

Atmospheric Dispersion of Pesticide Vapors: Analytical Methods Questioned

Glotfelty *et al.* recently presented the conclusion (1, p. 845) that "differences in molecular weight and structure cannot be neglected when one is comparing the coefficients of dispersion of vapors in turbulent air." This conclusion is contrary to knowledge about mass transfer through turbulent media and is based on an apparently erroneous interpretation of gradient information. Two processes combine to produce the behavior reported by Glotfelty *et al.*: eddy diffusion through the air and molecular exchange at the surface. A reanalysis of the concentration profiles illustrated in their figure 1a shows no evidence that the eddy diffusivities were different for the chemicals considered. The differences in concentration profiles that were observed were most likely due to molecular effects at the surface.

Atmospheric diffusivity is defined in terms of fluxes through the air and concentration gradients. In cases where direct measurements of fluxes are lacking, one may draw conclusions regarding diffusivities by looking at the curvature of concentration profiles. One can quantify curvature by using "shape functions," as

$$S = (C_1 - C_2)/(C_2 - C_3)$$

where C_1 and C_3 are, respectively, the concentrations at levels immediately below and above the intermediate level of measurement of concentration, C_2 . By stepping along each concentration profile, one can determine nine sequential shape functions. Expected values can be calculated directly from the standard micrometeorological relations. If we assume neutral stability, the geometric mean shape function should have been about 0.93 for the height intervals used in this particular case. The actual values found were 0.85 (± 17 percent) for heptachlor, 0.83 (± 27 percent) for chlordane, and 0.81 (± 20 percent) for trifluralin. In fact, conditions were not neutral, and values slightly different from 0.93 are to be expected. (The values given in parentheses are standard errors, evaluated logarithmically.)

To compare differences between the chemical species, it is informative to normalize evaluations of S for each species by using the heptachlor shape functions. The geometric means of normalized shape functions are found to be 0.98 (± 17 percent) for chlordane and 0.97 (± 4 percent) for trifluralin. These values are not significantly different from

the expected value of unity and certainly do not support the contention that there is a consistent effect of molecular diffusivity.

It seems that the finding of strange "shape functions" by Glotfelty *et al.* was imposed by the manner in which the data were analyzed. Glotfelty *et al.* normalized concentrations measured at each height, using concentrations of heptachlor at the same height, before subjecting the data to further analysis. Concentrations were normalized by concentrations rather than concentration differences by concentration differences. Normalization by the absolute values brings in another factor of interest—the efficiency of flux transfer across the layer of air immediately adjacent to the surface. Molecular (and Brownian) diffusivities affect fluxes at the interface between the atmosphere and the surface, where eddy and molecular diffusivities are indeed of similar magnitude, but they do not influence turbulent exchange well above the surface.

We are not aware of any "controversy" associated with this subject. In the context of atmospheric dispersion, eddy diffusivities far exceed molecular diffusivities, and mechanisms that might cause a molecular effect are difficult to imagine. The frequencies of turbulence involved in dispersion are sufficiently low that there is little fear that the inertia of large molecules will cause them to fail to respond to eddies, although this might not be the case for very large particles. Furthermore, the size of the molecules is not sufficient to cause them to sediment through the eddies, as might also happen in the case of particles that fall under the influence of gravity.

Inspection of the data presented in figure 1a of Glotfelty *et al.* shows them to be of very high quality. It is tempting to recommend that the data should be used to investigate the role of diffusivity on exchange processes at the surface. However, any such study would require evaluation of either the vertical fluxes or the concentrations in air in contact with the surface. Furthermore, the site used for the study of Glotfelty *et al.* does not seem adequate for this purpose. The shape functions discussed above indicate a large departure from constant-flux-layer predictions at the upper levels. (For this reason, data obtained above a height of 120 cm have been excluded from the evaluations of shape functions quoted above.) The insecticide data were ob-

tained in circumstances of 60- to 100-m uniform upwind fetch, at heights up to 1.9 m. Velocity measurements were made at heights up to 2.5 m. The surface was bare soil, with a roughness length sufficiently small that a guideline fetch/height ratio larger than 200 would have been advised. Instead, data were obtained for ratios sometimes less than 30. Thus, the data appear to have been obtained in a fetch-limited situation, in which the surface boundary layer was still slowly equilibrating after an upwind step-function change in surface flux.

In conclusion, the data must not be interpreted as evidence for a failure of existing knowledge concerning eddy diffusivity. The reason for the appearance of a discrepancy lies in the method of analysis, normalization of the data using concentrations rather than concentration differences. In reality, the set of data illustrated in figure 1a of Glotfelty *et al.* shows good agreement with the standard relationships and indicates that data obtained above about 1-m height are affected by the limited size of the experimental area. The analysis given here indicates that eddy diffusivities are the same for the species represented in the diagrams given by Glotfelty *et al.* The differences observed by them are due to diffusion across a quasi-laminar layer, which is dependent on the rate of evaporation and the molecular weight of the species.

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In a recent report Glotfelty *et al.* suggested (1) that the effective turbulent diffusivity of pesticide vapors in the surface layer of the atmosphere is a function of the pesticide. This conclusion was reached on the basis of differences between observed vertical concentration

Table 1. Vertical concentration profiles and estimated mass flux ratios from the data of Glotfelty *et al.*

Height (cm)	A Hepta- chlor ($\mu\text{g}/\text{m}^3$)	B Tri- fluralin ($\mu\text{g}/\text{m}^3$)	$(\frac{N_B}{N_A})^*$	C Chlordane ($\mu\text{g}/\text{m}^3$)	$(\frac{N_C}{N_A})^\dagger$
10	11	1.2		0.59	
15	8.7	0.88	0.14	0.45	0.026
20	7.3	0.74	0.10	0.39	0.043
25	6.5	0.66	0.10	0.35	0.05
40	5.4	0.53	0.12	0.28	0.064
50	4.5	0.42	0.122	0.25	0.033
70	4.0	0.37	0.10	0.22	0.06
90	3.6	0.32	0.125	0.20	0.05
120	3.0	0.27	0.083	0.18	0.033
150	2.4	0.21	0.10	0.15	0.05
190	2.2	0.19	0.10	0.14	0.05
Average			0.109 \pm 0.017		0.046 \pm 0.012

*Mass flux of trifluralin to that for heptachlor = $[(\bar{C}_n - \bar{C}_{n-1})_{\text{trif}} / (\bar{C}_n - \bar{C}_{n-1})_{\text{hept}}]$. † Mass flux of chlordane to that for heptachlor = $[(\bar{C}_n - \bar{C}_{n-1})_{\text{chlo}} / (\bar{C}_n - \bar{C}_{n-1})_{\text{hept}}]$.

profiles for each of the pesticides tested. This technical comment will indicate that the analysis of Glotfelty *et al.* is incorrect and that their conclusions are not justified by the reported data.

In their analysis, these investigators assumed that the pesticide concentration at a given height should be some constant multiple of the pesticide's concentration at a reference height. Thus, by normalizing this ratio for a given pesticide with the corresponding ratio for another pesticide, they expected to define a single "universal" concentration profile. Since a universal concentration profile was not observed, Glotfelty *et al.* presumed that the effective turbulent diffusivity was a function of pesticide properties.

Examination of the defining equation for the effective diffusivity,

$$\bar{N}_A = -D_{\text{eff}} \frac{d\bar{C}_A}{dy} \quad (1)$$

indicates that this normalization technique is valid only if \bar{N}_A is the same for all the pesticides. In Eq. 1, \bar{N}_A is the mean mass flux of pesticide A in the vertical (y) direction, $(d\bar{C}_A/dy)$ is the mean concentration gradient of pesticide A in the same direction, and D_{eff} denotes the effective diffusivity. The assumption of constant mass flux is clearly not justified in that the mass flux at the interface, which, under steady conditions, equals that through the surface layer, is approximately proportional to the vapor pressure of the pesticide (see Eq. 4). The pure-component vapor pressures, which may or may not reflect the actual vapor pressures at the air-ground interface, were given by Glotfelty *et al.* as 1.1×10^{-4} mmHg for trifluralin, 3×10^{-4} mmHg for heptachlor, and 1×10^{-5} mmHg for chlordane.

If the mass fluxes of two pesticides are not equal, the ratio of these fluxes is given by

$$\frac{\bar{N}_A}{\bar{N}_B} = \frac{(D_{\text{eff}})_A (d\bar{C}_A/dy)}{(D_{\text{eff}})_B (d\bar{C}_B/dy)} \quad (2)$$

If D_{eff} is a function only of the atmospheric properties (for example, wind speed, atmospheric stability, and height), then

$$\frac{\bar{N}_A}{\bar{N}_B} = \frac{d\bar{C}_A}{d\bar{C}_B} \sim \frac{\Delta\bar{C}_A}{\Delta\bar{C}_B} \quad (3)$$

Thus, the concentration difference between two heights for a given pesticide divided by the corresponding concentration difference for a different pesticide should give an estimate of the ratio of mass fluxes. Since the estimated mass flux ratio should be constant with height, analysis of the data by Eq. 3 should indicate the effect of differing molecular properties on the effective diffusivity. Table 1 summarizes the vertical concentration profiles of heptachlor, trifluralin, and chlordane reported by Glotfelty *et al.* Since the tabulated data were unavailable, it was necessary to estimate the information on concentration versus height from figure 1 of Glotfelty *et al.* As indicated in Table 1, however, the mass flux ratios of trifluralin to heptachlor (0.109 ± 0.017) and chlordane to heptachlor (0.046 ± 0.012) were relatively constant, despite the inaccuracy of the data. Thus, on the basis of the data reported by Glotfelty *et al.*, the effective diffusivity does not appear to be a function of molecular properties. Although it is true that molecular properties affect the volatilization rate of the pesticides, this should not be construed as a molecular effect on the atmospheric dispersal processes. The variation in concentration profiles observed by Glotfelty *et al.*

can be explained in terms of difference in the pesticide fluxes. The mass fluxes are ordered heptachlor > trifluralin > chlordane, qualitatively consistent with the magnitudes of the pure-pesticide vapor pressures.

Although molecular effects can be neglected throughout most of the lower layer of the atmosphere, they cannot be neglected very near the surface. Vertical mass transport in the laminar sublayer is via molecular diffusion. One can estimate the influence of molecular diffusivity on the overall vertical mass transfer rate by examining the defining equation for the mass transfer coefficient,

$$\bar{N}_A = k_A (C_{AS} - C_{A\infty}) \quad (4)$$

where k_A is the vertical mass transfer coefficient of A, C_{AS} is the surface concentration of A (mixture vapor pressure), and $C_{A\infty}$ is the mean concentration of A in the free atmosphere.

Experiments have made it possible to correlate k_A with flow conditions. The effect of molecular properties on turbulent mass transfer from a flat plate (which we will use to approximate the earth) is given by (2)

$$\frac{k_A}{k_B} \sim \left(\frac{D_A}{D_B} \right)^{2/3} \quad (5)$$

Since the molecular diffusivity of a gas is typically related to the inverse of the square root of its molecular weight, M ,

$$\frac{k_A}{k_B} \sim \left(\frac{M_B}{M_A} \right)^{1/3} \quad (6)$$

This suggests that molecular diffusion accounts for about a 7 percent difference in mass flux between trifluralin ($M = 335$) and chlordane ($M = 410$).

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2. L. J. Thibodeaux, *Chemodynamics—Environmental Movement of Chemicals in Air, Water, and Soil* (Wiley, New York, 1979), p. 86.

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Although presented in slightly different ways, both Hicks *et al.* and Reible raise the same issue: that ratios of concentration differences between two height intervals ("shape functions") should have been used to analyze our pesticide data rather than normalized ratios of concentrations. Owing to the need for brevity, we were unable to adequately discuss this point in our report (1), and it is clear that our remarks

regarding the shape-function test have been misinterpreted. Although it does support our contention that the rates of dispersion of pesticides above treated fields are dependent upon molecular size and shape, we found that the shape-function test can be very misleading. We thus chose to present the data in a manner that was more straightforward, more revealing, and less subject to error.

As defined by Hicks *et al.*, the shape function, S , for a particular component is given by the equation

$$S = (C_1 - C_2)/(C_2 - C_3) \quad (1)$$

where C_1 and C_3 are, respectively, the concentrations immediately below and above the intermediate level of measurement of concentration, C_2 . If the mass flux is constant through the profile, it follows that for component a

$$S_a = K_{2,3}^a/K_{2,1}^a \quad (2)$$

where $K_{2,3}$ and $K_{2,1}$ are the "eddy diffusivity" coefficients between the respective levels. One can compare the shape function for two separate components flowing through the same profile depths by using the equation

$$S^a/S^b = (K_{2,3}^a/K_{2,3}^b)/(K_{2,1}^a/K_{2,1}^b) \quad (3)$$

If the value of S^a/S^b is greater than 1.0, then the eddy dispersion of component a increases more rapidly with height than that of component b.

In order to clarify our position, it is necessary to introduce additional experimental data. Table 1 presents data on airborne heptachlor and trifluralin concentrations for a different sample interval from that reported earlier (1). These data are not unique but were selected from among a number of similar time periods in the original study (2). They are from the period centered at 1400 E.D.T. on the first day of the first experiment conducted at Beltsville, Maryland.

Calculation of the shape function S^t/S^h (where t is trifluralin and h is heptachlor) from the data in Table 1 gives values of 1.08 for heights of 5, 20, and 35 cm and 1.13 for heights of 35, 100, and 190 cm. According to Eq. 3, these shape functions clearly show that during this time period the rate of dispersion of trifluralin exceeded that of heptachlor, and that the difference increased with height.

Analysis in terms of relative concentration profiles (1) gives the same result. The concentration of trifluralin decreased by about 15 percent with respect to heptachlor throughout the profile. The foregoing S^t/S^h calculation is consistent

Table 1. Heptachlor and trifluralin concentrations and the ratios of concentration differences for a period during the first Beltsville experiment.

Height (cm) above bare ground	Concentration ($\mu\text{g}/\text{m}^3$)		N_T/N_H
	Hepta- chlor	Tri- fluralin	
5	86.6	40.2	0.57
10	77.4	35.0	0.49
15	68.6	30.7	0.48
20	59.4	26.3	0.33
25	57.6	25.7	0.51
35	49.5	21.6	0.48
45	40.6	17.3	0.49
60	35.1	14.6	0.45
80	28.9	11.8	0.45
110	24.4	9.77	0.41
150	19.8	7.90	0.44
190	16.7	6.55	

with our interpretation of this result: trifluralin declines with height with respect to heptachlor because it is dispersing more rapidly. Such relative concentration differences occurred very consistently for all the pesticides in nearly all the periods we sampled. In fact, the data in Table 1 yield a plot of normalized relative concentration that is remarkably similar to figure 1b of (1).

The data in Table 1 thus illustrate the case where K^t/K^h increases with height. A similar calculation of S^t/S^h based on the data of figure 1 of (1) (see Reible) gives values much closer to 1.0, as emphasized by Hicks *et al.* It should be noted that $S^a/S^b = 1.0$ in Eq. 3 does not imply that $K^a = K^b$, only that $K^a/K^b = Q$. This means that the shape function analysis will fail to detect any differences between the diffusivity coefficients as long as their ratio is constant over the measured profile. Such a case would arise if components a and b were transported at different rates by the same mechanism.

We believe this situation exists in the observations presented in figure 1 of (1), where regression analysis of the original concentration data reveals a highly rectilinear correlation between the concentrations (in micrograms per cubic meter) of trifluralin and heptachlor ($r^2 = 0.999$),

$$C_t = (0.110 \pm 0.005) C_h - (0.062 \pm 0.028) \quad (4)$$

where the \pm values represent the 99 percent confidence interval. In this case it is clear that $K^t/K^h = Q$, but the existence of the intercept value in Eq. 4 suggests that $Q \neq 1$. Trifluralin and heptachlor do not approach experimentally

undetectable levels at the same height in the profile. Since each has the same source, the field surface, and a negligible background air concentration, this indicates that the lower rate of dispersal of heptachlor caused some to remain when, upon extrapolation, trifluralin had disappeared. The result that $K^t/K^h = Q \neq 1.0$ is consistent with our contention that atmospheric transport of vapors occurs as a single coupled process between eddy dispersion and molecular diffusion.

The differences in profiles cannot be reconciled with the differences in mass fluxes from the surface. The ranking of diffusivities that we presented (1) does not correspond to relative volatilities. For example, Dacthal, one of the least volatile chemicals, is ranked between trifluralin and heptachlor, the two most volatile. All the questions raised by Hicks *et al.* and Reible are concerned with dilution rates at heights of 10 cm and more above the surface. At this distance the effects of any surface layers of laminar flow where molecular diffusion would be dominant can be neglected. Furthermore, the existence of any such layers at the surface of a porous body such as soil, where pressure fluctuations associated with turbulent air movement will penetrate into the body of the solid, is highly questionable (3).

Our reference to the existence of controversy over the interpretation of the actual physical nature of the dispersion of conservative entities in the atmosphere is supported by several references, including one that contains a classical application of shape-function analysis by the originator of the concept and discusses paradoxes that remain unresolved (4).

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