Reports

Atmospheric Dispersion of Vapors: Are Molecular Properties Unimportant?

Abstract. *Vapor profiles of pesticide mixtures over fallow agricultural fields reveal consistent rapid shifts in the relative proportions of the components in air. These relative concentration changes are correlated with molecular weight and size and reveal a significant molecular contribution to dispersion in turbulent air. Atmospheric studies that rely upon tracer gases, or use calculations that assume the equality of eddy dispersion coefficients, may be in serious error.*

The atmospheric diffusion and transport of vapor occur by two simultaneous processes: molecular diffusion arising from the thermal agitation of vapor molecules and eddy dispersion caused by physical mixing of the atmosphere. Under nearly all atmospheric conditions, molecular diffusion, as measured in the laboratory, is orders of magnitude slower than eddy dispersion. For this reason, and because turbulent mixing is a property of the atmosphere, it is usually assumed that the rate of eddy dispersion is independent of any molecular properties (*1*). We now question the validity of this assumption. From careful comparisons of the vertical concentration profiles of the vapors of several organic compounds (pesticides) in air over treated agricultural fields, we have discovered an apparent molecular contribution to eddy dispersion in the free atmosphere. Thus molecular properties play a significant role in vapor dispersal. This discovery has major implications in micrometeorology, atmospheric chemistry, and air pollution studies.

Field experiments were initially designed to measure postapplication pesticide volatilization losses (*2*). In each experiment, we sprayed an intimate mixture of two or more pesticides uniformly onto a fallow field and allowed it to remain on the soil surface (*3–5*). As the mixture volatilized and was transported by the wind, we sampled the vertical profiles of the component vapors with a sampling mast located 60 to 150 m downwind from the windward edge of the treated area. Air sampling began soon after each application and continued for chosen hourly periods for up to 50 hours. Vertical pesticide concentration profiles were obtained in 59 such sampling periods.

The air sampling mast and micrometeorological equipment are described in (*2*, *6*). Although other techniques are available, we chose to estimate vertical flux rates by the Thornthwaite-Holzman aerodynamic method because the necessary instrumentation is simple (*7*). We measured wind speeds at four or six levels between 25 and 250 cm, using cup-type anemometers. We estimated wind-speed gradients for each sample period by plotting the average wind speed versus the logarithm of height; this procedure adequately described wind profiles under nearly all conditions. We estimated temperature gradients between 30 and 80 cm by using ventilated ten-junction thermopiles in light-shielded sensors. We determined the atmospheric stability by calculating Richardson numbers. Over the 59 periods, a wide range of wind speeds and stabilities was observed during typical diurnal cycles. The soil surfaces were smooth and devoid of vegetation, and roughness lengths of 0.3 to 0.8 cm were measured from adiabatic wind profiles.

During each 1-hour period, air samples were taken simultaneously at 12 heights between 10 and 190 cm above the surface. Except for one period, wind speeds at all heights exceeded the face velocity of the sampler (18 cm/sec). At each height, approximately 3 m^3 of air was drawn through light-shielded sampling probes and the pesticides were quantitatively trapped by a plug of porous polyurethane foam (PPF) 4.5 cm in diameter and 5 cm long (*6*). The PPF plugs were Soxhlet-extracted with hexane, and the pesticide mixture in each air sample extract was analyzed by gas chromatography. During 23 sampling periods, we also drew air at six heights through glass fiber (GF) filters 4.7 cm in diameter, using a nearly identical mast at the same location. These samples were extracted with solvent and analyzed to measure the filter-retained pesticide components.

The concentrations of pesticides present in the air generally declined with time after application but gradually enough so that, after the first few periods, the change was small during each sampling period. The background concentrations of all pesticides were always at least several orders of magnitude less than the concentrations present in air over the treated fields. Figure 1a shows data for a typical period. Each point represents the time-averaged pesticide concentration at

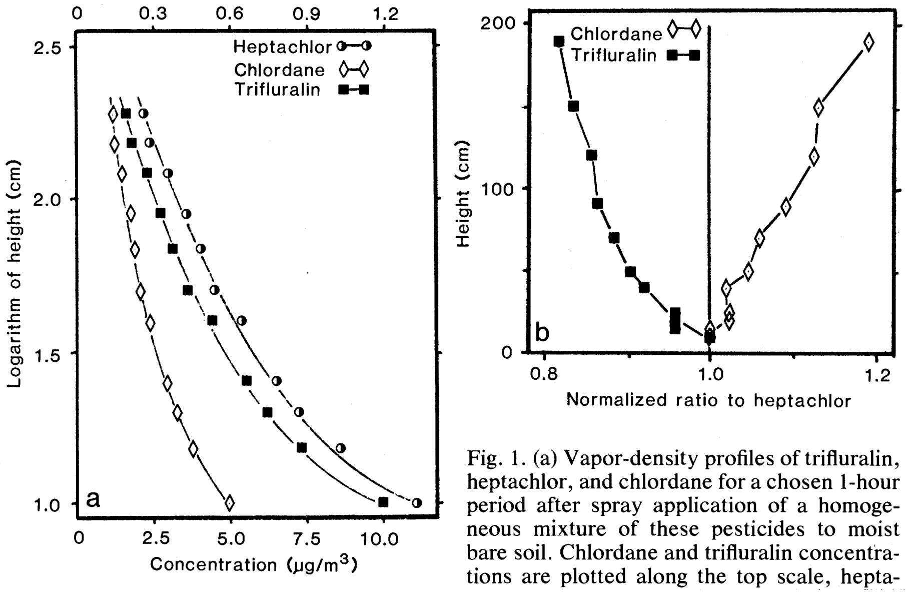

Fig. 1. (a) Vapor-density profiles of trifluralin, heptachlor, and chlordane for a chosen 1-hour period after spray application of a homogeneous mixture of these pesticides to moist bare soil. Chlordane and trifluralin concentrations are plotted along the top scale, heptachlor concentrations along the bottom. (b) Relative concentration profiles obtained by dividing the trifluralin and chlordane concentrations at each height in (a) by that of heptachlor and normalizing to the 10-cm value = 1.0. The central vertical line represents heptachlor.

that height during the sampling hour. During this period, the average wind speed at 1 m was 2.7 m/sec, the friction velocity was 0.23 m/sec, and the calculated eddy viscosity was 920 cm^2/sec, indications of turbulent conditions. The calculated Richardson number, −0.19, revealed moderately unstable thermal stratification. The smooth and nearly linear relation between pesticide concentration and the logarithm of height (Fig. 1a) is characteristic of eddy transport (*1*). Similar profiles were obtained in all periods, even in those much less turbulent than this one.

The relative concentration profiles of trifluralin, heptachlor, and chlordane for this period are shown in Fig. 1b. The trifluralin and chlordane concentrations were divided by that of heptachlor at each height, and these ratios were then normalized relative to the ratio at the lowest height. The trifluralin concentration decreases almost 15 percent with respect to heptachlor, whereas that of chlordane increases by about the same amount. The most important errors associated with determining the relative concentration profiles arose during the gas chromatographic analysis (*2*). These cause $\leq$ 1 percent relative standard error in the normalized profile points. The observed changes in Fig. 1b are thus easily measurable and highly significant.

Similar profile differences were observed in nearly all the sampling periods, which spanned a wide range of ambient conditions from fully turbulent to calm and from sunny to dark. Differential vaporization of pesticides from nearer and farther points in the field can be ruled out since there were frequent shifts of wind direction during each field experiment. The magnitude of the change in relative concentration was not closely connected to the level of atmospheric turbulence but did tend to be greatest during very light winds. The few periods in which relative concentration changes were not observed did not appear to be related to any particular level of atmospheric turbulence.

The direction of the profile differences was invariably the same for a particular pair of compounds; that is, trifluralin always decreased with height with respect to heptachlor and chlordane always increased as in Fig. 1b. In this manner, the profile changes always occurred in a definite order when all the chemicals were compared with each other.

A review of earlier studies of heptachlor and dieldrin volatilization from soil-incorporated residues under a corn canopy (*4*) and from exposed residues on orchard grass (*5*) revealed large profile changes whose significance had not been recognized. Heptachlor declined as much as sevenfold compared to dieldrin within and over the corn canopy. Photodieldrin, an isomer of dieldrin which formed on and volatilized from grass (*5*), was enriched with increasing height with respect to dieldrin.

We considered several explanations for the observed profile changes (*2*). For example, a chemical reaction such as photolysis or photochemical oxidation might cause a component to "disappear" from the profile. We calculated the exchange time represented by each vertical profile by dividing the integrated total amount of pesticide in the vertical profile by the vertical flux rate. During daylight hours these times were usually between 15 and 45 seconds, with generally longer intervals during quiet evening periods. Changes as small as 1 to 2 percent in relative concentration were measurable. For a 30-second exchange time and a reaction obeying first-order kinetics, this minimum detectable change in concentration corresponds to about a 30-minute half-life. Actually, the profile changes were usually much larger than 1 to 2 percent (Fig. 1b), representing even shorter half-lives.

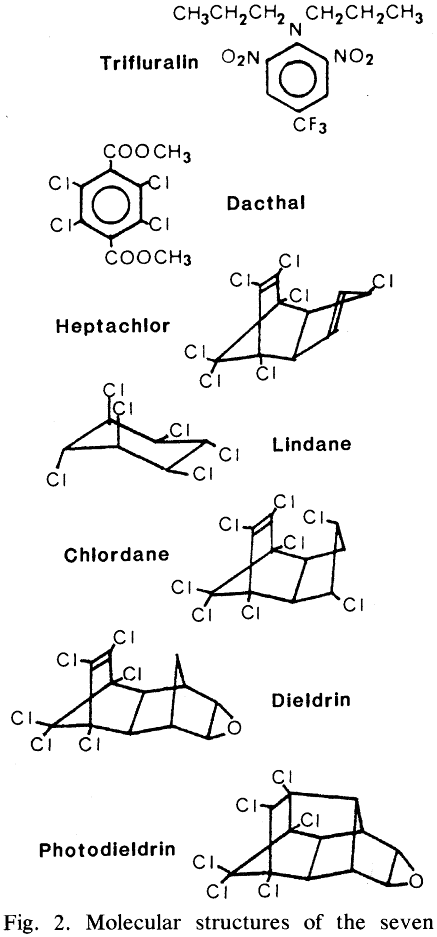

Fig. 2. Molecular structures of the seven pesticides ranked in order of profile depletion. Thus trifluralin and Dacthal are depleted with respect to heptachlor, which is in turn depleted with respect to heptachlor, which is in turn depleted with respect to chlordane, and so on.

Explanations for our profiles based on chemical processes, including photooxidation reactions with ozone or hydroxyl radicals, lead to untenable conclusions. For example, in one dark period the profile changes indicate that, if chlordane were stable, lindane, heptachlor, and trifluralin vapors must have half-lives of only 4 minutes, 47 seconds, and 15 seconds, respectively. This does not agree with the known chemistry of these compounds. For example, lindane persists in air long enough to be detectable in the mid-ocean atmosphere (*8*). For these reasons, we believe that the profile changes reflect physical rather than chemical processes.

On the basis of GF filter data, initial volatilization rates, and calculated collision frequencies with ambient aerosols, we conclude that trifluralin, heptachlor, lindane, and chlordane were evidently transported exclusively as vapor. Dacthal was different. During windy daylight periods GF filters retained about 30 percent of the total Dacthal in air, but in quiet evening conditions the amount of filter-retained Dacthal closely matched the small amounts retained from a laboratory vapor source. The particle component may have resulted from wind erosion of the wettable-powder Dacthal formulation from the soil surface. When both particulate and vapor-phase Dacthal were present, the particle fraction increased with height over the field: vapor diluted six- to tenfold, but particles diluted only two- to fourfold over the profile. Vapors apparently diffuse faster, leaving slower-moving particles behind. The Dacthal vapor profile, whether obtained in the evening when particles were absent or obtained by correction of the daytime profile for the particle component, tracked well with trifluralin, both decreasing with height to about the same extent relative to heptachlor.

Since there is no evidence for chemical reaction or particulate adsorption, it is necessary to reconsider the results in terms of the mechanism of dispersion of molecular vapors themselves. The normalized ratios in Fig. 1b represent the relative rates of dispersion of the vapors. Equal dilution of two vapors would result in all normalized values being equal to 1.00. This is to be expected if the dilution is controlled by eddy dispersion only. But this is not the case. Although linear regression analysis reveals a very high degree of correlation between the air concentrations of any two chemicals, implying the same basic transport mechanism for both of them, the fact that the relative concentrations do not remain constant with height shows that different vapor components approach zero concentration at different rates.

The relationship of the atmospheric profile to surface flux, particularly the energy elements momentum, sensible heat, and latent heat, is central in micrometeorology. One point of controversy is whether eddy dispersion is solely a property of atmospheric mixing and hence the same for all conservative entities (*9–11*). Resolution of this problem has often been hampered by instrumental errors and site-specific surface or atmospheric inhomogeneities. The fact that a different sensor is required to measure each energy property places severe demands upon instrument calibration and performance (*11, 12*). Measured profiles may be different because of systematic instrumental errors, unrecognized advected interferences, differences in the rates of eddy dispersion, or all three. Our experiment had no advected interferences, and all species were precisely measured in a single determination. Our data show that atmospheric dispersion rates are not the same for all conservative entities and also exhibit a clear reason why this is so.

The relative concentration changes among the pesticides always occurred in a definite order, and the pesticides may thus be ranked according to this order of profile depletion. This ranking is shown in Fig. 2 (*13*). According to the shape-function test of Swinbank and Dyer (*9*), profile depletion may be interpreted as a more rapidly increasing rate of eddy diffusion of the depleted component with height. The shape-function test thus reveals that eddy diffusivities increase more rapidly with height for components at the top of Fig. 2. The eddy diffusivities of the planar, aromatic herbicides trifluralin and Dacthal are greatest, and the eddy diffusivities tend to diminish as the degree of chlorination and the complexity of the ring structure increase. The ranking generally follows a pattern of increasing molecular weight (although lindane is an obvious exception), with further differences due to molecular shape, as suggested by the significant profile differences between the isomers dieldrin and photodieldrin.

The data show the effect of a single, continuous process in which vapors participate differently according to their molecular properties. Although the total transport rate is orders of magnitude greater, this predictable structuring of transport properties appears analogous to molecular diffusion. Because these pesticides have low vapor pressures, their vapor behavior is difficult to study in the laboratory and, as far as we know, measurements of their molecular diffusivity coefficients in air have not been reported. The actual molecular diffusivities are thus not known, but they would be expected to follow the ranking in Fig. 2, with the most rapidly diffusing components at the top.

We postulate that there exists a coupling of molecular diffusion and eddy dispersion into a single transport process in the free atmosphere, perhaps best described as an apparent acceleration of molecular diffusion as discussed by Monin and Yaglom (*14*). Therefore, differences in molecular weight and structure cannot be neglected when one is comparing the coefficients of dispersion of vapors in turbulent air.

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13. Dacthal was ranked for periods when particulate Dacthal was absent. Data for dieldrin and photodieldrin were from (*4, 5*). Chlordane and dieldrin were not directly compared in field studies; we judged their positions by comparing each to heptachlor.
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Attogram Detection Limit for Aqueous Dye Samples by Laser-Induced Fluorescence

Abstract. *A modified flow cytometer has been used to detect attogram quantities of aqueous rhodamine 6G by laser-inducd fluorescence analysis. A detection limit of 28 attograms (35,000 molecules) was obtained, nearly two orders of magnitude better than earlier measurements. The detection limit in concentration units was* 1.4×10^{-13} *mole per liter. During the 1-second measurement period, the total volume sampled was 0.42 microliter. On average, only half a rhodamine 6G molecule was present in the 6-picoliter probed volume.*

Laser-induced fluorescence analysis of liquid samples is of broad interest because of the exceedingly low detection limits attainable with the technique. Applications range from fluoroimmunoassay (*1*) to the detection of liquid chromatographic eluents (*2*). It is desirable to decrease the detection limits of the technique to allow analysis of smaller samples, minimize detector volume in high-performance liquid chromatography, and reduce the number of fluorescent tags needed in fluoroimmunoassay (*3*). We present here a straightforward method for the detection of attogram amounts (1 ag = 10^{-18} g) of aqueous dye based on the use of laser-induced fluorescence with an instrument designed for flow cytometry (*4*). More details of this work and a comparison of several flow cytometer experimental arrangements for fluorescence detection are presented in (*5*).

The hydrodynamic focusing technique used in flow cytometry provides a well-designed flow chamber that has been used for the analysis of small samples with laser-induced fluorescence (*6, 7*). By using a slow sample flow rate, one can analyze submicroliter volumes. Probed volumes in a flow cytometer can be as small as a few picoliters (1 pl = 10^{-12} liter). The optical arrangement of the flow cytometer provides an improved signal-to-noise ratio in comparison with conventional flow cells by