Endosulfan Transport: II. Modeling Airborne Dispersal and Deposition by Spray and Vapor

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ABSTRACT
Endosulfan (C₉H₆O₃Cl₆S; 6,7,8,9,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide) and other agricultural chemicals can be transported from farms to rivers by several airborne pathways including spray drift and vapor transport. This paper describes a modeling framework for quantifying both of these airborne pathways, consisting of components describing the source, dispersion, and deposition phases of each pathway. Throughout, the framework uses economical descriptions consistent with the need to capture the major physical processes. The dispersion of spray and vapor is described by similarity and mass-conservation principles approximated by Gaussian solutions. Deposition of particles to vegetation is described by a single-layer model incorporating contributions from settling, impaction, and Brownian diffusion. Vapor deposition to water surfaces is described by a simple kinetic formulation dependent on an exchange velocity. All model components are tested against available field and laboratory data. The models, and the measurements used for comparisons, both demonstrate that spray drift and vapor transport are significant pathways. The broader context, described in another paper, is an integrative assessment of all transport pathways (both airborne and waterborne) contributing to endosulfan transport from farms to rivers.

Acidity is the irrigated cotton (Gossypium hirsutum L.) industry in northern New South Wales, Australia, the insecticide endosulfan is widely applied by aerial spraying from November to January. A major water quality monitoring program (Cooper, 1996; Muschal, 1997, 1998) has shown that during and just after this spraying season, endosulfan concentrations in rivers near and downstream of cotton-growing areas are broadly in the range 0.02 to 0.2 μg L⁻¹, with occasional higher peaks. These values significantly exceed the present Australian environmental guideline for protection of ecosystems, currently 0.01 μg L⁻¹ (Australian and New Zealand Environment and Conservation Council, 1992). To manage and ameliorate such environmental contamination, it is vital to understand the pathways by which agricultural chemicals such as endosulfan move through the environment. Knowledge of the relative magnitudes and behavior patterns of these pathways is needed both for effective management of major pathways and also to avoid expensive efforts aimed at closing minor pathways.

This paper is the second of a pair, which have the overall aims of quantifying the magnitude, behavior, and relative importance of each of four major pathways (spray drift, vapor transport, dust transport, and runoff) by which endosulfan can move from farms to rivers, and elucidating management implications. The first paper (Raupach et al., 2001; henceforth Paper I) provides an overview, in which process models and data are combined to assess the contributions of each major transport pathway to riverine endosulfan concentrations. This paper provides modeling details for the airborne pathways. Parts of the work have appeared in several technical reports (Raupach et al., 1996; Raupach and Briggs, 1996, 1998; Briggs et al., 1998).

The present specific treatment of the major airborne pathways (spray and vapor) has several motivations. First, there is a need for a simple and robust framework for describing airborne pathways within the broader context of a complete integrative assessment of all transport pathways, undertaken in Paper I. Second, no adequate theoretical framework has hitherto existed for the vapor transport pathway. Third, many of the governing processes and conditions are common to both pathways, including turbulent dispersion and some aspects of source and deposition processes, so economy of description and proper comparisons between pathways are facilitated by using a single framework for these common processes.

Airborne transport pathways all involve three sequential processes, associated with (i) the source of the transported entity (spray droplets, contaminant vapor, or contaminant-bearing dust particles); (ii) the dispersion of the entity by wind and turbulence in the atmosphere; and (iii) the deposition of the entity to the water body. This paper assembles a suite of simple, compatible algebraic descriptions for the component processes, and tests these descriptions both separately and together with available experimental evidence. The major focus is on the spray and vapor pathways, since the dust pathway is not significant in the present context (Paper I).

The notation follows Paper I: subscripts “a” and “w” distinguish concentrations and other properties in air and water, and the α, β, and sulfate species are distinguished by superscripts α, β, or γ (where γ denotes the sulfate). Thus, the total endosulfan concentrations in air and water (in kg endosulfan m⁻³) are respectively Cₐ = Cₐ⁰ + Cₐ¹ + Cₐ² and Cₜ = Cₜ₀ + Cₜ¹ + Cₜ². A superscript s denotes an arbitrary species.

THEORY
Dispersion of Particles and Vapor

To determine contaminant transport via any airborne pathway (spray drift, vapor transport, or dust transport), it is necessary to calculate deposition from a cloud of particles or gas dispersing in the air. Here we use a simple model based on mass conservation and a Gaussian-plume assumption. The starting point is the conservation equation for a scalar entity in the air:
\[
\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = -\frac{\partial \phi_x}{\partial y} - \frac{\partial \phi_z}{\partial z} + S
\]  

where \(x, y,\) and \(z\) are along-wind, cross-wind, and vertical position coordinates (with \(z = 0\) at the ground), \(t\) is time, \(C\) is the scalar concentration, \(\phi_x\) and \(\phi_z\) are the cross-wind and vertical flux densities, \(S\) is the source density, and \(u(z)\) is the wind velocity. In this section the subscript "a", denoting air deposition, that is, the wind field is steady in time and horizontally homogeneous.

We restrict attention to "puff" releases of scalar, defined as releases that are localized in time (but not necessarily instantaneous), so that \(C, S, \phi_x,\) and \(\phi_z\) have finite integrals of the form:

\[
\hat{C}(x, y, z) = \int_{-\infty}^{\infty} C(x, y, z, t) \, dt
\]

where a caret denotes integration over all time. Then, time integration of Eq. [1] yields:

\[
u \frac{\partial C}{\partial x} = -\frac{\partial \phi_x}{\partial y} - \frac{\partial \phi_z}{\partial z} + S
\]

The time-integrated downward flux at the ground is the deposition \(D(x, y) = -\phi_x(x, y, 0)\), with units (kg m\(^{-2}\)). This is specified by a deposition velocity \(W_d\) which relates the downward flux of scalar at the surface to the concentration at a reference height \(z_i\) just above the surface:

\[-\phi_x(x, y, 0, t) = W_d \hat{C}(x, y, z_i, t) \quad \text{or} \quad D(x, y) = W_d \hat{C}(x, y, z_i)\]

Equation [4] is the lower boundary condition on Eq. [1] and [3]. The initial condition is that \(C\) is zero far upstream and as \(t \rightarrow -\infty\). We note the congruence between a time-integrated concentration field for a puff release and the concentration field for a steady plume release with the same source geometry; the former is described by Eq. [3] and the latter by Eq. [1] without the time derivative term, with similar boundary conditions in each case.

The deposition velocity \(W_d\) is a crucial parameter. In general, it is a conductance (a transfer coefficient with the dimension of velocity) specifying the air-to-surface flux of particles \((-\phi_x)\) through an equation of the form \(-\phi_x = W_d(C - C_s)\) where \(C\) and \(C_s\) are the air concentrations at the surface and at a reference level \(z_i\). For particles being deposited onto a surface it is generally assumed that \(C_s = 0\), yielding Eq. [4].

The deposition velocity is controlled by different processes for particles and gases, leading to different models for the two cases as described below.

Suppose now that mass \(Q\) of scalar is released from a source in the \(yz\) plane at \(x = 0\), not necessarily instantaneously or at a single point \((y, z, t)\), but from a source sufficiently localized that \(S(x,y,z,t)\) has a finite integral over \(t, y,\) and \(z\), and \(S\) is zero except at \(x = 0\). Then an integral mass balance over the \(yz\) plane \(x = 0\) shows that:

\[
Q = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u(z) \, \hat{C}(0, y, z) \, dy \, dz
\]  

Physically, this means that \(Q\) equals the total mass of scalar (the time-integrated mass flux) crossing the \(yz\) plane just downwind of \(x = 0\). However, as the scalar travels downwind it is removed by deposition to the surface. To describe this, we consider the mass fraction \(s(x)\):

\[
s(x) = \frac{1}{Q} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u(z) \, \hat{C}(x, y, z) \, dy \, dz
\]

which is the total mass of scalar crossing the \(yz\) plane at \(x\), normalized by the original mass \(Q\) of scalar at \(x = 0\). Clearly, \(s(0) = 1\). An equation for the evolution of \(s(x)\) can be found by integrating Eq. [3] over the \(yz\) plane. Using Eq. [3] to [6], taking \(W_d\) as uniform over all \(x\) and \(y\), and noting that fluxes vanish as \(y \rightarrow \infty\) and \(z \rightarrow -\infty\), we obtain:

\[
\frac{ds}{dx} = -\int_{-\infty}^{\infty} D(x, y) \, dy = -W_d \int_{-\infty}^{\infty} \hat{C}(x, y, z_i) \, dy
\]

It is necessary to close this equation by relating the final concentration integral to \(s(x)\). This can be done generally by means of a similarity hypothesis about the concentration field (as will be shown in a later paper), but here it is sufficient to use the more restricted assumption that the concentration field is Gaussian. In a Gaussian puff from a point release of mass \(Q\) at location \(x = 0, y = 0\), and release height \(z = h_0\), in a mean wind of speed \(u\) along the \(x\) axis, the time-integrated concentration is (Csanyi, 1973; Hanna et al., 1982):

\[
\hat{C}(x, y, z) = \frac{Q}{2\pi u \sigma_x \sigma_z} \exp \left( \frac{-y^2}{2\sigma_y^2} \right) \left[ \exp \left( \frac{-(z + z_i)^2}{2\sigma_z^2} \right) \right]
\]

where \(\sigma_x(x)\) is the plume width, \(\sigma_z(x)\) is the plume depth, and \(z_i(x)\) is the height of the plume centroid. We can refer to \(\sigma_x(x)\), \(\sigma_z(x)\), and \(z_i(x)\) as "plume" characteristics because, as noted above, the time-integrated concentration field from a puff is congruent with the concentration in a steady plume. If the scalar is settling under gravitation with terminal velocity \(W_s\), then the plume centroid can be assumed to obey \(z_i = \max(h_0 - xW_s/u, 0)\), while for a non-settling scalar material such as a gas, \(W_s = 0\) and \(z_i = h_0\). Empirical forms for \(\sigma_x(x)\) and \(\sigma_z(x)\) are often specified in terms of Pasquill stability classes, for example by Hanna et al. (1982) as summarized in Table 1. The relationship of these classes to more physical measures of stability, such as the dimensionless Richardson number, the Monin–Obhukov stability parameter, and the terrain roughness length, are given in Golder (1972) and Hanna et al. (1982). When the integral in Eq. [7] is evaluated using Eq. [8], we obtain:

\[
\frac{ds}{dx} = -\left( \frac{2}{\pi} \right)^{1/2} W_d s(x) \exp \left( \frac{-z_i(x)^2}{2\sigma_z^2(x)} \right) \frac{1^{1/2} W_s \sigma_x(x) \, u}{\sigma_z(x) \, u}
\]

which is an ordinary differential equation fully specifying \(s(x)\), given the starting condition \(s(0) = 1\). This is similar to the result of the source depletion method (Hanna et al., 1982), which calculates \(s(x)\) by using standard Gaussian formulae as if the source strength were \(Q(x)\). The present derivation makes the assumptions easier to identify and generalize.

Equation [9] is easily solved numerically once \(h_0, u, W_s, W_d\), and \(\sigma_x(x)\) are specified. Of these, \(h_0, u\), and \(W_s\) are measured parameters, and \(\sigma_x(x)\) is given in Table 1. The terminal velocity \(W_s\) is zero for a gas, while for particles it depends on particle diameter, particle-to-air density ratio, and air viscosity, and...
Table 1. Formulae recommended by Hanna et al. (1982) for the width \( \sigma_y(x) \) and depth \( \sigma_z(x) \) of a Gaussian plume from a point source near the ground, as a function of downwind distance \( x \) (km), valid for \( 0.1 < x < 10 \) km. A "super-unstable" class \( Z \) has been added.

<table>
<thead>
<tr>
<th>Pasquill stability class</th>
<th>Plume width ( \sigma_y(x) )</th>
<th>Plume depth ( \sigma_z(x) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z (super-unstable)</td>
<td>( 0.40x(1 + 0.1x)^{1/2} )</td>
<td>( 0.40x )</td>
</tr>
<tr>
<td>A (very unstable)</td>
<td>( 0.22x(0.6 + 0.1x)^{1/2} )</td>
<td>( 0.20x )</td>
</tr>
<tr>
<td>B (moderately unstable)</td>
<td>( 0.16x(0.6 + 0.1x)^{1/2} )</td>
<td>( 0.12x )</td>
</tr>
<tr>
<td>C (slightly unstable)</td>
<td>( 0.11x(0.6 + 0.1x)^{1/2} )</td>
<td>( 0.08x(1 + 0.2x)^{1/2} )</td>
</tr>
<tr>
<td>D (neutral)</td>
<td>( 0.08x(0.6 + 0.1x)^{1/2} )</td>
<td>( 0.06x(1 + 1.5x)^{1/2} )</td>
</tr>
<tr>
<td>E (slightly stable)</td>
<td>( 0.06x(0.6 + 0.1x)^{1/2} )</td>
<td>( 0.03x(1 + 0.3x)^{1/2} )</td>
</tr>
<tr>
<td>F (moderately stable)</td>
<td>( 0.04x(1 - 0.1x)^{1/2} )</td>
<td>( 0.016x(1 + 0.3x)^{1/2} )</td>
</tr>
</tbody>
</table>

can be calculated by standard methods summarized in Malcolm and Raupach (1991). The model for the deposition velocity \( W_d \) is described in the next subsection. In the restricted case where \( \sigma_y(x) = \sigma_z(x) \) (with constant \( a \) and the release height \( h_r = 0 \) (so that \( z_r = 0 \)), Eq. [9] has the analytic solution:

\[
\frac{s(x)}{s(0)} = \left( \frac{\sigma_z(x)}{\sigma_{z0}} \right)^b, \quad b = \left( \frac{2}{\pi} \right) \frac{W_d}{au} \frac{1}{\sigma_z} \tag{10}
\]

which provides a useful check on numerical solutions. We use the numerical solution in practice, because it is not subject to the restrictions on Eq. [10].

Once \( s(x) \) is determined, the deposition \( D(x, y, z) \) from a point release of mass \( Q \) of scalar is given from Eq. [4] and [8] by:

\[
D(x, y) = \frac{Qs(x)}{\pi u \sigma_y \sigma_z} \exp \left( -\frac{y^2}{2\sigma_y^2} \right) \tag{11}
\]

where the exponentials involving \( z \) in Eq. [8] have been simplified to unity by assuming that both the reference height \( z_r \) and the source height \( z_s \) are small compared with \( \sigma_z(x) \), which happens at sufficiently large \( x \) (in practice, quite quickly).

For line and plane sources, simpler expressions can be obtained by using mass conservation as expressed by the first equality in Eq. [7], which shows that for a unit source (a source of unit strength), the deposition is \(-ds/dx\). This applies both to the laterally integrated deposition from a unit point source, and to the deposition \( D(x) \) from a laterally uniform unit line source (an extensive line source across the wind direction). Extending to area sources, the deposition from a laterally uniform unit plane source (extending over \( 1000 \) m; spray release \( 5 \) km) is then the integral of the unit line-source deposition, \(-ds/dx\), over the plane source: \( D(x) = \int ds(x) \). Moreover, the actual plane source strength is \( D_0 \) and the deposition is \( D(x) \), then the deposition from a unit plane source is:

\[
\frac{D(x)}{D_0} = - \frac{1}{s'(x - x_i)} \int_{x_i}^{x} s'(x - x_i) \, dx_i = s(x) - s(x + x_p) \tag{12}
\]

where the prime denotes differentiation, so that \( s'(x) = ds/dx \). In a spraying operation, \( D_0 \) is the mass of spray released per unit area or the intended dose, and the ratio \( D(x)/D_0 \) is the drift deposition fraction \( f_{\text{drift}}(x) \) used in Paper I to quantify spray drift.

In practice, we are usually concerned with the dispersion of a cloud containing a distribution \( P(d) \) of particle sizes where \( d \) is the particle diameter. Particle size influences \( s(x) \) and hence the deposition \( D \) through the deposition velocity \( W_d \), which is a strong function of \( d \) (discussed in the next subsection). Hence, the deposition is calculated by solving separately for each particle size and summing the results, weighted by \( P(d) \).

An experimental test of this model is presented later. The basic behavior of the model is shown in Fig. 1, by plotting the depletion mass fraction \( s(x) \) and the deposition \(-ds/dx = -s'(x)\) for a laterally uniform line source (both found from numerical solution of Eq. [9]), and the drift deposition fraction \( f_{\text{drift}}(x) \) for a plane source (from Eq. [12]). Results are shown for several particle size distributions, in typical conditions specified in the figure legend and defined below.

The effect of particle size in limiting downwind drift is evident. In this work we do not explicitly consider the effects of spray droplet evaporation. However, present indications are that droplet evaporation is not a major factor for the application described in Paper I, as discussed there.

**Particle Deposition**

The deposition of particles to a vegetated surface occurs by three processes acting in parallel: direct gravitational settling to the surface, inertial impaction of particles on individual elements (leaves and stems), and Brownian diffusion of particles through the boundary layers of individual elements. The subject has been reviewed comprehensively by Davidson and Wu (1990). (Some authors, including Davidson and Wu, distinguish a fourth process, interception, which we treat as a form of impaction.) All of these processes are strong functions of particle diameter (Fuchs, 1964; Chamberlain, 1967): gravitational settling dominates for large particles (>100 μm), impaction dominates in a middle size range centred around 10 μm, and Brownian diffusion dominates for very small particles.
(<<1 μm). Consequently, a plot of $W_d$ against particle diameter exhibits a complex structure with a minimum at around 1 μm where none of the three processes is effective. Impaction and Brownian diffusion are also strong functions of the length scale of the canopy elements (such as a leaf width or stem diameter) and the local wind speed about the canopy elements, so $W_d$ also depends on wind speed and canopy architecture. The first models used to describe this complex set of processes were single-layer models in which the vegetated surface was treated as a composite, bulk entity (Owen and Thomson, 1963; Chamberlain, 1967; Shemel, 1980). Later work endeavored to resolve some of the complexities associated with the structure of the vegetation canopy through multilayer models that resolve the vertical variation of the wind field, particle concentration, and deposition processes inside the canopy (Bache, 1979a,b; Slim, 1982; Davidson et al., 1982; Ferrandino and Aylor, 1985; Raupach, 1993). While many of these multilayer models provide good representations of data from specific experiments, they are too demanding on data and parameterizations to be useful in the present context. Therefore, we use a single-layer model here.

The model is based on antecedents for single-layer models of gas transfer to vegetation (Chamberlain, 1966; 1967; Shreffler, 1978; Hicks et al., 1985), but makes use of more recent understanding of leaf-scale processes as reviewed by Davidson and Wu (1990). The deposition velocity is treated as a bulk (single-layer) conductance made up of three component bulk conductances acting in parallel:

$$ W_d = W_i + G_{imp} + G_{brow} \tag{13} $$

where $W_i$ (the terminal velocity) accounts for gravitational settling, $G_{imp}$ for impaction, and $G_{brow}$ for Brownian diffusion. Of these three, $W_i$ is a well-known function of particle diameter, particle-to-air density ratio, and air viscosity (Malcolm and Raupach, 1991). The bulk impaction conductance $G_{imp}$ and Brownian conductance $G_{brow}$ are both calculated by appealing to the analogy between particle transfer to the surface and momentum transfer.

The bulk aerodynamic conductance for momentum ($G_{aM} = \frac{u}{\nu_t}$, where $\nu_t$ is the friction velocity and $\nu_t$ the mean wind speed at the reference level $z'$) is a known property of the surface that can be specified in terms of the aerodynamic roughness length and thence the architecture of the canopy (Raupach, 1992, 1994). Two processes contribute to $G_{aM}$: form or pressure drag, and viscous or skin-friction drag (Thom, 1971), so we may write $G_{aM} = G_{aM}(form) + G_{aM}(visc)$. For a typical canopy, Thom (1971) estimated the ratio of the contributions of form and viscous drag to the total drag to be about 3:1. If $f_{form}$ is the fraction of the total canopy drag exerted as form drag, this implies that $G_{aM}(form) = f_{form}G_{aM}$ and $G_{aM}(visc) = (1 - f_{form})G_{aM}$, with $f_{form} = 0.75$.

Our hypothesis is that the Brownian conductance $G_{brow}$ is proportional to $G_{aM}(visc)$, and the impaction conductance $G_{imp}$ is proportional to $G_{aM}(form)$. For $G_{brow}$, the relationship is:

$$ G_{brow} = a_S e^{-\frac{St\rho}{\rho}} G_{aM}(visc) \tag{14} $$

where $Sc$ is the particle Schmidt number ($Sc = \frac{\nu_t}{\kappa}$, where $\nu_t$ is the kinematic viscosity of air and $\kappa$ the Brownian diffusivity for particles in air), and $a_S$ is a factor of order 1 accounting for different molecular diffusivities of particles and momentum. The factor $e^{-\frac{St\rho}{\rho}}$ accounts for the different molecular diffusivities of particles and momentum (Monteith, 1973). The Brownian diffusivity is given as a function of particle diameter $d$ by the Stokes–Einstein formula (Fuchs, 1964):

$$ \kappa = \frac{(1 + 2.5\eta_\text{air} d)}{(3\pi\eta_{\text{air}} d)} kT \left(\frac{m}{\pi \nu d}\right)^n, $$

where $k$ is the Boltzmann constant, $T$ the absolute temperature, $\rho$ the air density, and $\lambda$ the mean free path of air molecules (about $2 \times 10^{-6}$ m at sea level).

For the particle impaction conductance $G_{imp}$, the hypothesis is:

$$ G_{imp} = a_i E_{imp} G_{aM}(form) \tag{15} $$

where $E_{imp}$ is the particle impaction efficiency ($0 < E_{imp} < 1$) and $a_i$ is another factor of order 1 accounting for differential sheltering effects. The motivations for Eq. [15] are that a direct analogy between the conductances for particle impaction and form drag is only likely to be valid for particles with impaction efficiencies close to 1, and that the role of particle diameter in impaction can be quantified directly by the impaction efficiency. This can be specified as a function of the Stokes number $St$:

$$ E_{imp} = \left(\frac{St}{St + p}\right)^q; \quad St = \frac{2\tau_{\text{stoke}} U_0}{a_c}, \quad \tau_{\text{stoke}} = \frac{\rho_d d^2}{18 \rho \nu}, $$

where $\rho_d$ is the particle density, $d$ is the dimension of the canopy elements upon which impaction occurs, and $U_0$ is the flow velocity about the canopy elements (which we characterize by the friction velocity $u_*$). The stokes number $St$ is the ratio of the Stokes relaxation time $\tau_{\text{stoke}}$ to the radial traversal time $d/(2U_0)$. Equation [16] uses a commonly assumed empirical form for the function $E_{imp}(St)$, for which Bache (1981) and Peters and Eiden (1992) proposed $p = 0.8$ and $q = 2$ for several element shapes on the basis of fits to data.

Combining Eq. [13] to [15], the final form of the single-layer model for $W_d$ is:

$$ W_d = W_i + G_{aM}[f_{form}a_i E_{imp} + (1 - f_{form}) a_i Sc^{-\frac{3}{2}}] \tag{17} $$

in which $a_i$ and $a_S$ are parameters to be determined empirically. Although this model is a great simplification of the real, multilayer physics, it has advantages for the present purpose: it includes enough physics to capture the dependence of the three major processes (settling, impaction, and Brownian diffusion) on particle diameter and wind speed; its two empirical coefficients are sufficient to permit matching to experimental reality but not enough to introduce parameterization prob-
Vapor Deposition to Water Surfaces

For vapor transport of pesticides from fields to water bodies, the main deposition process of concern is deposition of vapor to the water body itself. For a species \( s \), the deposition flux of vapor into a water body is given by (Denmead and Freney, 1992):

\[
F_s(\text{vapour}) = V_d \left[ C_s - \frac{C_s}{A'} \right]
\]  

where \( V_d \) is a deposition velocity describing the (two-way) exchange of vapor between water and air, and \( A' \) is the water–air partition coefficient, defined as the partition of the species \( s \) between water and air in a system at thermodynamic equilibrium:

\[
A' = \left( \frac{C_s}{C_a} \right)_{eq}
\]

Thus, \( A' \) is the ratio of the water concentration \( C_s \) to the air concentration \( C_a \) when a vessel containing water, air, and the species \( s \) is allowed to come to equilibrium. Data reviewed in Paper I show that \( A' \) is of order 10\(^3\) for \( \alpha \)-endosulfan, 10\(^4\) for \( \beta \)-endosulfan, and 10\(^0\) for endosulfan sulfate, decreasing roughly by a factor of two for each 6°C increase in temperature.

Equation [18] shows that vapor deposition to water is driven by the difference between \( C_s \) and \( C_a \) (weighted by \( A' \)) and is a bidirectional process: endosulfan moves from air to water when \( C_s \) is high and revolatilizes back to air when \( C_s \) is low. More precisely, if the water concentration \( C_s \) in a water body of depth \( H \) responds to the air concentration \( C_a \) only by air–water exchange, then \( C_s \) obeys the mass balance equation

\[
\frac{\partial C_s}{\partial t} = F_s(\text{vapour})/H
\]

(see Paper I). This can be written as

\[
\frac{\partial C_s}{\partial t} = (A'C_a - C_s)/T'
\]

where \( T' \) is the time scale \( A'Ha/V_5 \). Hence, we have a first-order linear system in which \( C_s \) tends to track \( A'C_a \), with time averaging over a time of order \( T' \).

The vapor deposition velocity \( V_d \) determines the air–water flux. According to the Deacon model (Deacon, 1977; Denmead and Freney, 1992), the inverse of \( V_d \) is a transfer resistance \( R_d = 1/V_d \) given by the series sum of contributions from three sequential parts of the water–air pathway: transfer through the water \( (R_w) \), the quasilaminar air sublayer occupying the lowest millimetre or so of the air \( (R_a) \), and the turbulent atmosphere \( (R_t) \). This contrasts with Eq. [13] for particle deposition velocity, which is a parallel sum of three conductances describing different, parallel processes operating over the entire pathway from air to surface. The model gives the vapor deposition velocity as:

\[
V_d = \frac{1}{R_t + R_a + R_w/A'}
\]

\[
R_t^{-1} = k_{VK} u_t / \ln(z_t/z_5)
\]

\[
R_a^{-1} = 0.066(v_c/k_s)^{-0.61} u_t
\]

\[
R_w^{-1} = 0.082 \left( \frac{\rho_a}{\rho_w} \right)^{1/2} \left( \frac{v_c}{k_w} \right)^{-2/3} u_t
\]

where \( \rho_a \) and \( \rho_w \) are the densities of air and water, \( k_c \) and \( k_v \) are molecular diffusivities of endosulfan in air and water, \( v_c \) and \( v_v \) are the kinematic viscosities of air and water, \( u_t \) is the friction velocity, \( k_{VK} (= 0.4) \) is the von Karman constant, \( z_t \) is the reference height for the air concentration, and \( z_5 \) is the thickness of the quasilaminar air sublayer (given by \( z_5 = 50 v_c/u_t \)). The molecular diffusivities for endosulfan in air and water were estimated by multiplying the corresponding diffusivities for CO\(_2\) by \((M_a/M_w)^{1/2} = (44/407)^{1/2}\), where \( M_a \) and \( M_w \) are the molecular weights for CO\(_2\) and endosulfan, respectively.

Figure 4 shows the behavior of the model by plotting \( V_d \), \( R_t \), \( R_a \), and \( R_w/A' \) against \( u_t \). Typical values for \( V_d \) are about 2 mm s\(^{-1}\) at \( u_t = 0.2 \) m s\(^{-1}\), varying almost linearly with \( u_t \). All of the resistance terms in Eq. [20] are significant.

Source Terms for Spray Drift and Vapor Transport

Spray Drift

The source for spray drift is the intended deposition or dose \( D_s \) over the target area. Typically, the total dose of endosulfan in a single spray is \( D_s = 0.72 \) kg (endosulfan) ha\(^{-1}\) = 0.72 × 10\(^{-4}\) kg m\(^{-2}\), partitioned in the ratio 2:1 between
the crop into the air (kg m\(^{-2}\) s\(^{-1}\)) at time \(t\) since spraying, and \(T_s\) is a time constant for the volatilization of species \(s\), which can be determined from measurements (Kennedy et al., 1998). The air concentration produced by this flux can be evaluated using a simple Gaussian dispersion model (see above), yielding:

\[
C_s(x, y, t) = \frac{AF_s(t)}{\pi \sigma_x \sigma_y u} \exp \left( -\frac{y^2}{2\sigma_y^2} \right) \quad \text{[22]}
\]

where \(x\) and \(y\) are the downwind and crosswind coordinates of the receptor point relative to the source, and \(A\) is the area of the source (assumed to be a quasi-point source with dimensions small compared with \(x\) and \(y\)).

**RESULTS**

Comparison of Vapor Transport Model with Field Data

**Experiments**

Ahmad et al. (1995) and Edge et al. (1998) describe the field experiments used here for comparisons with the model. Two experimental sprays were carried out at Auscott Warren, NSW, at 0400 on 21 Dec. 1994 (Spray 1) and 1600 on 7 Jan. 1995 (Spray 2). In each spray, 3 L ha\(^{-1}\) of ULV Thiodan (240 g L\(^{-1}\) endosulfan) plus 0.5 L ha\(^{-1}\) of a Bt formulation was applied aerially to 182 ha of cotton in Fields 4 and 5 (see Fig. 5). Sampling of endosulfan in the environment was maintained for 5 d after each spray, as follows:

- Leaf samples were collected from Field 4 to determine the initial spray deposit and the subsequent loss rate of endosulfan species (Ahmad et al., 1995).
- Air samplers were placed within Field 4 and 200 m to its south at station S200m (Fig. 5). These yielded

**Fig. 5. Layout of the field experiment at Auscott Warren, 1994–1995.**
air concentrations of endosulfan species averaged over 4-h intervals for the first 24 h and then over 12-h intervals to 5 d. Unfortunately, no air concentration data were recovered from the S200m station for Spray 2.

- Water samplers consisted of water-filled galvanized iron trays, placed along four transects extending approximately south, north, east, and west of Fields 4 and 5, to distances up to 1000 m (Fig. 5). Each tray was 0.5 m² in surface area and 0.1 m deep, and was filled to depth 0.05 m with water. Tightly fitting lids were placed over the trays during spraying to prevent contamination of the water by direct spray drift. The lids were removed 1 h after spraying. Water samples were removed from the trays every 24 h, to 5 d, for analysis.

In addition to the above experiments, two additional experiments (Sprays 3 and 4) were carried out in the following season at Auscott Warren, on 18 and 27 Dec. 1995. In Spray 3, ULV Thiodan was applied aerially, in the same way as for Sprays 1 and 2, to 120 ha of cotton in Field 7 (adjacent to Fields 4 and 5, which were fallow). In Spray 4, Thiodan EC (350 g L⁻¹ endosulfan) was applied aerially to Field 7 at 2.1 L ha⁻¹ (together with Pix at 0.45 L ha⁻¹, with a total application rate of 20 L ha⁻¹). A major difference between Spray 4 and other sprays was in the droplet size distribution, which had a median of around 240 μm for the EC formulation (Spray 4) and around 80 μm for the ULV formulation (other sprays). The movement of volatilized endosulfan was determined after Sprays 3 and 4 using water-filled trays as described above. No air concentrations were measured. Site configuration prevented samples being taken more than 400 m from the edge of Field 7. The sampling periods were reduced from 5 d to 3 d (Spray 3) and 2 d (Spray 4), with sampling only every 24 h, because the results from Sprays 1 and 2 had shown that peak concentrations were achieved after 2 d. Because of these more restricted data sets we have not modeled Sprays 3 and 4 in detail, but we use them for qualitative comparisons.

Model Specifications

The vapor transport model was run for Sprays 1 and 2, using the parameters summarized in Table 2. These were assigned as follows:

- Volatilization parameters: The total applied dose of endosulfan per spraying, \( D_0 = 0.72 \times 10^{-4} \text{ kg m}^{-2} \), is partitioned 2:1 between the α and β isomers. There is no sulfate in the applied dose. Although some oxidation to sulfate occurs on leaves in the time between spraying and volatilization, this was assumed to degrade in situ because the vapor pressure of the sulfate is low compared with the α and β isomers (Paper I, Appendix A). The fraction volatilized was taken as \( f_{\text{vol}} = 0.5 \) for all species, to account for the sum of off-target spray drift and other removal mechanisms. The main alternative removal mechanism is probably assimilation into the soil, which can operate only on the fraction of the spray cloud that lands on the soil or is subsequently washed into the soil by rain. Endosulfan on the soil still volatilizes, though at a slower rate than from leaves (Hoechst Aktiengesellschaft, 1993).

The volatilization time scale in Eq. [21] was determined from the leaf samples, which showed that the endosulfan present on leaves decays exponentially as implied by Eq. [21], with time constants of 0.5 d (α) and 1.5 d (β) for Spray 1, and 1.0 d (α) and 5.0 d (β) for Spray 2. The longer decay time for the β isomer is caused by its lower vapor pressure (Paper I, Appendix A). The difference in decay times was caused by warmer conditions for Spray 1 than for Spray 2, and the strong dependence of the vapor pressure on temperature. The average maximum temperature for the 2 d after spraying was 40°C for Spray 1 and 29°C for Spray 2. These values for decay times are consistent with wind tunnel measurements by Hoechst Aktiengesellschaft (1993), who found values of less than 1 and about 3 d for the volatilization time scale of technical endosulfan from leaves and soil, respectively. Singh et al. (1991) found a much larger value, about 10 d, by exposing the liquid spray mixture in a petri dish on the roof of a laboratory, but this value is not applicable because of the unrealistic exposure technique.

- Meteorological parameters: Meteorological data including wind speed, wind direction, and air temperature were recorded at height 2 m during the months surrounding the trials by Dr. Nicholas Woods and colleagues, CPAS, Gatton College, University of Queensland. We used these data in half-hourly averaged form. Two gaps in the data (0830 to 1400 on 5 Jan. 1995, and 0700 on 8 January to 2230 on 9 January) were filled by copying data from periods of similar meteorological conditions, as judged from weather maps and data from

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Endosulfan dose</td>
<td>( D_0 )</td>
<td>kg m⁻²</td>
<td>( 0.72 \times 10^{-4} ), partitioned (2:1:0) between (α, β, γ)</td>
</tr>
<tr>
<td>Fraction volatized</td>
<td>( f_{\text{vol}} )</td>
<td>d</td>
<td>0.5</td>
</tr>
<tr>
<td>Volatization time scales</td>
<td>( T_a )</td>
<td>d</td>
<td>0.5 (Spray 1); 1.0 (Spray 2)</td>
</tr>
<tr>
<td></td>
<td>( T_b )</td>
<td>d</td>
<td>1.5 (Spray 1); 5.0 (Spray 2)</td>
</tr>
<tr>
<td>Elementary source area</td>
<td>( A )</td>
<td>ha</td>
<td>22.75 = 182/8</td>
</tr>
<tr>
<td>Wind speed</td>
<td>( u )</td>
<td>m s⁻¹</td>
<td>local measurements</td>
</tr>
<tr>
<td>Wind direction</td>
<td></td>
<td></td>
<td>local measurements</td>
</tr>
<tr>
<td>Stability classes for 8 three-hour periods</td>
<td></td>
<td></td>
<td>E,E,B,A,A,A,E,E (( u &gt; 2 \text{ m s}^{-1} ))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F,F,A,Z,Z,Z,F,F (( u &lt; 2 \text{ m s}^{-1} ))</td>
</tr>
<tr>
<td>Friction velocity</td>
<td>( u^* )</td>
<td>m s⁻¹</td>
<td>0.01a</td>
</tr>
<tr>
<td>Reference height</td>
<td>( z_r )</td>
<td>m</td>
<td>2.0</td>
</tr>
<tr>
<td>Water depth in trays</td>
<td>( H )</td>
<td>m</td>
<td>0.05</td>
</tr>
<tr>
<td>Endosulfan chemistry</td>
<td></td>
<td></td>
<td>see Paper I</td>
</tr>
</tbody>
</table>
nearby meteorological stations. Fortunately, the gaps occurred during periods of reasonably predictable wind and temperature. The missing 5.5 h on 5 January were filled using the same period on 11 January, and the missing 38.5 h on 8 and 9 January were filled with the same period on 3 and 4 January.

In the absence of direct information, stability classes were assigned according to time of day. Each 24-h period (0000–2400) was divided into eight 3-h blocks (0000–0300, ..., 2100–2400). The stability classes for these eight blocks were prescribed by the sequence (E,E,B,A,A,A,E,E) on occasions of moderate wind ($u > u_{\text{min}} = 2 \text{ m s}^{-1}$), and by the sequence (F,F,A,Z,Z,Z,F,F) for occasions of light wind ($u < u_{\text{min}}$). Sensitivity tests have confirmed that the model results are insensitive to the exact choice of stability classifications.

- Deposition and chemical parameters: The water depth in the trays was $H = 0.05 \text{ m}$. The deposition velocity for vapor of species $s$ to water, $V_{s}^{d}$, was determined by Eq. [20]. The chemical properties of endosulfan (Paper I, Appendix A) were evaluated by assuming that the temperature of the water in the trays was equal to the measured air temperature at the meteorological reference height. The friction velocity $u_{*}$ was estimated from the mean wind speed ($u$) at the reference height ($z_{r} = 2 \text{ m}$), since the ratio $u_{*}/u$ is reasonably independent of wind speed. Over a rough surface such as an agricultural area, this ratio is about 0.1. However, the water in each experimental tray was nearly aerodynamically smooth and was significantly sheltered by additional mechanisms, mainly a tray side wall extending 50 mm above the water surface. To account for this we assume a shelter factor (the ratio of $u_{*}$ within the tray to the ambient $u_{*}$) of 0.1. Thus, for the water in the trays, $u_{*} = 0.01u$. No stability corrections were applied. Sensitivity tests have shown that the model results are insensitive to assumptions about $u_{*}$. The reason is that $u_{*}$ affects only the deposition velocity $V_{s}^{d}$, and therefore the rate at which the air–water equilibration proceeds (that is, the rate at which the flux in Eq. [18] approaches zero when $C_{s}$ is steady). It does not affect the final equilibrium value of $C_{w}$, which is $A' C_{s}$. The rate of equilibration is given by the time constant $A'H/V_{s}^{d}$, which is fairly short (around 1.5 h for $H = 0.05 \text{ m}$, $A' = 1000$, $V_{s}^{d} = 0.001 \text{ m s}^{-1}$). Therefore, over time scales of a day or so, the air and water concentrations are close to equilibrium and the rate of the exchange (influenced by $u_{*}$) is nearly immaterial.

**Results of Comparisons**

We first consider air concentrations. Measurements of air concentrations were made at stations within Field 4 and at the S200m station, 200 m to its south (Fig. 5). These are compared with predictions from the model in Fig. 6. There is a strong diurnal cycle in both the predicted and measured air concentrations, caused by the entrapment of air with high concentrations near the ground at night when atmospheric dispersion is much weaker than by day. The measured concentrations are similar within Field 4 and at S200m. Total measured endosulfan concentrations within Field 4 for Spray 1 are overpredicted by the model for the first 24 h after spraying, but tend to be underpredicted at later times. The comparisons between model and measurements are quite good at S200m for Spray 1, and also for Spray 2 (for which only within-field data are available). It is concluded that, despite major simplifications, the model is capable of reproducing the order of magnitude of measured air concentrations. This is sufficient for the purpose at hand.

Turning to water concentrations, the model was used to predict the water concentrations ($C_{a}^{w}$, $C_{b}^{w}$, $C_{g}^{w}$ and the total $C_{w} = C_{a}^{w} + C_{b}^{w} + C_{g}^{w}$) at each receptor point (tray), for the 5 d following each spray. A representative sample of these predictions (the westward trays) are shown in Fig. 7 for Spray 1 (upper frames) and Spray 2 (lower frames), together with the measured concentrations at these trays. The predicted water concentrations rise rapidly from zero at the time of spraying to typical maxima around 0.5 g L$^{-1}$ for the trays close to the crop and 0.1 g L$^{-1}$ for more distant trays. There is a diurnal oscillation...
in the predictions (though less strong than in the predicted air concentrations), with highest concentrations occurring at night, because the water concentrations follow the air concentrations with a temporal smoothing.

To simplify quantitative comparisons, Fig. 8 shows the measured and modeled total concentrations $C_w$ at each tray, averaged in time over all five observation days. Each point represents one tray for one spray, and is an average over five values (the measurements at 24-h intervals and the predicted values at these times). For both Sprays 1 and 2 the model and measurements agree to within about 30% on average, a good result given the uncertainties involved in the modeling and the inevitable scatter in the measured data. Figure 9 compares measured and modeled time-averaged concentrations (over all 5 d of observation) for each endosulfan species. Again, each point represents one tray for one spray. For Spray 1 the $\beta$-endosulfan concentrations are overpredicted by the model while the other two species are underpredicted, leading to a reasonable prediction for the total endosulfan concentration (Fig. 9).

Fig. 7. Predicted and measured endosulfan water concentrations ($\alpha$, $\beta$, $\gamma$, total) at four westward receptor locations for Sprays 1 and 2.

Fig. 8. Time-averaged comparison (over 5 d) of measured and modeled total endosulfan concentrations at 13 receptor points, for Sprays 1 and 2.

Fig. 9. Time-averaged comparison (over 5 d) of measured and modeled endosulfan species concentrations ($\alpha$, $\beta$, $\gamma$, total) at 13 receptor points, for (a) Spray 1; (b) Spray 2.
out for 21 particle sizes determined by the particle size distribution $P(d)$. The final $f_{\text{drift}}$ for a spray with a broad particle size spectrum was calculated by integrating $f_{\text{drift}}(x,d)P(d)$ over $d$, where $f_{\text{drift}}(x,d)$ is the value appropriate at distance $x$ downwind of the field for a single particle size $d$.

For the "standard case" of Bird et al. (1996), 36 experimental replicates are available for a single-swathe aerial boom spray with a median droplet diameter of close to 250 μm and an approximately log-normal particle size distribution $P(d)$. We inferred mean measured values of $f_{\text{drift}}(x)$ from plots at three different wind speeds corresponding to the 20th, 50th, and 80th percentiles of the wind speed range covered by their 36 replicates. Figure 10 compares these data with predictions for each wind speed, using model parameters (given in the figure caption) selected to match the experimental conditions. The predictions capture the magnitude and the streamwise trend of $f_{\text{drift}}(x)$ well, slightly overestimating the magnitude of $f_{\text{drift}}(x)$ at higher wind speeds. Given the major simplifications of the model, this is a satisfactory result that provides confidence that the values of $f_{\text{drift}}$ being estimated by the model are reasonable.

**CONCLUSIONS**

We have developed and tested models for two significant airborne pathways transporting endosulfan and other agricultural chemicals from farms to environmental receptors, especially water bodies. For both pathways, the models consist of three components respectively describing source strengths, dispersion, and deposition. Economy of description has been gained by considering these pathways together, as much of the underlying process physics (especially for dispersion) is common to both. Throughout, we have used the simplest possible process descriptions consistent with often complex physical realities; for example, a Gaussian-plume model is used to describe both spray and vapor dispersion.

Spray drift depends not only on dispersion but also on deposition to the underlying (usually vegetated) surface. A single-layer model for this deposition process has been formulated that is well supported by the laboratory data of Chamberlain (1967) and that shows that for spray droplets of around 100 μm or smaller, impaction and related processes dominate over gravitational settling in particle deposition. By combining this model with a simple dispersion model based on a settling Gaussian plume, a model for spray drift is obtained that agrees very well with field data from Bird et al. (1996).

For vapor transport, the model consists of a simple exponential-decay assumption for the post-spray volatilization of endosulfan from a sprayed crop, the same dispersion model used for spray drift, and a model for deposition of vapor to a water surface due to Deacon (1977) and Denmead and Freney (1992), based on a kinetic formulation for the air–water exchange and a deposition velocity. The dispersion model and field measurements (Edge et al., 1998) both show that volatilization and dispersion of endosulfan from sprayed crops produces air concentrations ($C_a$) in the range 1 to 5
μg m⁻³ at sites within and adjacent to sprayed fields, immediately after spraying. Values are much higher at night than by day, because of entrapment of air with high concentrations near the ground at night. As volatilization proceeds, air concentrations decay with a time scale of 1 to 5 d, decreasing with increasing temperature.

The complete model of the vapor transport pathway (including volatilization, dispersion, deposition, and water chemistry) produces predicted endosulfan water concentrations ($C_w$) of order 0.1 to 0.5 μg L⁻¹ in a water body of depth 0.05 m within 1 km of a sprayed cotton crop, over the first few days after spraying. These predictions are in broad (though far from perfect) agreement with field observations by Edge et al. (1998). For experimental trays containing water of depth 0.05 m, they found water concentrations, averaged over the 5 d following spraying, ranging from 0.3 μg L⁻¹ (at a distance of 200 m from the crop) to 0.18 μg L⁻¹ (at 1 km) for Spray 1; the corresponding range for Spray 2 was 0.18 μg L⁻¹ (at 200 m) to 0.1 μg L⁻¹ (at 1 km). The highest observed concentrations in individual trays were around 0.5 μg L⁻¹, recorded around 48 h after spraying. Monitoring of two additional sprays (Sprays 3 and 4) in the following season gave similar (though somewhat lower) concentrations, but temperatures were also lower. No differences were observed between ULV and EC formulations, for which median spray droplet diameters are around 80 μm and 240 μm, respectively.

This level of agreement is sufficient for the purpose of establishing the overall significance of vapor transport relative to other possible transport pathways. However, modeling uncertainty remains in the physical and chemical properties of endosulfan species. It should also be noted that the water concentrations observed in the experimental trays cannot be directly scaled to infer the concentrations arising from vapor transport in a river, which has a quite different (generally much greater) depth and for which the exposure pattern is quite different. To make this conversion, one must consider the dynamical factors built into the model described in Part I.

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Profenofos Residues in Wild Fish from Cotton-Growing Areas of New South Wales, Australia

A. Kumar and John C. Chapman*

ABSTRACT

The organophosphorus (OP) pesticide profenofos (O-4-bromo-2-chlorophenyl O-ethyl S-propyl phosphorothioate) is used heavily in cotton-growing areas of eastern Australia toward the end of the growing season. European carp (Cyprinus carpio), bony bream (Nematalosa erebi), and mosquito fish (Gambusia holbrooki) were collected from the cotton-growing areas around Wee Waa, New South Wales, to determine the relationship between profenofos residues and acetylcholinesterase (AChE) activity in wild fish. Profenofos concentrations in water, sediment, and fish tissue reflected its general level of use; levels in March 1994 were significantly higher than in 1993 and generally decreased in May, 6 wk after cessation of spraying. Residues in carp and bony bream generally correlated with concentrations in water and sediment, although residues in fish tend to persist longer at some sites. Acetylcholinesterase inhibition was a useful indicator of profenofos exposure within a season, particularly if linked with residue measurements. Bony bream and gravid female mosquito fish recovered AChE levels more slowly than carp or nongravid mosquito fish. Recovery in creeks was generally more rapid than in lagoons.

Profenofos is a broad-spectrum organophosphorus (OP) insecticide registered in Australia for control of agricultural pests in cotton-growing areas, usually late in the growing season. It is usually applied by air at around 2 kg a.i./ha (Shaw, 1995), but there are currently not enough toxicity and fate data available to permit adequate risk assessment of sites adjacent to the spraying. Profenofos is reported to be highly toxic to some aquatic organisms (Shaw, 1995), but only limited ecotoxicology data are available. Batley and Peterson (1992) ranked its risk as about mid-range on the list of 12 priority cotton pesticides.

It is often assumed that the low bioconcentration potential of OPs by aquatic organisms rapidly reduces the risk of profenofos exposure in ecosystems (Eto, 1974; Yu and Sandborn, 1975) after application. Hence, evaluation of the rate of recovery of the ecosystem would permit adequate assessment of any long-term consequences of profenofos spraying.

Measurement of the concentrations of pesticide in spot samples of water may underestimate the exposure levels encountered by inhabiting aquatic organisms. However, an analysis of accumulated profenofos residues in the sediment or fish tissue may give a better indication of exposure (Nowak and Julli, 1991) and toxicological risk. In general, the most significant route of exposure for fish appears to be the direct uptake of insecticide from water (Tsuda et al., 1994). This study attempts to establish whether or not wild fish accumulate sufficient residues of profenofos for it to represent a risk to the aquatic system.

Acetylcholinesterase (AChE) activity in fish has been used as an indicator to monitor poisoning by OP pesticides (Coppage and Braidech, 1976; Zinkl et al., 1991). The use of AChE activity measurements in fish could be developed as a useful indicator, provided some prior

Abbreviations: AChE, acetylcholinesterase; ANOVA, analysis of variance; OP, organophosphorus; PCCM, Pearson Correlation Coefficient Matrix.

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