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Methane and Carbon Monoxide Emissions From Asphalt Pavement: Measurements and Estimates of Their Importance to Global Budgets

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We measured emissions of methane from asphalt surfaces used in pavement for roadways. Maximum emissions were 22 mg/m²/hr for 1- to 4-week-old pavement during maximum sunlight intensity. Emissions were much smaller at low sunlight intensity and dropped off to negligible amounts at night. Smaller emissions were observed for asphalt pavement of 2.5 to 3 years approximate age under similar conditions. Companion measurements of carbon monoxide emissions resulted in maximum emissions of about 2.6 mg/m²/hr for 1-week-old pavement. These findings indicate that emissions of CH₄ and CO are a function of both sunlight and temperature. Based on our results, methane emissions from asphalt pavement cannot be a significant source of atmospheric methane as compared to other identified methane sources. Therefore, although asphalt methane emissions are a form of fossil fuel methane, they cannot explain the relatively high fraction of ¹⁴C-depleted methane in the atmosphere.

INTRODUCTION

Measurements and interpretation of data involving atmospheric methane and its sources and sinks have become increasingly important in recent years. As the most abundant hydrocarbon in the atmosphere, methane plays the role of a principal greenhouse gas [e.g., *Donner and Ramanathan*, 1980; *Ramanathan et al.*, 1985] as well as taking part in many key tropospheric and stratospheric reactions [e.g., *Wofsy*, 1976; *Logan et al.*, 1981]. Escalation of the interest in understanding methane comes about partly because its concentration is increasing at a rate of about 1% per year over at least the last decade and a half [e.g., *Rasmussen and Khalil*, 1981; *Steele et al.*, 1987; *Blake and Rowland*, 1988]. Also, there is evidence from analysis of gases trapped in dated ice cores that atmospheric methane has more than doubled in concentration in the last 200 years and that its concentration stayed between 0.6 and 0.8 ppm over the last 3000 years [*Craig and Chou*, 1982; *Rasmussen and Khalil*, 1984; *Pearman et al.*, 1986]. Attempts to explain the recent increase depend upon the uncertain budget of atmospheric methane and may include increases in some methane sources, decreases in methane sink processes such as reaction with OH radical, or combinations of the two types of possibilities [e.g., *Stevens and Engelkemeir*, 1988; *Cicerone and Oremland*, 1988; *Tyler*, 1989].

Relative source strengths are not well known. For example, most early estimates presumed that biogenic sources of methane comprised 80 to 95% of all methane sources with radiocarbon "dead" (no carbon-14 present) sources making up the rest

[*Ehhalt*, 1974; *Ehhalt and Schmidt*, 1978; *Mayer et al.*, 1982; *Crutzen and Gidel*, 1983]. However, recent work by *Lowe et al.* [1988] and *Manning et al.* [1990] indicates that the contribution to CH₄ from dead sources such as fossil fuels is more probably 26% of the total contribution with a range of 23–32%. *Wahlen et al.* [1989] are in reasonable agreement with this value. Their reported value is 21 ± 3% for the fossil carbon contribution to atmospheric methane at the end of 1987.

Sackett and Barber [1988] propose that an overlooked radiocarbon dead source of atmospheric methane might be derivatives of fossil fuel carbon such as asphalts and road tars. They reported preliminary measurements of asphalt emissions of CH₄ using a laboratory test system. Tests consisted of experiments in which quartz tubes filled with asphalt were heated by exposure to UV light while emissions of CH₄ and other hydrocarbons were monitored. Their results indicate that up to 15% of total carbon in asphalt in this system may eventually be released as CH₄. Based on calculated U.S. production of asphalt they suggest that overall CH₄ emissions from newly produced asphalt may be as high as 5 Tg/year (Tg = 10¹² g). They speculate that world methane production from asphalt must be even larger and point out that other petroleum-derived products with uses such as roofing and other construction applications may also release CH₄ because of the materials' exposure to sunlight.

We have undertaken additional measurements of surface emissions of both old and new asphalt under natural conditions. Results are reported for CH₄ emissions from both old (greater than 2 years since paved) and new (1 week to 4 weeks since paved) asphalt pavement on outdoor surfaces of roadways and parking lots. Emissions are monitored over time, along with surface temperature and radiative flux from sunlight, to arrive at mean and maximum CH₄ fluxes as a function of these parameters. Companion data for CO fluxes from measured emissions are also reported.

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PROPERTIES AND USES OF ASPHALT

Because most of the readers of this paper are not likely to be familiar with the science and engineering of asphalt, it will be helpful to briefly discuss asphalt properties and usage before we report any of the experimental details or data analysis. After a search of the literature and discussions with staff at the Asphalt Institute in College Park, Maryland, we learned that journals and reports document the facts regarding world and U.S. usage and physical properties of asphalt rather incompletely. Furthermore, there is no uniform practice in aspects of asphalt mixing, paving, and repaving. Therefore we have relied on first hand knowledge from scientists or engineers who are in asphalt related businesses for many of the descriptions that follow. Their comments are noted in the text. Wherever possible, we have cited published reports.

Asphalt is derived from crude petroleum oil. Petroleum is a naturally occurring complex mixture consisting predominantly of paraffin, naphthene (i.e., cycloparaffin), and aromatic hydrocarbons in variable proportions. It also contains small amounts of organic compounds containing sulfur, nitrogen, and oxygen, and even smaller amounts of some trace metals. Many crude petroleum oils contain asphalt in amounts varying from 5 to 70%. Manufacturing takes place at relatively low temperatures using one of three processes: distillation, air-blowing conversion, or extraction with solvents. The production of asphalt should not be confused with the production of coal tars, pitches, and road tars which are produced by a coal carbonization process at high temperatures. Once produced, asphalt has a relatively high thermal stability in comparison to coal tars, pitches, and road tars and it is known that during the curing and application phases, some emissions of hydrocarbons takes place [Puzinauskas and Corbett, 1978].

Asphalt materials for paving applications include asphalt cement, cutbacks, and emulsified asphalt. In paving applications it is mixed with aggregate to form asphalt concrete. Although it is not strictly correct in a technical sense, asphalt concrete is commonly called asphalt pavement. Nonpaving uses include roofing asphalt cements, emulsions, and fluxes. World production capacity of asphalt for the year 1986 (excluding the United States) was 851,622 b/cd [Kinney, 1986] where b/cd is barrels per calendar day. This is equivalent to 5.09×10^{10} kg for the year 1986. Because all numerical quantities for both U.S. and world data are listed in units commonly used by the oil and petroleum or asphalt industries, we have left the numerical figures in the units first quoted but have endeavored to convert to SI units as soon as practicable. For conversion of units used here, a barrel is 42 gallons and there are 8.596 pounds in a gallon of asphalt in U.S. petroleum units. Although the Oil and Gas Journal (OGJ) report [Kinney, 1986] excluded U.S. production figures, we can calculate it from U.S. usage figures for the year 1986 given by Anderson [1988]. Total U.S. usage for that year was 3.13×10^7 short tons (where a short ton is 2000 pounds). This is equivalent to 2.84×10^{10} kg. However, of this total 2.20×10^6 short tons was imported from other countries. The world figure of 5.09×10^{10} kg included the amount used by all countries other than the United States as well as the amount exported to the U.S. Therefore we must subtract the amount exported to the United States so as not to double count it. World usage then becomes 4.89×10^{10} kg excluding the United States. Comparing the total 4.89×10^{10} kg to 2.84×10^{10} kg, one can see that the United States accounted for about one-third of the world asphalt usage in 1986. Similar

calculations for other years since 1984 lead to about the same result. Therefore we will generalize the uses of asphalt by describing the procedures used in the United States and note exceptions where they are known to us. United States figures for 1987 indicate that 85% of all asphalt consumed in the United States was for asphalt pavement [Anderson, 1988]. Of this, asphalt cements are 83%, cutbacks are 5%, and emulsions are 12%. (For descriptions of these three types of asphalt used in paving, see Anderson [1988]). A. Anderson (personal communication, 1988) noted that European asphalt contains some road pitch and is slightly more volatile than U.S. asphalt for roadways.

In the United States, asphalt paving is usually placed in 0.06 to 0.18 m thick sections while repaving (or overlays) is usually 0.05 to 0.10 m thick (J. Boyers, personal communication, 1988). It is placed hot with a median temperature between 104° and 138°C. According to Boyers (project engineer in the Public Works Department in Boulder County), no distinction is made between asphalt used on roadways and that used in parking lots in Boulder. He also stated that this holds true for many other places in the United States as well. The aggregate percentage for the two types of pavement may be slightly different but the asphalt is identical. The asphalt makes up anywhere from 4 to 6.5% of the total pavement volume.

The Asphalt Institute in Denver, Colorado, provided information which suggested a rough way of estimating asphalt lifetime and emissions (B. Brakey, personal communication, 1988). It seems probable that asphalt emissions do not occur over the lifetime of the road but are instead confined to some initial period after overlay because old pavement becomes dry and crusty with an oxidized coating. Also (for the United States at least), metropolitan and high density states have a higher percentage of paving done by the private sector (e.g., for California, about 60%, for Colorado about 40%, and for Wyoming, about 20%). This is important because about 50% of paving done by the private sector is repaving, while for county and state governments, about 85% is repaving and only about 15% is new. This kind of information does not translate to a quantitative estimate of old and new pavement or pavement lifetime very easily but it does indicate that a lot of paving is over previously laid pavement. With repavement thicknesses of 0.05 to 0.10 m, it means that a high percentage of old asphalt which might otherwise still be degassing, is locked up under newer layers and not exposed to sunlight. Depending on usage, repavement could be as seldom as 12 to 16 year intervals, but is probably between 3 and 8 years for most U.S. roadways.

Further, for U.S. asphalt usage, about 50% of emulsions (12% of all asphalt used in paving) are used for the top layer of asphalt and 50% are used to seal between layers. Emulsions are very stable and have no volatiles released over time. Cutbacks (5% of paving asphalt), which are the most volatile type of asphalt of those used for pavement, are being used less now and are not legal in high pollution metropolitan areas.

EXPERIMENTAL PROCEDURE

Asphalt emissions were measured using three different experimental set-ups. In each case, samples were collected by withdrawing air into 20 mL volume air tight syringes. Teflon septa were used to plug the syringe after sampling to prevent exchange of sample gas with outside air while transferring them to the laboratory. Experimental conditions were monitored during the collections including surface asphalt temperature, air

temperature, and UV light intensity. The UV light intensity was measured using an Eppley radiometer (spectral response range calibrated for 290–385 nm). All samples were analyzed within 2 hours of sampling against a CH₄ standard at 3.88 ppmv (NBS SRM 1660a) and a CO standard at 9.70 ppmv (NBS SRM 2612a). Instrument response for each compound was linear over the range of concentrations in this study and the precision of measurement is ± 0.01 ppmv for both CH₄ and CO. A model HP-5880 gas chromatograph fitted with a flame ionization detector and a 5A molecular sieve column separated CH₄ and CO for analysis. CO was passed through a methanizer consisting of a ruthenium carbonyl catalyst at 375°C prior to its detection.

Our initial tests were run using a fully enclosed tray of asphalt pavement which was obtained from a road paving crew along a new county road in Boulder, Colorado. The new and still hot asphalt (heated to 121°C at time of paving) was placed into a stainless steel tray of dimensions 0.61 m x 0.43 m x 0.15 m to a height of about 0.08 m. This asphalt pavement is designated as Marshall Asphalt Mix Design and is 100%, 3/4-in. aggregate with a specific gravity of 2.634 for the mix and a composition of up to a maximum of 6.1% asphalt. Immediately after returning to the laboratory at NCAR, we enclosed the entire tray in a large FEP teflon bag (2 mil thickness, about 0.05 mm) and heat sealed the bag edges to make the enclosure as airtight as possible. (Tests on the transparent teflon sheet by UV-spectrophotometer show that it transmitted 95% of all UV light.) Corrections were made for air exchange by injecting butane as a tracer into the bag at the beginning of the experiment and monitoring its decrease over time. A port in the bag allowed us to withdraw syringe samples and also to fill the bag with background air at the start of a new experiment. A measured amount of air was used to allow bag volume calculations for each experiment. Because of the relatively large volume of air surrounding the enclosed tray and the collapsible nature of the teflon enclosure, withdrawing samples had negligible effect on subsequent samples in determining methane flux values and little exchange between outside air and the bag took place through the septum.

More experiments were run using this enclosed tray system over the next few weeks. These tests were made to monitor emissions over time as the initially hot asphalt cooled and set in the tray. We investigated the effects of bright sunshine on asphalt and also the effects of laboratory heating of asphalt to typical outdoor pavement temperatures in the absence of light. External concentrations of CH₄ and CO were monitored at all times during the enclosure measurements for experiments run both outdoors and indoors. In addition, CH₄ and CO blanks were established for similar teflon enclosures without asphalt inside.

A different experimental setup was used to monitor emissions from road and parking lot surfaces outdoors. The procedure is described below for a relatively old section of asphalt pavement in a townhouse parking lot. This pavement was about 2.5 years old and was sampled by covering a section with a large 1.31 m by 1.64 m teflon sheet. The center was raised to a height of about 0.25 m by using a dummy 1-L jar as a centerpiece under the sheet. Two meters of teflon 9 mm OD tubing were run from the central air space under the sheet to the edge of the sheet to allow us to take syringe samples. The approximate volume of the air cavity under the sheet was 21.5 L as determined by inflating the sheet with a measured background

air source prior to beginning sample collections. The sheet edges were held down by wet sand to diminish air exchange into the enclosure. The leak rate was determined by doping the enclosed airspace with SF₆ and monitoring its decrease over time.

RESULTS

Experimental data are summarized in Table 1. The maximum flux of CH₄ and CO measured during each experiment is shown with values for UV intensity and the asphalt surface and air temperatures at the time of maximum methane emissions. In each case, average fluxes over the whole time period were much smaller. The values in parentheses are maxima for the temperature and UV intensity during the respective experiments without regard to the time of maximum methane emissions. Fluxes were calculated by first determining the leak rate constant for incremental time intervals using the data from an inert tracer gas. The methane and CO production rates determined from concentration data were then corrected to account for leakage. Finally a flux was determined from the enclosure dimensions and the concentration data.

In the first experiment, values for emissions from fresh (7 day old) asphalt show that methane flux peaked at about 22 $\mu\text{g}/\text{m}^2/\text{hr}$ while carbon monoxide flux peaked at about 2.6 $\text{mg}/\text{m}^2/\text{hr}$ in the enclosed tray. The value for CO emissions proved to be the highest obtained for any of our experiments with asphalt. The value for CH₄ emissions was effectively equal to the highest value obtained in a subsequent experiment using relatively fresh (26 day old) asphalt. The methane emission peaked slightly before the time of maximum surface temperature (57°C) and close to the time of maximum UV sunlight (33 W/m^2). Figures 1 and 2 detail results of this test (which correspond to the first day of testing listed in Table 1). Figures 1a and 1b are CH₄ and CO fluxes from the asphalt in the enclosure versus time. Figures 2a and 2b are surface asphalt temperature versus time and the UV radiometer reading in watts/m^2 versus time (where the radiometer is calibrated as 0.594 $\text{mW}/\text{cm}^2/\text{mV}$).

In the laboratory when the same asphalt sample was heated to 58°C (day 21), methane and carbon monoxide emissions were about one-third as high, about 8.9 $\mu\text{g}/\text{m}^2/\text{hr}$ and 0.8 $\text{mg}/\text{m}^2/\text{hr}$, respectively. When the asphalt sample was exposed to sunlight again (day 26) emissions built up to approximately the original level seen at the 7 day mark, although the asphalt surface temperature (47°C) and UV sunlight intensity (27 W/m^2) were slightly lower than for the 7 day mark. These findings indicate that emissions of CH₄ and CO are functions of both sunlight and surface temperature.

As described in the experimental section, a teflon sheet setup was deployed to make similar tests on asphalt pavement used for parking lot surfaces and roadways. On a parking lot surface known to be about 2.5 years old, maximum emissions were lower than in the fresh asphalt cases, as shown in Table 1. Maximum surface asphalt temperature (22°C) and UV sunlight intensity (2.0 W/m^2) were lower than for previous tests. Some of the decrease in emissions may have been due to conditions of less sunlight on the day of the test but the data clearly showed that for equal surface temperature, the older asphalt was not as productive as the fresh asphalt. This test was repeated several months later at the same location (asphalt age now about 3 years) to monitor emissions of CH₄ on a day with bright sunlight and a hotter pavement surface. This time emissions of

TABLE 1. Measured Maximum Emissions of Methane and Carbon Monoxide From Asphalt

Description of Test	Date	Maximum CH ₄ Emission, μg/m ² /hr	Maximum CO Emission, mg/m ² /hr	Surface Temperature at Max CH ₄ Emission, °C	Shade Temperature at Max. CH ₄ Emission, °C	UV Reading at Max. Emission, W/m ²
7 day old asphalt in teflon enclosure outdoors	Sep. 29, 1988	22.0	2.62	53(57)	22(22)	31(33)
21 day old asphalt in teflon enclosure indoors	Oct. 13, 1988	8.9	0.84	58(58)	---	---
26 day old asphalt in teflon enclosure outdoors	Oct. 18, 1988	22.2	2.00	45(47)	21(22)	24(27)
2½ day old asphalt under teflon sheet outdoors	Nov. 8, 1988	0.45	0.17	19(22)	13(18)	1.5(2.0)
3 year old asphalt under teflon sheet outdoors	June 15, 1989	3.9	---	72(72)	22(22)	35(38)
6 day old asphalt (rubberized) under teflon sheet outdoors	July 19, 1989	8.3	---	73(73)	30(30)	40(40)
21 day old asphalt under teflon sheet outdoors	Aug. 24, 1989	15.7	---	73(73)	34(34)	40(40)

Numbers in parentheses are maxima for entire experiment.

CH₄ reached a maximum of 3.9 μg/m²/hr at the time of maximum temperature and sunlight. This flux was higher than the previous measurement for old asphalt but well below that for fresh asphalt, although surface temperature (72°C) and UV sunlight intensity (38 W/m²) were the highest yet measured.

Because the summer of 1989 provided much higher sunlight intensity than the fall of 1988, we made two additional experiments to test fresh asphalt using the teflon sheet method. In one experiment we tested fresh (21 day old) asphalt of the kind used in all previous experiments. This is the asphalt

described in detail in an earlier section as the common type of Boulder County asphalt. In spite of higher surface temperatures (73°C) and more UV sunlight intensity (40 W/m²), maximum CH₄ emissions were only 16 μg/m²/hr this time as compared to 22 μg/m²/hr for asphalt of similar age tested last fall. A likely explanation for this difference in emissions for two nearly identically-aged asphalt sections is that their usages differ since being lain down. Our tray asphalt (26 day old) was never tamped down nor driven over, while the road surface asphalt (21 day old) was immediately put into use to serve traffic needs.

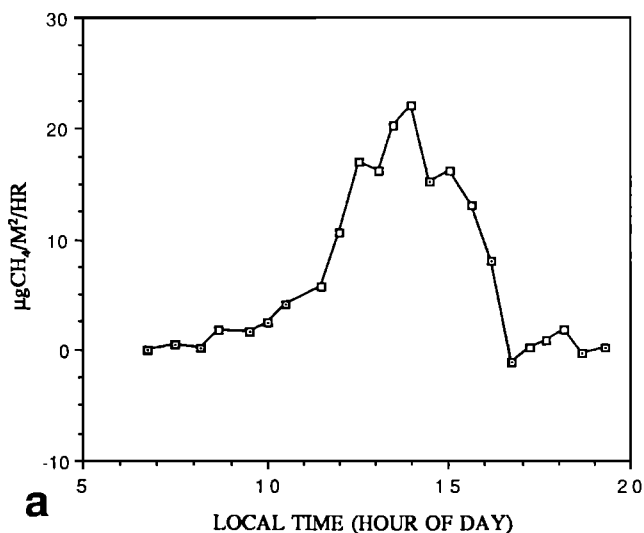


Fig. 1a. Methane flux versus time of day for 7-day-old asphalt in enclosure (September 29, 1988).

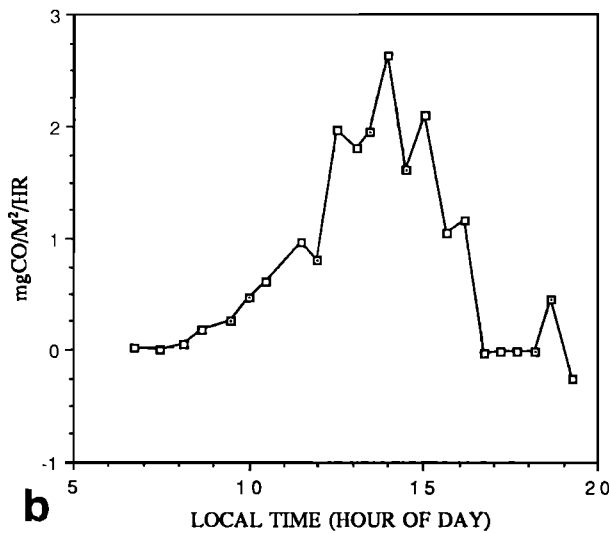


Fig. 1b. Carbon monoxide flux versus time of day for 7-day-old asphalt in enclosure (September 29, 1988).

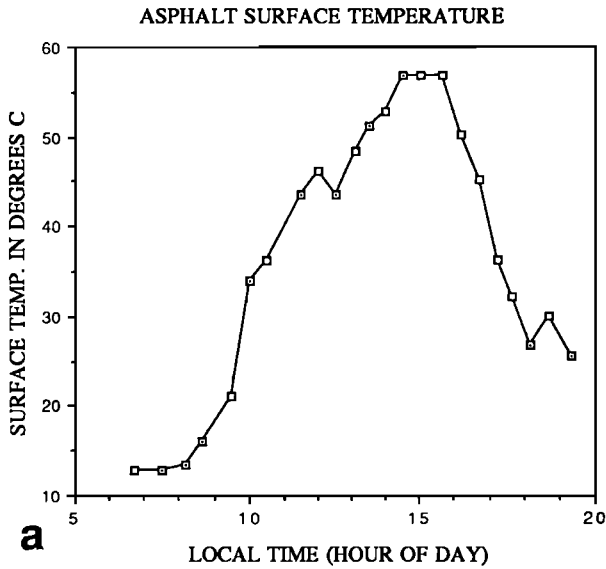


Fig. 2b. UV intensity (unadjusted for sun angle) versus time of day for 7-day-old asphalt in enclosure (September 29, 1988).

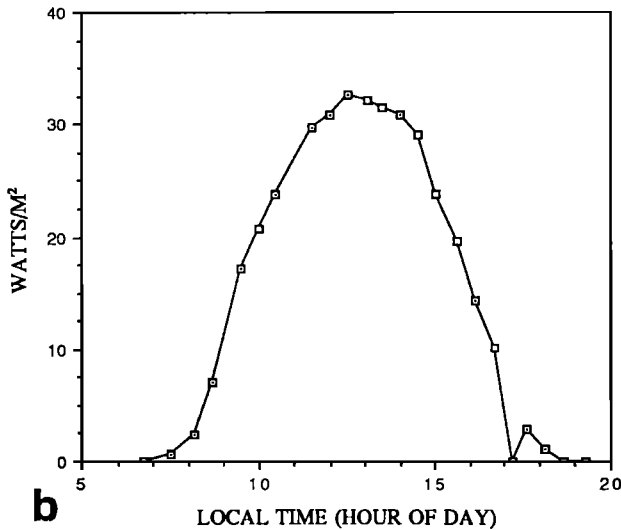


Fig. 2a. Asphalt surface temperature versus time of day for 7-day-old asphalt in enclosure (September 29, 1988).

In the other experiment a different kind of asphalt was tested. According to C. Stuka of Brannon Sand and Gravel in Denver, Colorado, this asphalt, designated plant mix seal AC-20, is a harder asphalt with neoprene rubber mixed in (C. Stuka, personal communication, 1989). It is being used more and more in states like Colorado, where because of weather conditions, properties such as better long-term wear, better skid resistance, and water resistance are needed. We tested this asphalt on a newly paved street in Boulder, Colorado where the asphalt overlay was 6 days old. Maximum CH₄ emissions of 8.3 μg/m²/hr were found at the maximum surface temperature and UV sunlight intensity of 73°C and 40 W/m², respectively.

A brief discussion of errors is in order. The largest potential error is in estimating the volume of the enclosures used. For the tray experiment this error is ±5% at the start of the enclosure time. The effects of wind could cause this enclosure volume to

decrease, lessening the volume. This would cause fluxes to be somewhat larger than calculated. We estimate that this error is no more than 10% and that this exceeds all other kinds of errors. The two largest fluxes in Table 2 are therefore about 22.0±1.1 μg/m²/hr based on the identifiable error of precision and may be underestimated by about 10%, making them as high as about 24 μg/m²/hr.

For the experiments with the teflon sheets, the volume error could be somewhat greater. Again, the estimate of the initial enclosure volume of 21.5 L is good to about 5%, but the wind effect during the time of enclosure could decrease the volume by possibly 20%. This is again a visual estimate. From Table 2, the value for 21 day old asphalt under the teflon sheet becomes 15.7±0.8 μg/m²/hr but in the worst case may be underestimated by about 20%.

In every test we have described we are dealing with differences between accumulated source and background concentrations. These differences can be small enough that the error of the FID measurement is as much as 3%. Background air over the pavement surface typically had concentrations of about 2.00 ppmv of CH₄ while concentrations of emissions of CH₄ ranged from a few tenths of a ppmv above background to about 5.00 ppmv. For the smallest flux in Table 2 (0.45 μg/m²/hr), where the accumulated concentration was calculated from 2.30±0.1 - 2.00±0.1, an additional error of 3% could be added to the volume error of 5%. The uncertainty in the value found by accumulating these errors is 6%, making the value 0.45±0.03 μg/m²/hr. Errors in the FID concentration measurements become smaller in determining the fluxes in Table 2 as the concentrations, and hence fluxes, increase.

ESTIMATE OF ASPHALT EMISSIONS

Estimating asphalt emissions of CH₄ and CO will be difficult since several assumptions are involved in extrapolating to world averages. Using figures from the preceding sections we can try to estimate total asphalt surface area in the world. This will only be a very rough estimate but it should overestimate world asphalt surface area. It will use typical or average values for figures in the calculation where those values are known to be reasonable worldwide. Where world values for figures in the calculation are less, well known estimates will be made which allow for the greatest possible asphalt emissions to occur. We will also make other estimates of the importance of asphalt pavement emissions by comparisons to some other sources of methane.

A reasonable estimate for the total asphalt usage in 1986 is found by combining the two values 4.89 x 10¹⁰ kg (world except United States) with 2.84 x 10¹⁰ (U.S. production) to get 7.73 x 10¹⁰ kg. From Anderson [1988], we have figures to show that the United States uses about 85% of its asphalt for paving, while Canada uses only about 76% for the year 1987. The rest of the asphalt is used for applications such as roofing and other miscellaneous uses. Assuming that 85% is the world average, then 6.18 x 10¹⁰ kg were used as paving asphalt in 1986. Since a typical mix proportion for asphalt pavement is 6% asphalt and 94% aggregate, total asphalt pavement by weight is 1.03 x 10¹² kg. Such an aggregate mix has a density of 144 lbs/ft³ (about 2310 kg/m³) and if it is laid 0.05 m thick (very thin for new pavement and about average for repavement) then 1.03 x 10¹² kg will cover about 8.92 x 10⁹ m². This then is the maximum amount of asphalt pavement surface area covered in 1986. If we

TABLE 2. Methane Flux Measurements for Selected Sources (Compiled From the Recent Literature)

Source Area	Average Flux, gCH ₄ /m ² /d	Estimated Area for Total of Like Sources* 10 ⁹ m ²	Reference
Southeastern U.S. Cypress Swamps	0.0046-0.068	1087	<i>Harriss and Sebacher</i> [1981]
California Rice Paddies	0.075	1450	<i>Cicerone and Shetter</i> [1981]
	0.25	1450	<i>Cicerone et al.</i> [1983]
Spain Rice Paddies	0.096	1450	<i>Seiler et al.</i> [1984]
Alaskan Sites			
Moist tundra	0.0049		
Wet tundra	0.040		
Water-logged tundra	0.119 0.106	897	<i>Sebacher et al.</i> [1986]
Boreal marsh	0.289		
Alpine fen			
Amazon, Brazil			
Open lake	0.027	---	
Flooded forest	0.192	1087	<i>Bartlett et al.</i> [1988]
Grass mats	0.230	1008	
Amazon, Brazil			
Open lake	0.120	---	
Flooded forest	0.110	1087	<i>Devol et al.</i> [1988]
Grass mats	0.590	1008	

*From *Matthews and Fung* [1987].

assume 50% of this is new pavement and 50% is used for repaving existing asphalt based on information in the section on properties and uses of asphalt, then the contribution to the potential asphalt surface area calculation is maximized with respect to new versus old pavement. Then assuming that repavement takes place globally every 12 years (12 years is almost certainly too long for a global average, but the value leads to a greater amount of pavement than would exist if repavement is more often), 50% of $8.92 \times 10^9 \text{ m}^2$ represents about one-twelfth of all asphalt roadways and the total asphalt surface area is $0.5 \times 8.92 \times 10^9 \text{ m}^2 + 12 \times 0.5 \times 8.92 \times 10^9 \text{ m}^2 = 5.80 \times 10^{10} \text{ m}^2$.

Using the maximum value for fresh asphalt of $22 \mu\text{g}/\text{m}^2/\text{hr}$ as the CH₄ flux and assuming 12 hours of maximum intensity UV sunlight over the globe, the CH₄ released from asphalt is $0.0964 \text{ g}/\text{m}^2/\text{yr}$. Therefore yearly methane emissions are about $0.0964 \text{ g}/\text{m}^2/\text{yr} \times 5.80 \times 10^{10} \text{ m}^2 = 5.59 \times 10^9 \text{ g}/\text{yr}$ or only about 0.01 Tg/yr (1 Tg = 10^{12} g). In using this figure we must keep in mind that for most of the day asphalt emissions do not approach the maximum flux used in this calculation and we do have evidence that asphalt emissions drop off significantly as the asphalt becomes old.

For the purposes of this work, it is important to compare measured methane fluxes from asphalt, a fossil fuel source, with measurements from other sources of methane that have been studied previously. Table 2 lists both average flux of methane

and a reasonable estimate of the total land surface area covered for several previous studies of tropical and temperate wetlands and rice paddies. As can be readily seen, the sources listed typically have fluxes several orders of magnitude larger than the maximum flux value of $0.0003 \text{ g}/\text{m}^2/\text{d}$ ($22 \mu\text{g}/\text{m}^2/\text{hr} \times 12 \text{ hr}$) found for asphalt. The estimated land area for these sources is also larger than the estimate derived above for asphalt pavement surface area.

Recent estimates for several methane sources of all types, including estimates made by compiling data such as in Table 1 for wetland areas, show that biogenic sources may range from 100–200 Tg/yr for natural wetlands and 60–170 Tg/yr for rice paddies, while fossil fuel sources such as coal mining and gas drilling, venting, and transportation losses may range from 25–45 Tg/yr and 25–50 Tg/yr, respectively [*Cicerone and Oremland*, 1988]. In recalling the estimated value for asphalt CH₄ emissions of 0.01 Tg, it is evident that methane asphalt emissions are not only small compared to several biogenic sources, but to other fossil fuel sources as well.

If similar calculations are made for the CO emissions from asphalt comparisons can be made with emissions of CO from other sources. For example, the first test with the 7 day old asphalt (see Figure 2b) had a maximum emission of $2.62 \text{ mg}/\text{m}^2/\text{hr}$. Integrated emissions for this day result in $10.0 \text{ mg}/\text{m}^2/\text{d}$, assuming a 14-hour day with at least some light and no nighttime emissions. Since the greater metropolitan area of

Denver is about 210 km², one can make a liberal estimate of city asphalt emissions by assuming that 20% of the total surface area of the metropolitan area is asphalt including both parking lots and roadways. Then 10.0 mg/m²/d x 2.1 x 10⁸ m² x 0.20 = 4.2 x 10⁸ mg/d. We can compare this to the amount of estimated daily CO emissions by motor vehicles in the Denver area. According to D. Stedman (personal communication, 1988), Denver traffic emits somewhere between 1200 and 1700 metric tons (one metric ton equals 1000 kg) of CO per day. That is equivalent to a range of (1.2–1.7) x 10⁶ kg/d. Asphalt emissions of 4.7 x 10⁸ mg/d are equal to 420 kg/d so they are only a small portion of the amount emitted by motor vehicles in Denver.

CONCLUSIONS

Based on our measurements we conclude that methane emissions from asphalt pavement cannot be a significant source of atmospheric methane on a global basis. Maximum emissions were 22 µg/m²/hr for 1- to 4-week old pavement during peak sunlight intensity. Emissions were much smaller for other times of day and dropped off to negligible amounts at night. Smaller emissions were observed for asphalt pavement of 2.5–3 years approximate age under similar conditions. Making the most favorable assumptions regarding total surface area of exposed asphalt pavement globally, our calculations indicate that asphalt methane emissions are only about 0.01 teragram per year even when using our maximum observed emission rate as the average rate of emissions for all exposed asphalt on the globe.

These calculations can only serve as estimates as it is difficult to extrapolate to global surface area of asphalt from asphalt production figures. For instance, lifetime of emissions from asphalt pavement cannot be well known nor can the age of the many and varied roadways. Also there are different UV spectrums at the surface in locations around the globe. Asphalt cement as a percentage of total asphalt mix varies from region to region. Furthermore, different asphalt aggregates may have slightly different densities leading to different changes as they are compressed and hence differences in the release of volatile gases. Not only do the aforementioned examples cause problems in estimating total emissions, but European and other asphalts used for paving may have higher emissions than the asphalt used in the United States on which our measurements are based. Other nations use some road pitch mixed in with asphalt cement and it is known to be more volatile. Nevertheless, the differences in composition among the world's asphalts and their chances for increased volatility and methane release above that of the U.S. asphalt we studied cannot be very great (B. Brakey and A. Anderson, personal communications, 1988).

Sackett *et al.* [1988] have expanded on the work reported by Sackett and Barber [1988]. Because asphalt has other uses such as roofing and construction applications which may also be exposed to sunlight, they are also testing other surfaces made from petroleum products such as synthetic rubber, plastics, and spilled oil. These authors have found that some of these emit several times more CH₄ than asphalt surfaces. Nevertheless, it would seem that the total CH₄ released from all of these additional potential sources must be very small as the actual global surface area of asphalt pavement exposed to sunlight must dwarf all the other mentioned petroleum-derived sources combined.

The recent article by Cicerone and Oremland [1988] puts a value of 1 Tg/yr for asphalt methane emissions in perspective.

In their Table 4 they list total annual release of methane by identified sources. One column lists HEDC, the hypothetical equivalent dead carbon methane which might be expected from various sources. If the radiocarbon dead methane sources have been underestimated in the past and are in fact as much as 32% of total methane released to the atmosphere [Lowe *et al.*, 1988], then there are other more likely explanations for overlooked dead methane sources than methane from asphalt. These explanations include the release of biologically produced but ¹⁴C-depleted methane escaping from older carbon substrates in peat bogs and boreal wetlands, and release of methane from gas hydrates in continental shelf areas. These are in addition to the possibility that radiocarbon dead sources such as venting and flaring of gas, and coal and lignite mining are underestimated as sources. One other possibility is that the modern "live" biogenic methane sources have been overestimated and that current existing estimates for dead methane source strength actually represent a greater portion of the total methane budget than believed. For this last possibility to be true, estimates of constraints on the atmospheric lifetime of CH₄ and the magnitude of methane sinks would have to be in error significantly.

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