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. On 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 ($\pm$ 17 percent) for heptachlor, 0.83 ($\pm$ 27 percent) for chlordane, and 0.81 ($\pm$ 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 ($\pm$ 17 percent) for chlordane and 0.97 ($\pm$ 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 obtained 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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Reference

1. D. E. Glotfelty, A. W. Taylor, W. H. Zoller, *Science* **219**, 843 (1983).

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 (μg/m^3)	B Tri-fluralin (μg/m^3)	$\left(\dfrac{N_B}{N_A}\right)$*	C Chlordane (μg/m^3)	$\left(\dfrac{N_C}{N_A}\right)$†
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 ± 0.017		0.046 ± 0.012

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

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,

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

indicates that this normalization technique is valid only if $\overline{N}_A$ is the same for all the pesticides. In Eq. 1, $\overline{N}_A$ is the mean mass flux of pesticide A in the vertical (y) direction, $(d\overline{C}_A/dy)$ 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

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

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

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

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 volatization 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 affects 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,

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

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)

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

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

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

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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References

1. D. E. Glotfelty, A. W. Taylor, W. H. Zoller, Science 219, 843 (1983).
2. L. J. Thibodeaux, Chemodynamics—Environmental Movement of Chemicals in Air, Water, and Soil (Wiley, New York, 1979), p. 86.

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

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