (BTEX)	ESTIMATED CONC. (ppbv)
Inman01	04/23/98	Grab Sample (1158 hrs)	Upwind ~180' East of RR	Benzene Toluene Ethyl benzene Total Xylenes	<0.20 0.37 <0.20 1.57
Inman04	04/23/98	Grab Sample (1407 hrs)	Downwind Fenceline	Benzene Toluene Ethyl benzene Total Xylenes	<0.20 0.30 <0.20 0.76
Inman05	04/23/98	Grab Sample (1438 hrs)	Residential 234 West Colonial	Benzene Toluene Ethyl benzene Total Xylenes	0.65 1.88 <0.20 0.52

The following table lists the toxic air pollutants tentatively identified in the five SUMMA canister samples collected during this investigation. As previously mentioned quantification of BTEX and other compounds (hexanes) in the Inman02 and Inman03 samples could not be conducted due to out of range concentrations and overlapping peaks. The other toxic air pollutants, acetic acid and methyl ethyl ketone, detected at low-levels in the upwind, downwind, and residential SUMMA canister samples, were not quantified due to a lack of an calibration standard.

TOXIC AIR POLLUTANTS TENTATIVELY IDENTIFIED BUT NOT QUANTIFIED				
INMAN01 Upwind (~180'E of RR)	**INMAN02** Railcar Port (Open)	**INMAN03** Tank 15 Roof Vent	**INMAN04** Downwind Fenceline	**INMAN05** Residential (234 W. Colonial
Acetic Acid	Xylenes	Xylenes	Acetic Acid	Acetic Acid
Methyl Ethyl Ketone	n-Hexane	n-Hexane	Methyl Ethyl Ketone	Methyl Ethyl Ketone
		Hexane Isomers		

Page Three
Inman Asphalt Terminal (ATAST #98015)

The following four tables summarize BTEX concentrations detected by the portable GC/MS during this investigation.

-TABLE I-[BENZENE]

RUN #	SAMPLE ID	DESCRIPTION	ESTIMATED BENZENE CONC. (ppmv)
1	98042303	50 ppbv BTEX Standard	0.05
2	Inman 01	Upwind on Inman Property (~180'E of RR)	< 0.02
3	Inman 02	Railcar Port (Open)	1.2
4	Inman 03	Storage Tank 15 Vent During Fill Process	2.6
5	Inman 04	Downwind at Fenceline	< 0.02
6	Inman 05	234 West Colonial Drive	< 0.02
7	Inman 06	Zero Air Blank	< 0.02
8	Inman 07	50 ppbv BTEX Standard	0.05

-TABLE II-[TOLUENE]

RUN #	SAMPLE ID	DESCRIPTION	ESTIMATED TOLUENE CONC. (ppmv)
1	98042303	50 ppbv BTEX Standard	0.05
2	Inman 01	Upwind On Inman Property (~180'E of RR)	<0.02
3	Inman 02	Railcar Port (Open)	2.5
4	Inman 03	Storage Tank 15 Vent During Fill Process	9.1
5	Inman 04	Downwind At Fenceline	<0.02
6	Inman 05	234 West Colonial Drive	<0.02
7	Inman 06	Zero Air Blank	<0.02
8	Inman 07	50 ppbv BTEX Standard	0.07

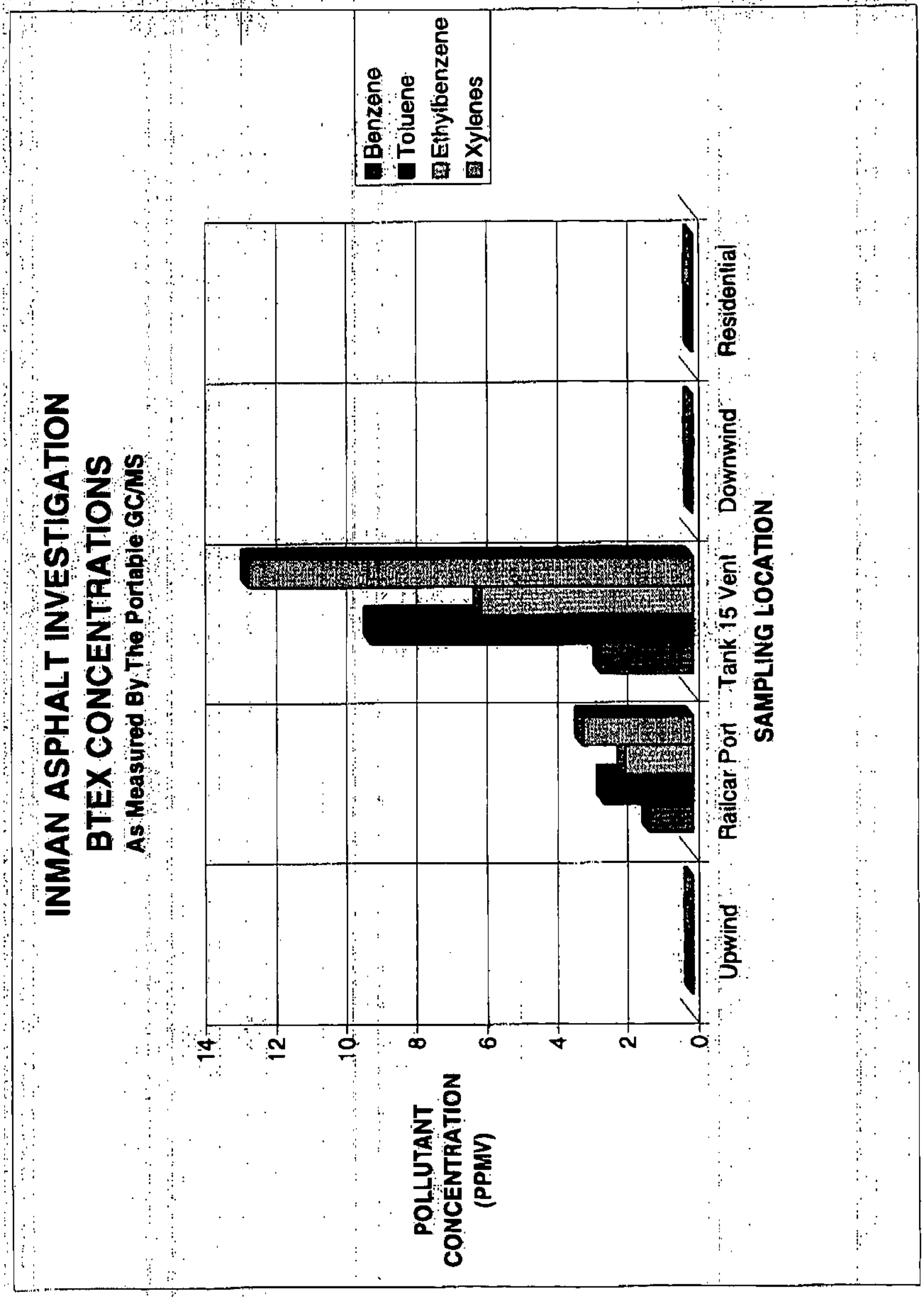
-TABLE III-[ETHYL BENZENE*]

RUN #	SAMPLE ID	DESCRIPTION	ESTIMATED ETHYLBENZENE CONC. (ppmv)
1	98042303	50 ppbv BTEX Standard	0.05
2	Inman 01	Upwind On Inman Property (~180'E of RR)	0.04
3	Inman 02	Railcar Port (Open)	1.9
4	Inman 03	Storage Tank 15 Vent During Fill Process	6.0
5	Inman 04	Downwind At Fenceline	0.04
6	Inman 05	234 West Colonial Drive	0.04
7	Inman 06	Zero Air Blank	<0.02
8	Inman 07	50 ppbv BTEX Standard	0.05

*Ethyl benzene currently is not listed as a North Carolina Toxic Air Pollutant and therefore does not have an ambient fenceline standard or AAL (Acceptable Ambient Level).

-TABLE IV-[TOTAL XYLENES]

RUN #	SAMPLE ID	DESCRIPTION	ESTIMATED TOTAL (m,p,o) XYLENES CONC. (ppmv)
1	98042303	50 ppbv BTEX Standard	0.05
2	Inman 01	Upwind On Inman Property (~180'E of RR)	<0.02
3	Inman 02	Railcar Port (Open)	3.1
4	Inman 03	Storage Tank 15 Vent During Fill Process	12.6
5	Inman 04	Downwind At Fenceline	<0.02
6	Inman 05	234 West Colonial Drive	<0.02
7	Inman 06	Zero Air Blank	<0.02
8	Inman 07	50 ppbv BTEX Standard	0.04



INMAN ASPHALT INVESTIGATION
BTEX CONCENTRATIONS
As Measured By The Portable GC/MS

The following table displays results of the Organic Vapor Analyzer samples collected during this investigation.

READING	LOCATION	CONCENTRATION
1	Background At Trailer	~1.2 ppm
2	Upwind At Inman (~180' East Of RR tracks)	~1.3 ppm
3	Liquid Asphalt Railcar Port (Liquid Asphalt Heated To ~320 F)	~600 ppm
4	Liquid Asphalt Tank 15 (Roof Vent During Tank Loading)	~200-500 ppm
5	Liquid Asphalt Truck Loading Rack (Tanker Truck Hatch During Truck Loading)	~400-600 ppm
6	Downwind Fenceline (North Side Of Property-Near NW Corner)	~1.2-2.2 ppm
7	Residential Property-234 W. Colonial (Upwind At Time Of Sampling)	~1.2 ppm

CONCLUSIONS

Facility Assessment Summary

ATAST's goal of assessing the ambient impact of emissions from the Inman Asphalt Terminal was met by performing air sampling through the use of SUMMA canisters, the portable GC/MS, and the Organic Vapor Analyzer, at several locations in and around the facility. Currently, there are no devices in place for controlling fugitive emissions during railcar unloading, tanker truck loading, and storage tank filling. ATAST recommends that the Mooresville Regional Air Quality Office assist the Inman Asphalt Terminal in developing a control strategy for these fugitive emissions. This recommendation is based on the significant emissions of BTEX compounds from the railcar hatch and the storage Tank 15 vent. Additional complaints may warrant the need to perform computer modeling. The proximity of the property boundaries to the emission sources may challenge the facility during a modeling exercise. During the investigation ATAST briefly met with several residents from the neighborhood northeast of the Inman Asphalt Terminal. The residents expressed

CONCLUSIONS (Continued)

an interest in the establishment of a vegetation buffer along Jake Alexander Boulevard for the purposes of odor and noise mitigation as well as aesthetics. ATAST also recommends that the Mooresville Regional Air Quality Office examine the concept of a vegetation buffer in addition to assisting the Inman Asphalt Terminal in developing a fugitive emissions control strategy. These options were well received by Cheryl Buehring, an Inman Asphalt Terminal consultant, during a telephone conservation with ATAST member William Steinmetz.

Ambient Monitoring Summary

The citizens lodging air quality complaints against the Inman Asphalt Terminal reside in a neighborhood located northeast of the facility. Therefore, complaints would be expected during either calm or southwesterly wind conditions. It should be noted that weather conditions during this investigation included easterly and southeasterly winds. Asphalt-like odors were not encountered in the residential area or upwind of the Inman Asphalt Terminal during this investigation. However, occasional faint asphalt-like odors were encountered at the facility's downwind fenceline. Upwind, downwind, and residential air samples collected by the portable GC/MS in the vicinity of the Inman Asphalt Terminal revealed estimated benzene, toluene, and xylene concentrations below 0.02 ppmv, with ethyl benzene concentrations reading 0.04 ppmv. As previously mentioned, ethyl benzene is currently not listed as a North Carolina Toxic Air Pollutant and therefore does not have a health-based fenceline ambient air standard or AAL (Acceptable Ambient Level).[1] The SUMMA canisters collected at the same locations (upwind, downwind, and residential) which were analyzed with the more sensitive Finnigan GC/MS resulted in estimated concentrations ranging between <0.20 -0.65 ppbv for benzene, 0.30-1.88 ppbv for toluene, and 0.52-1.57 ppbv for total xylenes.

The health-based North Carolina Acceptable Ambient Level (AAL) for benzene is 0.04 ppbv averaged annually. However, according to the Agency for Toxic Substance and Disease Registry (ATSDR), benzene concentrations in urban air typically range from 2.8 to 20 ppbv.[2] Furthermore, benzene concentrations at the background/rural air monitoring site associated with the Paw Creek Air Study II (ATAST #95010) averaged 0.22 ppbv from August 8, 1996 through August 11, 1997. Based on this information the benzene concentration of 0.65 ppbv encountered at 234 West Colonial in Salisbury on April 23, 1998 was more typical of clean air.

The Acceptable Ambient Level (AAL) for toluene is 1227 ppbv averaged over a 24-hour period. According to the Environmental Protection Agency, toluene concentrations in urban and suburban air typically range from 0.26 to 7.9 ppbv.[3] Therefore, the toluene concentrations which ranged from 0.30-1.88 ppbv during this investigation are typical for urban and suburban air and well below the health-based North Carolina AAL.

The Acceptable Ambient Level (AAL) for xylene is 610 ppbv averaged over a 24-hour period. According to the ATSDR, xylene concentrations in the industrial areas and cities of the Unites States

CONCLUSIONS (Continued)

and Europe range between 0.70 and 90 ppbv.[4] Based on this information, the xylene concentrations which ranged from 0.52 to 1.57 ppbv during this investigation are somewhat cleaner than typical urban air and well below the health-based North Carolina AAL.

In conclusion, the ambient air samples collected during this Inman Asphalt investigation found BTEX concentrations to be typical of, or cleaner than, urban air. However, the BTEX concentrations acquired while collecting air samples from the railcar port and the Tank 15 vent indicate the need for the development of a control strategy. A vegetation buffer to mitigate odor and noise should also be considered. Analysis of the liquid asphalt sample collected during this investigation is incomplete and will therefore be provided at a later date.

William K. Steinmetz June 8, 1998
William K. Steinmetz, Environmental Specialist Date

Lorene P. Cherry 6-8-98
Lori P. Cherry, Supervisor, Toxics Protection Branch Date

cc: Alan Klimek
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Central Files

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