10 September 2013

TECHNICAL MEMORANDUM

To: Anne LeHuray, Pavement Coatings Technology Council

From: Robert DeMott, Thomas Gauthier, Michael Masonjones, ENVIRON International, Corp.

Subject: Volatilization of PAHs from Coal-Tar-Sealed Parking Lots

Introduction

Two papers recently published by Van Metre and coworkers (2012a, 2012b)[1] on the volatilization of polycyclic aromatic hydrocarbons (PAHs) from coal-tar-sealed (CT-sealed) parking lots suggest that volatilization losses represent a potentially significant source of PAHs to urban air, and that annual PAH emissions are larger than annual vehicle emissions of PAHs for the United States.

Both papers rely on short-term ambient air concentrations measured at the parking lot surface and complex modeling strategies with numerous underlying assumptions to calculate their estimates of PAH emissions. The models were initially developed for estimating pesticide emissions from soil and water evapotranspiration rates from agricultural fields. We find that the simplifying assumptions applied by the authors to instead model PAH emissions from a parking lot surface result in an overestimation of emissions by a factor of about 2.5 to 3. In addition, comparisons made to PAH concentrations detected in other studies, and PAH mass loss based on changes in sealer concentrations over time, which are intended to substantiate the flux measurements, are inherently flawed.

In one paper, PAH concentrations detected at the parking lot surface are compared to ambient air PAH concentrations reported elsewhere to support their claim that emissions are potentially significant. However, the authors inappropriately compare short-term (2-hour average) daytime-only measurements collected during the hottest part of the day to longer-term (12 hours to 4 months) average concentrations that include cooler nighttime levels. The authors bias their comparison by not including PAH concentrations detected during cooler nighttime conditions in their own study averages (when estimated emission rates were five times lower) even though other studies in the table represent longer-term averaging periods including day and nighttime conditions.

---

[1] Van Metre, P.C., M.S. Majewski, B.J. Mahler, W.T. Foreman, C.L. Braun, J.T. Wilson and T.L. Burbank. 2012a. Volatilization of Polycyclic Aromatic Hydrocarbons from Coal-Tar-Sealed Pavement. *Chemosphere* 88(1):1 - 7.

Van Metre, P.C., M.S. Majewski, B.J. Mahler, W.T. Foreman, C.L. Braun, J.T. Wilson and T.L. Burbank. 2012b. PAH Volatilization Following Application of Coal-Tar-Based Pavement Sealant. *Atmospheric Environment* 51: 108-115.

In a second paper, the authors attempt to substantiate their estimated PAH emission rates with changes in PAH concentrations detected in parking lot scraping samples. This type of sampling is prone to inclusion of the underlying substrate which serves to dilute sealer PAH concentrations and overestimate losses. In addition, although there is some mention of alternative loss pathways (e.g. photolysis, runoff, wind transport) no quantitative assessment is presented to establish the relative importance of these loss pathways. In other studies, photodegradation has been reported to be much more significant than volatilization (for example, as reported by Kim et al., 2009).[2] Even the authors used a sample of product that was "dried indoors **in the dark** for 3 days" as the starting concentration for the parking lot scraping samples – apparently recognizing a concern for photodegradation losses. It is a notable observation, not mentioned by the authors, that PAH losses after volatilization for 3 days in the dark were much less than PAH losses from the combined effects of volatilization and photolysis after one day in the field.[3]

The following critique considers the appropriateness of the study design, the applicability of the model used to characterize air emissions, and the associated uncertainties of the estimates used to develop conclusions. In brief, our analysis finds that the selected modeling equations and simplifying assumptions used bias the estimated emissions high by at least a factor of 2.5-3-fold. Emissions 2.5-3-fold lower than estimated by the authors would, for example, not make coal tar sealers appear to be a larger source of PAHs than vehicles – one of the key conclusions reached. Moreover, given that the in-use parking lots examined in the *Chemosphere* paper were evaluated under extreme high temperature conditions, and that the follow up study of emission rates over time is based on a single CT-Sealer application made during these same extreme high temperature conditions, there is considerable uncertainty in using these data to draw conclusions about PAH emissions from CT-sealed parking lots under more typical conditions and on an annual basis.

Background

The first paper, published in *Chemosphere*, presents "summertime" gas phase PAH concentrations in ambient air collected at two heights (3 cm and 1.28 m) above ten in-use parking lots (6 CT-sealed lots, 1 asphalt-sealed lot and 3 unsealed lots) in Austin, Texas. The exact ages of the sealer on the parking lots were unknown, but estimated to range from about 3.6 to 8 years based on Google earth photography, with an uncertainty of about 0.5 to 2 years according to the authors. The samples were collected during the hottest part of the day (from about 2:30 to 4:30 pm), and are characterized as representing "likely daily summertime maximum concentrations and fluxes." From the paired ambient air concentration measurements, PAH emission flux rates were estimated using models for emission flux developed for pesticide emissions from soil (the Scholtz method)[4] and

[2] Kim, D., B.M. Kumfer, C. Anastasio, I.M. Kennedy and T.M. Young. 2009. Environmental aging of polycyclic aromatic hydrocarbons on soot and its effect on source identification. Chemosphere 76: 1079-1081.

[3] Because no temperature is reported for the drying time indoors, it is unclear to what extent differences in temperature may account for differences in PAH losses.

[4] Scholtz, M.T., E. Voldner, A.C. McMillan and B.J. Heyst. 2002. A pesticide emission model (PEM) Part I: model development. *Atmospheric Environment* 36: 5005-5013.

water evapotranspiration rates (using the Thornthwaite – Holzman (T-H) equation)[5] from agricultural fields and forests.

All the parking lots were sampled once in August, 2009 during the hottest part of the day and five of the lots were sampled a second time from about 5:00 to 7:00 am when temperatures were cooler. The sampling methodology follows an approach developed by Meijer et al. (2003) for estimating pesticide emissions from soil and utilizes a 1.3 m diameter stainless steel disk collecting air at 3 cm above the surface of the parking lot and a high volume air sampler mounted on a stand collecting air at a height of 1.28 m. At the end of each sampling event, a dust sample was also collected from the surface of the parking lot using a vacuum device and the fine fraction (< 0.5 mm) was retained for analysis.

The authors analyzed air samples for 19 individual PAHs, but only eight PAHs [phenanthrene (PHE), anthracene (AN), 4,5-methylphenanthrene (45MP), 1-methylphenanthrene (1MP), fluoranthene (FLU), pyrene (PY), chrysene (CHY) and benzo(b)fluoranthene (BbF)] were detected frequently. The authors referred to these 8 PAHs as ΣPAH8. Not surprisingly, the ΣPAH8 concentrations detected in ambient air were higher above the CT-sealed lots compared to unsealed lots. However, the authors found no difference between concentrations above CT-sealed lots and the asphalt-sealed lot.

In a second paper, published in *Atmospheric Environment*, the authors used the same approach (i.e., collecting ambient air samples at 3 cm and at 1.28 m) to estimate PAH flux rates from a newly applied CT-sealed parking lot surface after 1.6 hours, and after 1, 5, 16, 45, 149, 232, 328 and 376 days following application. After each sampling event, a sample of sealer was scraped from the parking lot surface to estimate total PAH losses (volatilization and degradation) from the CT-sealed parking lot for comparison.

The authors reported a decrease in ambient air concentrations over time with the highest levels recorded during the curing period (within 24 hours) and a significant decrease in ambient air concentrations (and estimated flux rates) over the 16 days following the application. Within these first 16 days following application, PAH emissions were dominated by PHE and AN, which comprised about 85% of the total PAH emissions during this time period. Once this initial drying period is complete, the volatilization flux rate is likely controlled by temperature.

Analysis

Based on our analysis of the data, we find that the experimental approach for estimating PAH flux rates from sealed parking lot surfaces under the environmental conditions of the study is flawed and results in an overestimate of emission rates. In particular we find the following.

The flux calculation method used by the authors includes inappropriate simplifying assumptions.

The flux calculation method used by the authors (following Scholtz, 2002 and Louis, 1979[6]) includes inappropriate simplifying assumptions about friction velocity, wind speed profiles, and surface

---

[5] Thornthwaite, C.W., and B. Holzman. 1939. The determination of evaporation from land and water surfaces. *Monthly Water Review* 67: 4-11.

boundary layer thickness. These factors relating to the model result in overestimating flux rates by a factor of about 2.5 to 3 due to the resulting biases in the calculations themselves. A full treatment of this portion of the analysis can be found in the attached Appendix.

In brief, flux calculations are sensitive to the roughness length parameter, which is necessary to scale atmospheric stability. The authors do not provide a value for this parameter, and it appears from their supplemental documentation that they simplified the full Scholtz/Louis method to avoid including this parameter. At the same time they also appear to ignore (or at least greatly simplify) the thermal effects that a hot parking lot surface would create on the turbulence scale. Efforts at reconstructing their analysis using the full Scholtz/Louis treatment reveal their equivalent choice of roughness length to be inconsistent, ranging from 3 to 15 cm, depending on which paper and which calculation they are performing (wind speed or flux multiplier). This is why their results appear to be corroborated by the simpler Thornthwaite-Holzman model developed for pesticides volatilizing from soil, since these roughness lengths are similar to what would be appropriate for an agricultural field. However, these values are far above the appropriate value for a parking lot, which is relatively flat. Choosing a more appropriate value of 0.5 cm, as suggested by the literature, results in lower estimated fluxes.

The modeling estimates are also expected to be biased high due to experimental design.

Assumptions about the turbulent surface layer thickness of 3m used in their calculations are found to be inappropriate when tested using a full boundary layer theory approach (Monin-Obukhov) for verification. As a consequence, chemical measurements, temperatures, and wind speeds were often sampled well above the predicted layer where the Scholtz/Louis approximations to the Monin-Obukhov theory apply, and also above where traditional calculations place the concentration boundary layer for cross flow over a flat evaporating plate at a certain fetch distance from the upstream edge. Further compounding the bias is that wind speed and temperature measurements are taken at different elevations than the chemical measurements, which violates the assumptions of Scholtz/Louis, and attempts to correct for this with logarithmic profiles are invalid outside the surface layer. The end result of the flaws in the experimental design is that flux calculations are biased high. A more thorough discussion can be found in the attached Appendix.

Ambient air concentrations above aged CT-sealed parking lots were measured under extreme (record high temperature) conditions which serve to overestimate emission rates and yield atypical results.

The authors recorded "summertime" gas phase PAH concentrations collected during the hottest part of the day (from about 2:30 to 4:30 pm) between August 10, 2009 and August 28, 2009. Average temperatures recorded at 1.28 m above the parking lot surface ranged from 97.7 to 110 °F, and at the surface of the parking lot from 123 to 142 °F.

---

[6] Louis, J.F., 1979. A parametric model of vertical eddy fluxes in the atmosphere. Boundary Layer Meteorology 17:187-202.

These temperatures represent extreme high temperatures for Austin, Texas. For example, the average daily high temperature recorded at Austin Mabry Airport in August ranges from 95 to 98 °F (NOAA).[7] The highest temperature ever recorded in Austin is 112 °F.

In fact, during the USGS sampling, record high temperatures were occurring in Austin. Daily record highs for August 6 (105 °F) and August 11 (105 °F) were recorded in 2009. Since Parking Lot CT_1 was sampled on August 11, 2009, it is not surprising that the highest flux rates were estimated by the authors for this parking lot. At lower temperatures, with a more solid substrate, diffusion would have been slower, and flux rates due to volatility would be far less, particularly since vapor pressure increases rapidly with temperature, as described by the Clausius-Clapeyron equation.

As previously noted, the authors used a sampling approach developed by Meijer et al. (2003) for estimating organochlorine pesticide emissions from agricultural soils. The authors of that pesticide study note "the temperature in the very small boundary layer at the air soil interface is most likely to control the partitioning." Thus, the specific approach used by the authors notes the significance of temperature at the emitting surface, making it obvious that the extreme temperatures encountered in this study would be expected to yield atypical results with respect to most CT-sealer applications.

Comparison of PAH concentrations in the *Chemosphere* paper is flawed because of significant differences in temperatures and averaging times.

The authors pose the question "Does the high rate of volatilization of PAHs from sealed pavement mean that sealer is an important source of PAHs to urban air?" and then proceed to make a series of flawed comparisons to PAH concentrations reported in other papers. The PAH measurements collected above the sealed parking lots represent short-term, 2-hour average concentrations collected during the daytime[8] under extreme high temperatures ranging from 37 to 43 °C (99 to 110 °F). For comparison, Van Metre et al. include a number of studies but none are based on short-term samples and none were collected under extreme temperature conditions.

It is well established that peak concentrations decrease with increasing averaging times. For example, peak one-hour average concentrations are generally about 2 to 3 times higher than corresponding 24-hour average values and 4 to 9 times higher than corresponding peak monthly average values.[9] In addition, vapor phase PAH concentrations above a source area (*i.e.,* a parking lot) depend strongly on temperature. Even the authors note that flux rates were five times lower during "nighttime" concentrations when temperatures ranged from 76 to 77 °F compared to daytime temperatures of 99 to 110 °F.

---

[7] http://www.srh.noaa.gov/ewx/?n=austinmabryclidata.htm
[8] Note that the authors did not include the lower nighttime concentrations in the average values reported in the table.
[9] Trout, D.A. 1980. The ratio of peak 1-hour average concentrations to peak concentrations of other averaging times for various pollutants and differing sources. USEPA Region V.

For example, the data reported by Motelay-Massei et al. (2005)[10] in Table 1 represent average concentrations over a 4-month integration period between the months of July and October, 2000. The average temperature over that sampling period was reported to be approximately 16 °C (61 °F). Week-long samples were collected at roof top level every other week for two years in the study reported by Halsall et al. (1994).[11] Weekly average temperatures were not reported but were likely within the range of monthly average temperatures in London which range from about 35 to 75 °F.

The data attributed to Gigliotti et al. (2005)[12] represent the arithmetic means of 24-hour average samples collected over multiple years at monitoring sites in New Jersey; and consecutive 12-hour day and night samples were collected over four days in January, 2 days in May, and eleven days in July from the roof of a building and from on board a ship anchored in Lake Michigan at a height of approximately 10 meters above the surface of the water in the data reported by Simcik et al. (1997).[13] Temperatures were recorded and ranged from a low of 32 °F in January to 84 °F in July.

Clearly, comparing PAH concentrations detected in January at a height of 10 m above the surface of Lake Michigan with PAH concentrations detected in August at a height of 1.2 meters above a hot parking lot under extreme high heat conditions provides little insight as to whether or not sealer is an important source of PAHs to urban air.

The authors' statement that concentrations are higher than other reported concentrations even though they represent only gas-phase concentrations while several other studies represent gas-phase and particle-phase concentrations is misleading and distracts the reader from the real differences among the studies (*i.e.,* temperature and averaging time). Gigliiotti et al (2005) report, "particle-phase PAH concentrations are often an order of magnitude or more lower than gas-phase PAH concentrations" and Halsall et al. show that the most predominant PAH, phenanthrene, "exists almost exclusively in the vapor phase." Thus, neglecting particle phase PAH concentrations has little effect on total PAH concentrations in the Van Metre study.

Comparison of estimated flux rates with PAH mass loss based on changes in sealer concentration over time neglects competing loss pathways.

Although there is some mention of alternative loss pathways (e.g., photolysis, runoff, wind transport) no quantitative assessment is presented to establish the relative importance of these loss pathways. The authors have assumed that changes in PAH concentrations over time for applied

---

[10] Motelay-Massei, A., T. Harner, M. Shoeib, M. Diamond, G. Stern and B. Rosenberg. 2005. Using passive air samplers to assess urban-rural trends for persistent organic pollutants and polycyclic aromatic hydrocarbons. 2. Seasonal trends for PAHs, PCBs, and organochlorine pesticides. *Environmental Science & Technology* 39:5763-5773.
[11] Halsall, C.J., P.J. Coleman, B.J. Davis, V. Burnett, K.S. Waterhouse, P. Harding-Jones and K.C. Jones. 1994. Polycyclic aromatic hydrocarbons in U.K. urban air. *Environmental Science & Technology* 28:2380-2386.
[12] Gigliotti, C.L., L.A. Totten, J.H. Offenberg, J. Dachs, J.R. Reinfelder, E.D. Nelson, T.R. Glen IV and S.J. Eisenreich. 2005. Atmospheric concentrations and deposition of polycyclic aromatic hydrocarbons to the mid-Atlantic east coast region. *Environmental Science & Technology* 39:5550-5559.
[13] Simcik, M.F., H. Zhang, S.J. Eisenreich and T.P. Franz. 1997. Urban contamination of the Chicago/coastal Lake Michigan atmosphere by PCBs and PAHs during AEOLOS. *Environmental Science & Technology* 31:2141-2147.

sealer (i.e., scrapings from sealed parking lots) are primarily attributed to volatilization losses. In fact, concentration changes reflect a number of loss pathways including tire abrasion, wash off, and photodegradation, in addition to volatilization. Neglecting these additional loss pathways yields an inflated estimate of losses attributed to volatilization. The importance with regard to the modeled flux estimates is that the loss of PAHs over time from applied sealer is used by the authors to provide a check on the reasonableness of their estimated flux rates. Artifactually increasing the apparent volatilization loss from the applied sealer allows the measurements to appear to support higher modeled flux estimates. In other studies, these same authors have estimated PAH removal rates due to tire abrasion and wash off - processes that are claimed to be significant enough to represent the dominant source of PAHs to nearby watersheds – yet quantitative discussion of these processes is excluded in these volatilization studies.

Photodegradation is another significant loss pathway that has been shown to be much more significant than volatilization by other researchers (e.g., Kim et al., 2009).[14] This process alone can explain the gap in mass balance that would occur if the emissions flux is 2.5 to 3 times smaller than calculated by the authors. Kim et al. (2009) examined the loss of PAH in soot particles exposed to artificial light. Loss rates for PAHs measured under irradiation conditions and in the dark indicate that photodegradation rather than volatilization is the primary PAH loss pathway for soot-borne PAH in this study. For example, the loss rate for pyrene under irradiation conditions was nine times greater than in the dark. The authors also observed an obvious two phase photodegradation loss for the lowest molecular weight PAHs [naphthalene (N), acenaphthene (ACE), acenaphthylene (ACY) and fluorene (FL)]. Loss rates for the initial phase were 5 to 40 times higher than the second phase loss rates – potentially related to initial loss of PAH at the surface followed by a slower diffusion-limited loss of PAH originating in the interior of the soot particles.   For higher molecular weight (4 to 6 ring) PAHs, however, only a single loss rate was observed.

In other studies, Matsuzawa et al. (2001)[15] estimated the photodegradation half life of phenanthrene in diesel particulate matter deposited on the ground at about 120 hours (5 days) under artificial light conditions. Behymer and Hites (1988)[16] measured the rates of photolysis of PAHs coated on a variety of substrates. For darker colored substrates the half lives measured for a variety of PAHs, corrected for losses in the absence of light, ranged from 125 to 263 hours (about 5 to 11 days) under artificial light conditions (Behymer and Hites, 1988).   For black substrates, the authors concluded that the carbon content and color of the substrate controls the reactivity of the PAHs.

In another study, Plata et al. (2008)[17] studied the photolysis of PAHs in No. 6 fuel oil coated on rocks at a beach in North Falmouth, MA by measuring PAH loss over time and comparing it to modeled

[14] Kim, D., B.M. Kumfer, C. Anastasio, I.M. Kennedy and T.M. Young. 2009. Environmental aging of polycyclic aromatic hydrocarbons on soot and its effect on source identification. Chemosphere 76: 1079-1081.

[15] Matsuzawa, S., L. Nasser-Ali and P. Garrigues. 2001. Photolytic behavior of polycyclic aromatic hydrocarbons in diesel particulate matter deposited on the ground. *Environmental Science & Technology* 35: 3139-3143.

[16] Behymer, T.D. and R.A. Hites. 1988. Photolysis of polycyclic aromatic hydrocarbons adsorbed on fly ash. *Environmental Science & Technology* 22: 1311-1319.

[17] Plata, D.L., C.M. Sharpless and C.M. Reddy. Photochemical degradation of polycyclic aromatioc hydrocarbons in oil films. 2008. *Environmental Science & Technology* 42: 2432-2438.

degradation due to photolysis. For the four ring PAHs evaluated in the study (benzo[a]anthracene and chrysene), the authors estimated that photolysis accounts for about 10% to 20% of the observed loss.

These studies suggest that photodegradation is a significant loss pathway for PAHs and that measuring PAH concentrations in scrapings from sealed parking does not provide a suitable metric for evaluating potential volatilization losses without considering losses from photodegradation and other potential loss pathways. If losses in PAHs from applied sealer due to abrasion, runoff and photodegradation were considered, the remainder attributable to volatilization loss would not be high enough to support the modeled estimates selected by the authors.

Analysis of sealer scrapings tend to overestimate PAH losses due to volatilization.

The experimental design involving scraping the cured sealer from the underlying pavement is prone to inclusion of the underlying substrate which serves to dilute sealer PAH concentrations and overestimate losses. No duplicate analyses were conducted to verify the precision of this sampling approach.

For example, CHY is included in the ΣPAH8 category, yet a statistical analysis of sealer scraping concentrations over time shows no significant trend of decreasing concentrations over time. The same conclusion also holds true for benzo(b)fluoranthene, which is also included in the ΣPAH8 category. So, while the authors infer extensive volatilization loss based on results for some of the PAHs, the limited loss of CHY and BbF point out the uncertainty in their assumptions.

In addition, in the initial days after application of the sealer, the estimated flux rate of phenanthrene and anthracene represents 83% to 85% of the total estimated vapor flux of ΣPAH8.   However, analysis of the sealer scrapings indicates that phenanthrene and anthracene represent only 38% of the PAH lost between one and five days after application. This illustrates that on actual sealed parking lots other significant loss mechanisms in addition to volatilization are operating (e.g., photodegradation). To compare to their modeling, however, the authors are attributing all of this loss to volatilization.

The PAH emissions measured in these studies are primarily low molecular weight (2-3 ring PAHs).

The PAH emissions measured in these studies are primarily low molecular weight (2-3 ring PAHs). PAH's in automobile exhaust reflect a broader range of PAH's, and tend to be less biodegradable, less photolyzable, and more toxic than the low molecular weight PAHs dominating the volatilization estimates of these papers. The authors make comparisons between the sealer emissions modeled and automobile exhaust, concluding that CT-based sealers represent a larger contribution than automobiles. This type of comparison fails to make clear to a generalist audience that automobile exhaust PAH mixtures represent different and more significant environmental impacts than the low molecular weight PAH mixture measured by the authors, which is expected to degrade more rapidly.

Conclusions

Based on our analysis, we find that the two papers recently published by Van Metre and coworkers (2012) overstate the volatilization of PAHs from coal tar sealers. These papers employ a set of modeling assumptions and experimental study design approaches that consistently bias their

findings to overestimate PAH volatilization from sealed parking lots. Our analysis finds that this bias is high by at least a factor of 2.5-3-fold. Emissions 2.5-3-fold lower than estimated by the authors would, for example, not make coal tar sealers appear to be a larger source of PAHs than vehicles – one of the key conclusions reached. Moreover, given that the study was conducted under extreme high temperature conditions, and based on a single CT-Sealer application, there is considerable uncertainty in using these data to draw conclusions about PAH emissions from CT-sealed parking lots under more typical conditions and on an annual basis.

Appendix

Methods for Calculating Boundary Layer Effects on Flux from a Flat Surface

Estimation of flux of a volatile substance from a flat surface has been studied in the literature for decades. Though an exact analytical solution exists and has been verified for laminar flow, a corresponding turbulent theory presents significant complications, mostly centering on the uncertainty in the size and strength of the eddies, which provide the bulk of the transport. As an approximation, most researchers use some form of boundary layer theory whereby a solution is established via scaling to experimentally verified situations, valid only within a certain distance away from the surface according to geometric and flow dimensions. Typically, the flux N_A of a species A is written as:

$$N_A = -k \frac{\partial C_A}{\partial z} = -Ku*(C_{A1} - C_{A0})$$

Where:
k and K are transfer coefficients, in full and unitless form
u* is the shear (or friction) velocity, which typically scales as the bulk flow velocity according to turbulence conditions, and
C_{Ai} is the concentration of species A at height z_i from the source surface.

The papers under review here use a simplified assumption of an unstable atmosphere with a boundary layer 3 m thick, and u*=0.17u, where u is the average windspeed in the boundary layer. To aid in further discussion, a review of the relevant calculation methods is discussed here. The first two methods relate to the estimates made by the authors, the third and fourth are more of a "textbook" solution for mass transfer off a flat plate, and the last is one we believe is most appropriate for flat parking lots in a real atmosphere. Method 5 represents an improvement over Methods 1 and 2 in that it will also provide a better approximation for u* and the boundary layer length scale.

Method 1 - Thornthwaite and Holzman, 1939, derived an estimate of K for water evaporation from agricultural fields:

$$Ku* = \kappa^2 (u_1 - u_0) / \ln(z_1 / z_0)^2$$

Where:
κ is the Von Karmann constant = 0.4, and
u_i are the wind speeds measured at heights z_i, optionally relative to a "zero plane displacement height".

The application of this method relies on velocity measurements being sufficiently above the roughness length of the vegetative material (about 1/10 the height of the vegetation, below which viscous flow dominates and the equation blows up), yet inside the boundary layer where the logarithmic velocity profile is valid (much less than the Obukhov length, which is dependent on

atmospheric stability, and ranges from the order of meters during the day to hundreds of meters at night).

Method 2 – Scholtz et al., 2002, derived a more sophisticated estimate of K for pesticide emissions from crops, where:

$$K = \frac{1}{1/K_T + \frac{2}{\kappa}(\frac{Sc}{Pr})^{2/3}}$$

Where Sc is the Schmidt number, $= \mu/\rho D$
Pr is the Prandtl number for air, $= \mu c_p/k$
μ = viscosity
c_p = heat capacity
k = thermal conductivity
D = diffusivity of chemical in air
ρ = density
K_T depends on the stability of the atmosphere, and given by Louis, 1979 as:

$$K_T = \frac{\theta *}{T - T_0} = \frac{a^2 u(\theta - \theta_0)}{0.74 u * (T - T_0)} F(Ri_B(z)),$$

$$\text{where } F(x) = \left\{ \begin{array}{l} 1 - \dfrac{bx}{1 + c|x|^{1/2}}, x < 0, (unstable) \\ \dfrac{1}{(1 + 0.5bx)^2}, x >= 0, (stable) \end{array} \right\}$$

Where Ri_B is the bulk Richardson number $= gz(\theta - \theta_0)/u^2 T$
T, T_0 = temperature height z, z_0
θ, θ_0 = potential temperature = $T(P_{std}/P)^{R/Cp}$ at height z, z_0
P, P_0 is pressure at height z, z_0
P_{std} is standard atmospheric pressure at sea level
R is the universal gas constant = 8.314 J/molK
g is gravity = 9.8m/s^2,
u is windspeed at height z
a = $\kappa/\ln(z/z_0)$,
b = 9.4,
c = 5.3a^{2}b(z/z$_0$)$^{0.5}$, and
z_0 = roughness length

Note that the authors of the papers under consideration chose u*=0.17u as an approximation valid for all turbulent conditions.

Note also that the position of 0.74 in the denominator follows Louis/Scholtz, but may contradict Monin-Obukhov's contention and the Wang and Bras paper referenced by the authors that it should be in the numerator.

Method 3 - Sharma and Rahman, 2002, derived a somewhat more applicable semi-empirical model for horizontal flow over a flat plate, along with experimental verification. They also provide a parameterized formula for u*, which is responsive to evolution of the boundary layer thickness as fetch distance increases.

$$u^* = u(\lambda^n \, \mathrm{Re}_b)^{-(\frac{1}{n+1})} = 0.15u \, \mathrm{Re}_b^{-0.125}$$

Where n=7, and λ=8.74 are empirical parameters,
and $\mathrm{Re}_b = \rho \upsilon \delta / \mu$, where δ is the depth of the momentum boundary layer, given by:

$$\delta = \left(\frac{\lambda^{-2n} \left(\frac{(n+3)(n+2)}{n} \right)^{n+1}}{\mathrm{Re}_x^2} \right)^{1/(n+3)} x = 0.371x \, \mathrm{Re}_x^{-0.2}$$

Where $\mathrm{Re}_x = \rho \upsilon \xi / \mu$, and
x is the "fetch" distance (from the upstream edge of the slab).

A little math gives the relation:

$$u^* = 0.17u \, \mathrm{Re}_x^{-0.1}$$

This derivation goes on to suggest that, locally:

$$Ku^* = 0.1982(8.55Sc^{0.37})^{-0.889} Sc^{-0.1270} \, \mathrm{Re}_x^{-0.2} u = 0.0294 \, \mathrm{Re}_x^{-0.2} Sc^{-0.456} u$$

Averaging over the entire fetch distance gives us something more common to compare to against other sources:

$$Ku^*_{avg} = \frac{0.1982}{0.8}(8.55Sc^{0.37})^{-0.889} Sc^{1-0.1270} \, \mathrm{Re}_x^{0.8} D/x = \frac{0.0368 \, \mathrm{Re}_x^{0.8} Sc^{0.544} D}{x}$$

Method 4: - As a general check, Venkanna, 2010 provides a textbook formula for the average mass transfer from a flat plate in turbulent flow:

$$Ku^*_{avg} = \frac{0.0296 \, \mathrm{Re}_x^{0.8} Sc^{0.43} D}{x}$$

This has a very similar form to the Sharma derivation, corroborating the approach in Method 3 for obtaining a local transfer coefficient.

Method 5: - A more formal derivation of the original Monin-Obukhov theory (1954) as summarized by Louis (1979), has the advantage that u* and the applicable vertical scale, L, are accounted for but

do not need to be known or approximated ahead of time. However, it requires solving an implicit set of equations relating the unknowns u*, θ*, and L:

$$u* = \kappa u / (\ln(\frac{z}{z_0}) - \psi_m(\frac{z}{L}) + \psi_m(\frac{z_0}{L}))$$

$$\theta* = \kappa\theta / 0.74(\ln(\frac{z}{z_0}) - \psi_h(\frac{z}{L}) + \psi_h(\frac{z_0}{L}))$$

$$\psi_m(x) = \ln((1 + y^2)(1 + y)^2 / 8) - 2\tan^{-1} y + \pi / 2$$

$$\psi_h(x) = \ln((1 + y^2)^2 / 4)$$

$$y = (1 - 16x)^{0.25}$$

$$L = \frac{\theta u *^2}{\kappa g \theta *}$$

Where L is the Monin-Obukhov Length, the limit of applicability of the surface layer in Boundary Layer theory.

Note that only the unstable atmospheric case for z<L is shown here for brevity, but the complete set of equations accommodating other cases (following Louis, 1979, Kader, 1990, Holtslag, 1990) was used when performing the calculations for this review.

This method does not provide for a specific method of calculating K, but the approximation made by the authors in Method 2 is still appropriate, taking into account diffusion through a very thin laminar sublayer below the Surface Layer. This time, however, K_T is not approximated by the empirical relations of Louis, and is just taken from its definition as $\theta*/(T-T_0)$, since $\theta*$ is now readily available.

<u>Summary of Problems with the Applied Methods</u>

- Method 1 is derived for crops, not parking lots. With its assumption of logarithmic velocity profiles, it is not useful or applicable for very small roughnesses, very unstable conditions, or measurements that are close to the extremes of the boundary layer domain, where the assumptions break down and location accuracy of the measurement equipment is on the order of the heights of interest. All of these conditions occur in a parking lot in full sun, when most of the reported measurements were taken. Though generally aligned with Method 2 results (see Table 1), as stated by the authors, Method 1 tends to overpredict fluxes, even when only compared against Method 2.

- Method 2 attempts to account for thermal effects and atmospheric stability, but it is still derived from and supported by crop evidence, and these extra effects are almost certainly different over a bare parking lot in the sun than over a vegetated field evaporating water. Though Method 2 is subject to the same limitations on logarithmic velocity profiles as Method 1, it is formulated in such a way that a single velocity can be used that is far from the surface, provided you know the thickness of the boundary layer. The authors of the papers under consideration give a constant thickness of 3 m with no justification, while it is almost certain that this thickness changes significantly with wind and solar heating conditions. Table 1 provides a comparison of the Method 2 calculations, as we have

interpreted the Scholtz paper referenced by the authors, and also as the authors themselves reported. Though slightly different from the reported values, we can see that the Method 2 calculations generally agree very well, and slight differences are probably due to the exact physical constants used, degree of formal use of the Scholtz/Louis equations, or the roughness length, which was not reported by the authors. The following are some specific significant issues that were found with the authors' stated vs. actual use of the Scholtz/Louis methodology and the appropriateness of their approximations:

- It is evident in the supplemental documentation that the authors did not actually follow the full Scholtz/Louis method (Method 2) and instead made some approximations for which we could find no justification or explanation (e.g., $F_M = u*^2$, in place of a more complex formula in Louis, and a simple factor of $0.74*K_M$ instead of a full treatment with temperature difference for K_T). Further hindering the ability to reproduce the authors' calculation was a lack of use of roughness length, what should be a key parameter in establishing wind speed, temperature and concentration profiles. Without a roughness length, it is noted that the authors resorted to an exponential velocity profile in the boundary layer zone which starts at 0, whereas a logarithmic profile based on the friction velocity and roughness is more appropriate for a turbulent boundary layer.

- The Scholtz/Louis theory requires measurements of temperature, wind speed and concentration at the same height. These heights range from 0.6 to 1.8 m in these studies, varying by as much as a factor of 3, further complicating the issue that these heights are also well outside the surface layer thickness in most cases. This represents a flaw in the experimental setup that should be fixed.

- Despite the questionable simplifications to the Method 2 approach, the author's calculation results can nevertheless be reasonably matched with roughness lengths of approximately 6 cm in one paper and 3.5 cm in the other, for the case calculating average velocity based on a constant 3m boundary layer and logarithmic profile. The value that enables matching of their reported results to the full proper Scholtz/Louis method (Method 2) is more consistent with approximately 15 and 12 cm for the same papers. These roughness lengths are probably reasonable for crops, making the favorable match reported to Method 1 results understandable, but they are in any case all very high values for roughness of flat pavement. These abnormally large scales chosen have a net effect of overpredicting fluxes, and a quick literature search confirms 5 mm is a more appropriate scale, and that is what is used in the present analysis.

- Choosing a constant Surface Layer thickness of 3 m and a u* of 0.17 times the average wind speed in that zone leads to a number of problems found with the calculation. A hot parking lot generates a significant temperature gradient near the surface, and when combined with the use of a more realistic roughness length, results in length scales more typically below 1 meter, according to Monin-Obukhov theory. This is very important when calculating u* from the average wind speed in the Surface Layer, since the assumption of logarithmic dependence of wind speed with height, used to calculate the average from a single measured height, breaks down outside this zone. Though we have confirmed that u*=0.17u is appropriate in

some circumstances, it is overly simplistic when dealing with varying thermal buoyancy conditions and long fetch lengths. More typically, u* is calculated via Method 5 to be a somewhat smaller fraction of u, as much as 2 to 3 times less under the conditions investigated here. Compounded with the tendency to use an average wind speed that is too high in many cases owing to the overestimation of Surface Layer thickness, this results in calculated fluxes that are higher than actual fluxes.

- Though Methods 3 and 4 result in very similar formulas for overall transfer coefficient, in effect corroborating each other, the primary interest is in the accompanying implications for u*. The dependence on fetch gives a reality check of whether a flat u*=0.17u, as used in the papers being investigated here, is appropriate in this circumstance. This assumption turns out to be reasonable if the boundary layer thickness is well known, so that an applicable u can be derived, and fetch distance is small (less than a meter or so). These conditions are not met consistently for the USGS studies. Also, the weak dependence on Re_x is nevertheless enough that u* may easily be a half or a quarter this value at the fetch lengths used in this investigation. Table 1 reports the u* derived from Method 5, and we see it is generally a factor of 2 to 3 lower than the simpler estimate used by the authors.

- Of further concern is that Methods 3 and 4 are meant to be used in a transition from zero ground concentration to nonzero, and it takes time and downwind distance for the concentration profile to develop to macroscopic scales that can be measured. This was pointed out by the authors themselves, and the issue is confirmed here, as most boundary thicknesses calculated by these methods, given local atmospheric conditions and fetch lengths, are well below the height of the chemical measurement apparatus at 1.28m (see Table 1). In fact, only one extreme case of the longest fetch (79m) at the lowest wind speed satisfied the condition (Sealed CT_6a_am). This results in measured off-ground concentrations that are well below what they should be if the Method is to be applied consistently. This will tend to cause overestimation of the flux from the surface.

- It should be further noted that Methods 3 and 4 completely ignore thermal buoyancy effects, which are expected to be fairly strong over a hot parking lot, and thus are probably not very applicable here, unless the conditions are stable or neutral. Indeed, Methods 3 and 4 were found to produce flux estimates that are about 3 to 10 times lower than the more formal Method 5 (see Table 1).

- Method 5 gives a more formal check on whether the equations being used (notably the log-scale dependence of velocity on height) are within the appropriate range for the original Boundary Layer theory of Monin-Obukhov. Note that Method 5 is similar to Method 2, except that L, θ* and u* are calculated instead of being approximated or taken from correlations ahead of time. The underlying assumptions that go into those approximations may be easily violated in the final answer, and Method 5 provides the post-check feedback necessary to verify the validity of the assumptions when using Method 2. Table 1 provides an estimate of L for each experimental condition, and we can clearly see in most cases that L is very different and in most cases much smaller than the globally assumed thickness of 3m used by the authors.

- Though Method 5, like Method 2, does not specifically provide for the effect of fetch distance, we have learned from analysis of Methods 3 and 4 that the parking lots are probably not big enough for a full concentration profile to develop over them. Thus, as noted previously for limitations on Method 2 due to inadequate fetch length, Method 5 will also give us only an upper bound on the actual flux. In all cases, even this upper bound was calculated to be significantly lower than the authors' Method 2 approach by about a factor of 2 to 3 (geometric mean of 2.3 and 3.0 for the papers being investigated, see Table 1).

Because of numerous compounding problems with application of theory and experimental design, the authors of the papers being analyzed report flux estimates that are at least a factor of 2 to 3 too high. This is a conservative estimate, because more aggressive pursuit of proper experimental conditions (fetch distance, height of measurement appropriate to weather conditions, experimental verification for a smaller roughness length), will all only increase that value.

References

Holtslag, A.A.M., deBruijn, E.I.F. and Pan, H.-L. 1990. A high resolution air mass transformation model for short-range weather forecasting, *Monthly Weather Review* 118:1561-1575.

Kader, B.A., Yaglom, A.M. 1990. Mean fields and fluctuation moments in unstably stratified turbulent boundary layers. J. Fluid Mechanics 212:637-662.

Louis, J.F., 1979. A parametric model of vertical eddy fluxes in the atmosphere. Boundary Layer Meteorology 17:187-202.

Monin, A.S., Obukhov, A.M. 1954. Basic Laws of Turbulent Mixing in the Surface Layer of the Atmosphere. Tr. Akad. Nauk SSSR Geophiz. Inst. 24(151):163-187.

Scholtz, M.T., E. Voldner, A.C. McMillan and B.J. Heyst. 2002. A pesticide emission model (PEM) Part I: model development. Atmospheric Environment 36: 5005-5013.

Sharma, R.N. and S.U. Rahman. 2002. A simple model for turbulent boundary layer mass transfer on flat plate in parallel flow. Chemical Engineering Journal 85: 35-39.

Thornthwaite, C.W., Holzman, B. 1939. The determination of evaporation from land and water surfaces. Monthly Weather Review 67: 4-11.

Venkanna, B.K. 2010. Fundamentals of Heat and Mass Transfer. PHI Learning Pvt. Ltd. Ch. 5.

Table 1: Comparison of Flux Calculation Methods for Phenanthrene

Sample	Previously Reported Friction velocity, u* (m s^{-1})	Method 5 Monin Obukhov Length (Surface Layer Thickness) L (m)	Method 5 Friction velocity, u* (m s^{-1})	Conc. Bound Layer (m) (Methods 3/4)	Ku* (m/s) Method 1	Ku* (m/s) Method 2	Ku* (m/s) Method 3	Ku* (m/s) Method 4	Ku* (m/s) Method 5	Previously Reported Ku* (m/s) for Phenanthrene (c.f. Method 2)	Previous / Method 5 Ku* Ratio
Sealed ASP	0.29	-0.66	0.15	0.350	0.0216	0.0195	0.0017	0.0011	0.0084	0.020	2.3996
Sealed CT_1	0.33	-0.64	0.17	0.609	0.0244	0.0221	0.0018	0.0011	0.0095	0.022	2.3568
Sealed CT_2	0.42	-1.37	0.21	0.212	0.0316	0.0278	0.0023	0.0019	0.0106	0.028	2.6294
Sealed CT_2_am	0.67	-9.46	0.29	0.193	0.0503	0.0423	0.0032	0.0036	0.0133	0.041	3.0642
Sealed CT_3a	0.35	-0.88	0.18	0.353	0.0260	0.0231	0.0019	0.0013	0.0094	0.024	2.4936
Sealed CT_3b	0.15	-0.18	0.10	0.416	0.0115	0.0109	0.0011	0.0006	0.0060	0.011	1.8828
Sealed CT_3a_am	0.08	-0.24	0.06	0.457	0.0072	0.0067	0.0008	0.0005	0.0035	0.006	1.6919
Sealed CT_4	0.56	-2.94	0.26	1.006	0.0418	0.0359	0.0025	0.0018	0.0125	0.035	2.8137
Sealed CT_4_am	0.29	-2.09	0.15	1.119	0.0245	0.0213	0.0016	0.0011	0.0077	0.020	2.5688
Sealed CT_5	0.19	-0.36	0.11	0.450	0.0144	0.0133	0.0013	0.0008	0.0064	0.014	2.1556
Sealed CT_6a	0.65	-3.82	0.29	1.016	0.0490	0.0419	0.0028	0.0021	0.0142	0.040	2.8145
Sealed CT_6b	0.27	-0.57	0.15	1.213	0.0202	0.0183	0.0013	0.0008	0.0080	0.019	2.3483
Sealed CT_6a_am	0.09	-0.20	0.07	1.437	0.0087	0.0082	0.0007	0.0004	0.0044	0.007	1.6182
Unsealed_1	0.21	-0.36	0.12	0.282	0.0159	0.0146	0.0015	0.0009	0.0071	0.015	2.1423
Unsealed_2	0.31	-0.90	0.16	0.378	0.0231	0.0206	0.0017	0.0012	0.0084	0.021	2.5360
Unsealed_2_am	0.11	-0.33	0.08	0.446	0.0101	0.0094	0.0010	0.0006	0.0046	0.008	1.7886
Unsealed_3	0.15	-0.30	0.09	0.941	0.0115	0.0107	0.0009	0.0005	0.0054	0.011	2.1060
PIC.1	0.731	-10.21	0.30	0.190	0.2162	0.0440	0.0034	0.0039	0.0141	0.043	3.0675
PIC.2	0.833	-13.15	0.35	0.185	0.2471	0.0500	0.0037	0.0044	0.0158	0.047	2.9983
PIC.3	0.649	-5.47	0.28	0.195	0.1915	0.0395	0.0031	0.0033	0.0131	0.039	3.0084
PIC.4 REP	0.398	-5.20	0.17	0.215	0.1174	0.0243	0.0021	0.0022	0.0081	0.026	3.2757
PIC.4	0.461	-7.68	0.19	0.209	0.1359	0.0279	0.0024	0.0026	0.0090	0.030	3.3127
PIC.5	0.314	3.01	0.10	0.225	0.0927	0.0163	0.0018	0.0017	0.0037	0.022	5.8415
PIC.6	0.440	14.05	0.17	0.210	0.1297	0.0253	0.0023	0.0027	0.0070	0.029	4.0973
PIC.8	0.272	-0.56	0.14	0.232	0.0803	0.0180	0.0016	0.0011	0.0078	0.019	2.4291
PIC.9	0.418	-1.15	0.20	0.213	0.1235	0.0267	0.0022	0.0018	0.0104	0.028	2.6395