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 (± 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 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).

30 March 1983; accepted 15 September 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

Science

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Science **224** (4651), 905.
DOI: 10.1126/science.224.4651.905