Transport of Heavy Chlorinated Hydrocarbons in the Atmosphere

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■ Fluxes of aerosol polychlorinated biphenyl (PCB, 54% chlorine mixture) ranging from 2×10^{-9} to 9×10^{-7} (average: 3×10^{-7}) g m^{-2} day^{-1} were measured at La Jolla, Calif., during February and October 1972. A model for mesoscale aerosol transport which treats the plume as a superposition of Gaussian-shaped puffs diffusing isotropically in the plane of the horizon was used with the assumption that deposition occurs irreversibly to compute source strength, aerosol half-life, and isopleths of deposition flux. Hourly wind velocity and daily deposition flux measurements made during a one-month period were used to calibrate the model, and a second month of data provided a check for the predictive capacity of the method. On the basis of flux measurements and model calculations, arguments are presented for most dry deposition of aerosol PCB introduced into the troposphere to occur within 100 km of the source.

Polychlorinated biphenyls (PCB) are used to plasticize paints, adhesives, and plastics and are among the most refractory of synthetic organic chemicals. In Southern California, where this study took place, open burning has been largely supplanted by landfill disposal, but high temperatures in landfills as well as weathering of products containing PCB could contribute to the emission of this material as an aerosol. Volatilization of PCB used as a fireproofing agent is also a possible source of aerosol since about 400 fires occur daily in Los Angeles, of which 5% are structure fires. The manufacturer of PCB in the U.S. voluntarily restricted sales of PCB to closed system applications (heat transfer, dielectric, lubricant, and hydraulic fluids) in 1971. This action is not likely to reduce the emission of aerosol PCB until the service life of the products involved has expired and they are safely disposed of.

Distribution of Sources and Sinks and Relationship Between Deposition Flux and Aerial Concentration

Location of Sources. A correlation between measured fluxes and the component of the wind trajectory in the assumed direction of the source weighted by the reciprocal of the wind speed has been shown (1). This correlation supports the hypothesis that the location of the source of aerosol PCB is in the Los Angeles area. The susceptibility of the flux data to a rectification by an empirical, qualitative calculation suggests that a more quantitative model would be capable of predicting source strength, half-life in the atmosphere, and isopleths of the deposition flux from the same type of wind velocity and deposition flux data. Physical considerations and experimental observations which are fundamental to such a quantitative aerosol transport and deposition model are developed in the following paragraphs.

Procedures for flux measurement and analysis have been described (1) which involve the use of 0.17 m^2 mineral oil-coated glass deposition plates. The deposited chlorinated hydrocarbons (CHC) are scavenged from the mineral oil on an active silica-gel column, eluted from the column with n-hexane, concentrated under vacuum, and analyzed by gas chromatography with electron-capture detection.

Half-Life of PCB in Soil and Secondary Emission. To invoke the principle of conservation of mass in a practical aerosol transport model, the most important sources and sinks must be identified. In particular, the reemission of material which has deposited on the earth's surface (secondary emission) must be accounted for.

If the flux of PCB (54% chlorine mixture) over the last 30 years is approximated by a linear increase from zero to that found in 1972, the total input to the soil at La Jolla would be about 3×10^{-3} g m^{-2}. At undisturbed uneroded gently sloping locations near the aerosol sampling site, the amount of PCB in the upper 10 cm of soil was measured at an average surface concentration of 1.6×10^{-3} g m^{-2} (range, 0.5×10^{-3} to 3.0×10^{-3} g m^{-2} from 12 cores). Steep slopes and exposed ridge-crests yielded low surface concentrations while alluvial deposits were rich in CHC only if they had a high "fines" (passing a 100-μm screen) content. The concentration of PCB in the soil at a depth of 10 cm was typically 0.2 of the concentration at the surface of adobe cores and as high as 0.8 for more permeable soils. It is apparent that CHC is being transported by hydraulic action vertically down into the ground.

Given the linear increase of deposition flux with time assumed in the previous paragraph and the observed surface concentrations, the half-life of PCB in the top 10 cm of soil can be calculated. Equate the time rate of change of surface concentration, dC_2/dt, with the assumed input from aerosol, $k_2 t$, minus the concentration-dependent term describing the disappearance via the combined agencies of secondary emission and leaching downward, $k_1 C_2$, to give $dC_2/dt = k_2 t - k_1 C_2$ which is solved by $C_2(t) = k_1^{-1} k_2 t [1 - \exp(-k_1 t)]$. With $k_2 = 6 \times 10^{-6}$ g m^{-2} yr^{-1} and $C_2(t = 30$ yr$) = 1.6 \times 10^{-3}$ g m^{-2}, k_1 is calculated to be 0.114 which corresponds to a half-life of PCB in the top 10 cm of soil due to leaching and secondary emission of 6 years.

This approximate result agrees substantially with the 10-year half-life found by Nash and Woolson (2) for the disappearance of DDT from experimental plots which were provided with good drainage. Residence times in soil of DDT and PCB should be approximately equal since the two compounds have similar solubilities, vapor pressures, and adsorption properties on solid surfaces. Woodwell et al. (3) divided the amount of DDT retained in soils in the continental U.S. by the annual rate of application to arrive at an estimate of the lifetime in the soil of 4.5 years. However, our results and those of

Tarrant and Tatton (4) show that soil concentrations of CHC in areas not subject to direct application are *increasing* so that the assumption of a steady state cannot be made. Since the disappearance of CHC from soil is due to leaching as well as volatilization or mobilization on aerosol particles (secondary emission), the half-life for secondary emission alone should be longer than 10 years.

If the secondary emission half-life is sufficiently long, the process of deposition of aerosol on the ground can be considered to be irreversible. Our assertion that secondary emission can be neglected when considering a primary aerosol source 100 km distant is also based on observations during easterly winds of PCB fluxes less by a factor of 500 than during winds from the direction of Los Angeles (Figure 1). If no primary sources are located east of the measuring site, then any PCB flux during easterly winds should be attributable to secondary emission. Low fluxes during easterly winds are consistent with the earth's surface as a good *reflector or* a good absorber of aerosol PCB. Since a substantial portion of the time integrated deposition of PCB is accounted for in the soil, the most reasonable interpretation of these data is that the earth's surface can be treated as a good absorber of aerosol PCB.

Near a source, where concentrations in the soil are high, it is reasonable to expect that secondary emission could become appreciable. A convenient model for a primary source surrounded by a region of diffuse secondary emission is a Gaussian distribution of source strength.

Deposition Velocity, Deposition Flux, and Atmospheric Stability. A relation between the concentration of material in the air and the flux of material from the air to the earth's surface must be found to construct a transport model. If turbulence in the atmosphere were homogeneous in space and time, and if we are far from the source so that the aerosol size distribution is relatively constant in space and time, then the assumption that the deposition velocity, V_d, remains constant would provide such a relationship: Flux, $F = V_d\chi(z = 0)$, where z is altitude and $\chi(z = 0)$ is the ground level aerial concentration. However, a synoptic knowledge of both $\chi(z = 0)$ and turbulence conditions will actually be required to account for the inhomogeneity that is present in the atmosphere.

Within a few kilometers downwind of a source under stable conditions, deposition velocity decreases with distance from the source (5). This is probably due to depletion from the plume of large ($\gtrsim 10 \ \mu m$) particles whose gravitational fall velocity is significant in comparison to the deposition velocity resulting from turbulent motion. However, a submicron particle, even under stable conditions, can have a deposition velocity which is 5–50 times faster than its sedimentation velocity, V_s, in the absence of turbulence. For unstable conditions, V_d is two to three orders of magnitude larger than V_s for 1-μm particles, and the data show too much scatter to detect any decrease of V_d with distance from the source. Values for V_d computed from dispersion models and material balance considerations (5) are larger than V_d determined directly from wind tunnel tests (6). For downwind distances of more than a few kilometers, sedimentation due to gravity is insignificant in comparison to the influence of turbulence on deposition velocity.

Concurrent flux and ground level concentration measurements were made to determine the effect of various states of turbulence on deposition velocity. To be above the laminar boundary layer which would be expected to be depleted by deposition, ground level aerial concentrations were measured at $z = 10$ cm above a flat surface by drawing air through a 10 mm diam × 75 mm long column of oil-impregnated glass wool in series ahead of an oil-filled impinger. CHC was recovered from the mineral oil by the same methods used for the flux measurements. Sampling periods of 4–8 h duration were made to coincide with the presence of either stable (inversion, stratified) or unstable (lapse, well-mixed) atmospheric conditions. Stable conditions occurred during night and morning hours and were frequently accompanied by a stratum of smog about 500 m thick over the ocean trapped by a surface-based inversion. Unstable and neutral conditions in which the atmosphere was being mixed by thermal convection or mechanical turbulence occurred in the afternoon and were evidenced by strong insolation and brisk sea breezes (3–8 m s^{-1}). The results of these measurements are shown in Table I.

When the atmosphere is stratified, high ground-level concentrations occur together with low deposition velocities. Conversely, when the atmosphere is well mixed, low $\chi(z = 10$ cm) accompanies large V_d. The deposition velocities measured for PCB were similar to those found for [131]I (7) and for uranin particles by Islitzer and Dumbauld (5) and show the increase with instability noted in the latter work. Islitzer and Dumbauld used particles with a diameter of about 1 μm which is comparable to the average mass mean diameter of Los Angeles smog particles (8).

Although changes in atmospheric stability strongly influence the vertical profile of aerial concentration in a plume, the decay or onset of turbulence does not affect the quantity of material in the air above a unit area:

$$\chi_{vi} = \int_0^\infty \chi(z)dz$$

Table I shows that ground level concentration and deposition velocity are both much more sensitive to the prevailing state of atmospheric turbulence than is the deposition flux. A second set of flux measurements was made to test the extent to which changes in $\chi(z = 10$ cm) and V_d with changing turbu-
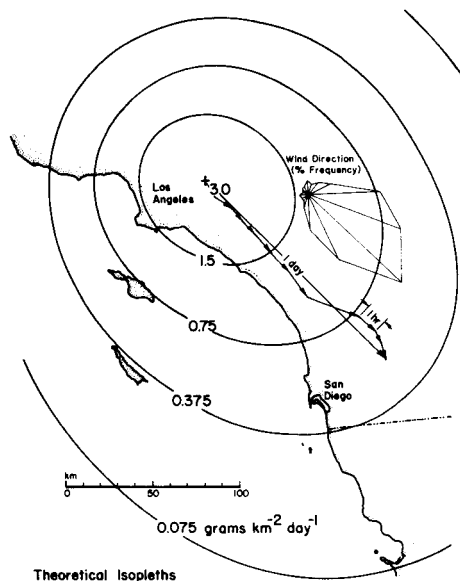

Figure 1. Model parameters for calculation of this series of isopleths: deposition coefficient, $k = 0.146$ h^{-1}; exponential dispersion parameter, $n = 0.25$; linear dispersion parameter, $c = 14.7$; source strength, $Q = 3.0$ kg h^{-1}

Wind data for October 1972 used, and isopleths reflect average for whole month. Isopleths for February 1972 are much the same. Emission from San Diego not included in calculations. If position of model source displaced more than 35 km in any direction from position shown, constant flux fits measured fluxes better in least-squares sense than transport model predictions

lence conditions might compensate to give a flux which is approximately independent of turbulence. The occurrence of this set of circumstances is requisite for the validity of our approximation, $F = k\chi_{vi}$, that deposition flux is proportional to the vertically integrated aerial concentration. This approximation avoids the difficulty of quantifying atmospheric turbulence and reduces the transport problem to two dimensions.

A consecutive series of flux measurements was made with the duration of each measurement confined to periods of stationary turbulence. That is, a new sampling period was begun each time a change in stability or state of mechanical turbulence was observed in the atmosphere. The average of six PCB deposition flux measurements made during unstable conditions was 15.3×10^{-9} g m^{-2} h^{-1}, while the average flux for six stable periods during the same week of observations was 9.3×10^{-9} g m^{-2} h^{-1}. Some of the difference between fluxes during stable and unstable periods is likely to be due to noncompensating effects of turbulence on $\chi(z = 10$ cm) and V_d. However, stable periods during which winds are slight to calm can be expected to yield lower fluxes since depletion of the plume by deposition is not made up for by advection. This set of measurements therefore shows the maximum influence that turbulence can have on deposition flux. A 24-h sampling period was chosen to minimize possible error caused by diurnal variation of atmospheric stability when the result of this sampling was to be compared with model calculations based on the approximation that flux is independent of turbulence.

Wind velocities were measured at Montgomery Field which is located on level terrain about 10 km east of the flux receptor site. Hourly wind velocities to be used in the transport model calculations were averaged to obtain mean wind bearings for October and February 1972 (data deposited with the ACS Microfilm Depository Service). These bearings were close to those computed from U.S. Naval Synoptic Surface Meteorological Observations (SSMO) (9) which combines data from vessels in the region 31° to 34° North and the coastline to 120° West: for October, 304.6° vs. 305.6° (SSMO) and for February, 323.4° vs. 322.9° (SSMO). These results indicate that the wind field in the neighborhood of the measuring site is free from terrain-induced distortions and that velocities measured there are representative of winds over the whole Southern California coastal and nearshore region.

Gaussian Puff Deposition Model

The assumptions and approximations that are contained within the model are: (1) The source is of constant strength and Gaussian shape, (2) eddy diffusivity is isotropic in the horizontal plane, and (3) deposition flux is proportional to the vertically integrated aerial concentration (the amount of material in the air above a unit area):

$$\text{Flux, } F(x, y) = k \int_0^\infty \chi(x, y, z)dz = k\chi_{vi}(x, y)$$

Deposition flux is assumed to be independent of other factors such as wind velocity, horizontal wind shear, temperature and lapse rate.

To describe the two-dimensional concentration of material in a puff originating at the point $r = 0$ at time $t = 0$ diffusing isotropically in the plane of the horizon and falling irreversibly from the atmosphere, the expression

$$\chi_{vi}(r, t) = \frac{Q}{2\pi\sigma^2} e^{-kt}e^{-r^2/(2\sigma^2)} \tag{1}$$

was employed where Q is the quantity of material in the puff, σ^2 is the dispersion, k is the deposition coefficient of assumption 3, and r is the distance from the center of mass of the puff (Lagrangian coordinate).

Mo./day, 1973	Wind speed, m/s (stability)	Ground level concn, (g/m³) × 10⁻⁹	Flux (g/m² h) × 10⁻⁷	V_d, cm/s
3/28	2.5 (Neutral)	0.45	0.24	1.5
3/2	1 (Strong surface-based inversion)	14.0	1.6	0.31
3/15 (a.m.)	1 (Weak surface-based inversion)	4.8	0.76	0.44
3/15 (p.m.)	4 (Lapse)	1.4	1.5	3.0
4/6	6.5 (Lapse)	1.26	0.46	1.0

When $\sigma^2 = 2 Kt$ (with K the Fickian eddy diffusivity), this Gaussian distribution (Equation 1) provides a solution to the gradient diffusion equation:

$$\frac{\partial \chi_{vi}}{\partial t} + k\chi_{vi} + K\left(\frac{\partial^2 \chi_{vi}}{\partial x^2} + \frac{\partial^2 \chi_{vi}}{\partial y^2}\right) = 0, x^2 + y^2 = r^2$$

which requires that the time rate of change of χ_{vi} be balanced by the deposition flux, $k\chi_{vi}$, and by eddy diffusion, $K\nabla^2\chi_{vi}$.

The Gaussian distribution (Equation 1) also serves as a basis for many successful plume diffusion models in which the dispersion is not limited to a linear dependence on t. Based upon an interpolation formula for the Lagrangian velocity correlation coefficient, Sutton (10) derived the expression

$$\sigma^2 = \frac{1}{2} C^2([u]t)^{2-n}, (n \text{ and } C \text{ constant, } 0 < n < 1) \tag{2}$$

for the dispersion of a Gaussian-distributed cluster of diffusing material. The time over which the instantaneous wind, $u(t)$, was averaged to obtain the mean speed, $[u]$, was long enough to ensure that $[u]$ would represent a virtual steady flow.

A transport model that can take deviations from steady flow into account is more capable of predicting the dispersion of pollutant plumes than one that does not. Consider the dispersion, σ_1^2, of a puff after a time $2\Delta t$ with wind speed (u) compared to the dispersion, σ_2^2, which would result after time Δt at speed $(2 u)$ followed by an hour of calm. If the wind speed were to be averaged over the whole time period $2\Delta t$, the predicted dispersion would be the same for both cases. When the eddy diffusion is considered to take place in two successive intervals of length Δt, the predicted dispersions for the two cases would be

$$\sigma_1^2 = 2(C^2/2)(u\Delta t)^{2-n} \text{ and } \sigma_2^2 = (C^2/2)(2 u\Delta t)^{2-n}$$

That $\sigma_2^2 > \sigma_1^2$ is reasonable since the higher wind speed in case 2 could be associated with greater atmospheric turbulence and eddy diffusion.

An anemometer was observed for several minutes to estimate the average over this time period of the wind speed and direction. Velocities were found in this way each hour, and the results of each measurement were presumed to approximate the mean velocity which would result from an average taken over the whole hour. Hourly velocities are summed to show a typical daily trajectory in Figure 1.

The spreading of each puff in the plume was considered to have taken place during a succession of hour-long intervals.

Within each interval the eddy diffusion was described by the Sutton expression for the dispersion of the distribution of material. The increase in the dispersion of the puff during the ith hour due to effective eddies is

$$\sigma_i^2 = \frac{1}{2} c^2 (r_i)^{2-n} \qquad (3)$$

where $r_i = u_i \Delta t$ is the trajectory length for the ith hour. A lower-case c is used to distinguish the virtual eddy diffusion coefficient used here (for $\Delta t = 1$ h) from C in Equation 2 which applies for $\Delta t >$ (source to receptor transit time, h hours). For the dispersion of a puff which has traveled the distance $R_h = \sum_{i=1}^{h} (r_i)$, the expression

$$\sigma^2(R_h) = \sum_{i=1}^{h} \sigma_i^2 + \sigma_0^2 \qquad (4)$$

was used where σ_0^2 accounts for the finite size of the source.

Equation 1 and assumption 3 give for the deposition flux from a puff

$$F(r, t) = \frac{kQ}{2 \pi \sigma^2} e^{-kt} e^{-r^2/(2\sigma^2)} \qquad (5)$$

which satisfies $\int_0^\infty \int F(r, t) 2 \pi r dr dt = Q$. (All that is emitted eventually is deposited on the earth.)

Wind velocity measurements made 15 m above the ground best represent the mean motion of a cloud released near the surface (11). Since wind velocities for this work were observed at only 7 m elevation above the ground, a parameter, α, was introduced which was applied to the observed wind speeds to yield larger effective speeds: u_i(eff) $= \alpha u_i$(obs).

Surface wind velocities and directions were measured hourly throughout the fallout sampling period and for 4 days (96 h) preceding the first 24-h measuring period. A puff of material containing Q grams of pollutant was assumed to have been emitted each hour. The lifetimes, positions, and trajectory lengths for 96 puffs emitted prior to each hour of measurement were computed to find the contribution of each puff to the total hourly deposition flux. The hourly fluxes were then totaled to give computed daily fluxes which could be compared with the measured daily fluxes.

After physically plausible initial values were chosen for the various parameters, each parameter was varied in turn to minimize $\delta =$ (sum of squares of the differences between measured and predicted fluxes). The variation of the model parameters was repeated until no further improvement could be made in the least-squares fit of the predicted to measured fluxes. The source strength, Q (g h^{-1}) was fixed by the requirement that the monthly average measured and predicted fluxes should be equal.

The value of the deposition coefficient, $k = 0.15$ h^{-1}, which minimized δ was within 5% of the value of k which caused the source strength to be a minimum while still predicting the correct monthly average flux. The source strength predicted by the model would be little changed by the requirement that the deposition coefficient be chosen to reproduce the monthly average flux with the smallest possible source.

The optimum (δ minimized) value for the exponential horizontal dispersion parameter, $n = 0.25$. lies in the midst of other experimental results and is equal to that found by Sutton in his original measurements. This result could be expected since this model is a straightforward adaptation of the Sutton model for variable wind velocity. Minima with respect to δ were found for the virtual diffusion coefficient and the wind speed scaling parameter at $c = 14.7$ and $\alpha = 1.8$. Model predictions and flux data are shown in Figure 2.

To compare the crosswind dimensions of the plume predicted by this model with dispersions measured during other atmospheric transport experiments, a computation of concentrations in various parts of the plume was performed using

the parameters optimized by the iterative procedure described above. Experimental wind speeds were used in this concentration calculation, but hourly variations in wind direction were ignored. The crosswind profiles of this hypothetical "straightened" plume are shown in Figure 3. The influence of large-scale (greater than about 20 km radius of curvature) eddies or meanders on the plume spreading was separated from smaller-scale eddy diffusion effects in this computation of crosswind dispersion to provide a more realistic comparison with measurements made of plumes from noncontinuous sources. From Figure 3, the predicted variance of the crosswind concentration at 120 km, which is the distance from Los Angeles to La Jolla, is 69 km with the variance of the source (source diameter) set at its optimized value of 10 km. These dimensions compare favorably with published experimental values (12) which fall in the range 30–80 km. Although there was a rapid degradation of the least-squares fit of calculated to measured fluxes (increasing δ) when σ_o was increased beyond 20 km, only a slight increase in δ was noted when the model source was contracted to a point.

Eddies in the horizontal plane larger than $O(u_i \Delta t \sim 20$ km) are explicitly accounted for from our knowledge of hourly wind velocities. Sutton's theory, together with the assumption of steady flow, would yield $\sigma^2 = \frac{1}{2} C^2 R_h^{2-n}$ which implies that the scale of effective eddies would continue to increase as trajec-
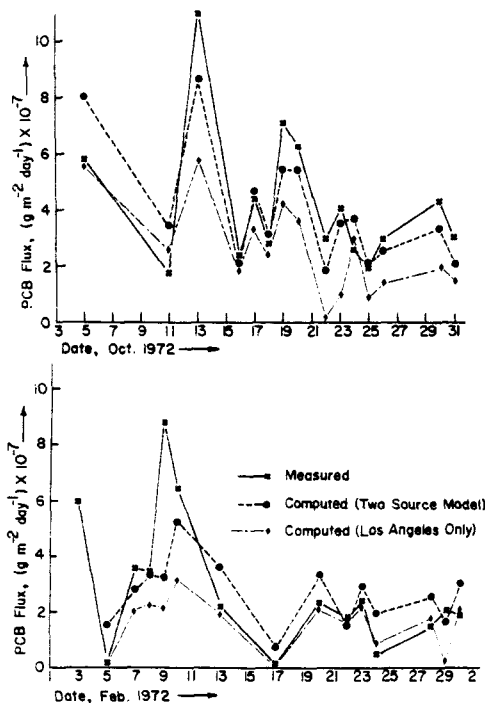

Figure 2. Best fit to measured flux data achieved with Los Angeles having source strength of 7.0 times that of San Diego

Source strength which must be assigned to Los Angeles to reproduce correct monthly average measured flux was 3 kg h^{-1} 54% chlorine PCB for October 1972 and 2.4 kg h^{-1} for February 1972. Other model parameters used in computations were $n = 0.25$, $c = 14.7$, $k = 0.146$ h^{-1}, and the initial source diameters, σ_o, were 10 km for Los Angeles and 1 km for San Diego. October data used to calibrate model, and values found in this process used to compute model predictions for February

tories lengthen. Equation 4 allows the size of effective eddies to be limited to less than $O(u_i \Delta t)$.

A thinner planetary boundary layer exists over the smoother ocean so that winds observed from ships are closer to geostrophic than measurements made at land stations. Thirty-year mean surface winds at Southern California stations in rougher terrain than Montgomery Field (U.S. Weather Bureau data) reflect the influences of the local topography and show a generally more onshore and less geostrophic flow than the ship-based SSMO data. Since model predictions using the Montgomery Field data (which are similar to ship-based observations) correlate well with measured pollution levels, most of the pollutant transport 120 km distant from the source must occur above the slower moving surface layer which is of the order of tens of meters deep and is directed more nearly along the generally onshore gradients of pressure.

Terrain-induced inhomogeneities in the wind velocity field smaller than the cross-wind plume dimensions (about 50 km) are anticipated to be accounted for in the model by a horizontal dispersion which is larger than would be found for locations (at sea, for instance) having smoother terrain. Inhomogeneities that persist after spatial averaging over a scale of ~50 km would influence the trajectory of the plume centerline and cause predictions of the source location based on a mean wind field with straight and parallel streamlines to be in error. Inspection of the spatially smoothed contours of the Southern California coast and inland mountains allows an estimate of this error of no more than about 50 km in the crosswind direction. However, it was the purpose of this study to discover the atmospheric residence time of aerosol PCB and the strength of the source rather than its accurate location which is better accomplished by a grid of receptors nearer the source (13).

Implications of Transport Model Results

Residence Time in Atmosphere. The deposition coefficient, $k = 0.15$ h^{-1}, which provides the best least-squares fit of model predictions to measured fluxes, corresponds to an atmospheric half-life for PCB of 4.6 h. Since this result is considerably different from the 4-year time constant assumed for DDT by Woodwell et al. (3), the following considerations are presented to support the contention that the atmospheric half-life of surface-released aerosols whose deposition at the earth's surface is largely irreversible is of the order of hours or at most a few days. Factors which inhibit reemission of material deposited from an aerosol or vapor state are low vapor pressure or high affinity for solid surfaces or for solution. The last factor would be active in the case of sulfur dioxide for which Meetham (14) found an atmospheric half-life of between 8 and 10 h using deposit gauge data and estimates of emission during coal burning.

We can approximate the integral in assumption 3 as:

$$F = k \int_0^\infty \chi(z)dz \approx k\chi(z = 0)z_m$$

where z_m is a suitable height above the surface. Using the definition of deposition velocity, $F = V_d\chi(z = 0)$, we get $k \approx V_d/z_m$. During unstable conditions the deposition velocity of PCB is in the range 1–4 cm s^{-1}, and z_m is the thickness of the atmospheric mixed layer, which is estimated by the heights of cumulus clouds at 1–3 km. These considerations place k in the range 0.01–0.14 h^{-1}. For stable atmospheric conditions, V_d is about 0.4 cm s^{-1}, and z_m is the depth of the surface-based inversion layer. The smog layer trapped by the surface-based inversion was estimated to be 300–800 m thick on the days when V_d was measured. Thus, k should be from 0.02 to 0.05 h^{-1} during stable conditions. If it should happen that the concentration of PCB remains constant throughout the
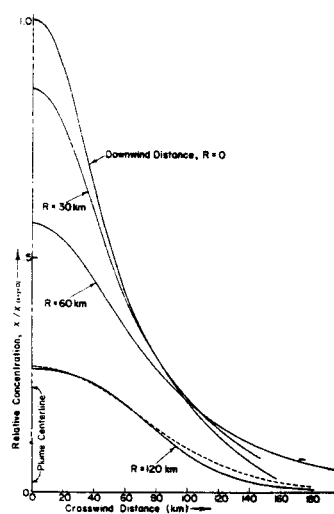

Figure 3. Predicted cross-wind plume dimensions at various distances from source

One month of wind speed data used to generate average concentration distribution. Instantaneous concentrations can be considerably different from average. Profile at $R = 0$ different from that of source since diffusion in wind direction allows puffs whose centers have been moved downwind to continue to contribute to concentration at $R = 0$. Broken line is Gaussian with $\sigma = 69$ km

depth of the mixed layer during stable conditions, then the smallest value for k would be about 0.005 h^{-1} for a half-life of 140 h. Such a long half-life would prevail only if the atmosphere never becomes turbulent. A constant flux equal to the experimental average flux fits the data better in a least-squares sense than model predictions using $k = 0.005$ h^{-1}. In addition, a source strength of over 250 metric tons yr^{-1} of the 54% chlorine grade PCB would be required from Los Angeles for this model to predict the correct measured average flux when this long half-life is assumed. Five percent of the U.S. population reside in the Los Angeles area. If the U.S. production of about 5×10^3 metric tons yr^{-1} of (54% Cl) PCB is allocated on a per capita basis, only about 250 metric tons yr^{-1} would be used in Los Angeles. A half-life in the atmosphere as long as six days would imply that dispersal into the atmosphere is the principal fate of PCB. Current estimates (15) are that landfill disposal accounts for the majority of waste PCB.

Relative Importance of Rain Scavenging and Dry Deposition. The concentration of PCB and chlorinated pesticides in two samples of rainwater from squalls which approached the sampling site from the seaward (southwest) direction was less than our detection limit of 2×10^{-12} g ml^{-1} (16). However, dry deposition measurements made during and immediately after the passage of the front yielded CHC fluxes which were also less than our detection limit of 10^{-9} g m^{-2} h^{-1}. These low values are reasonable in light of the fact that during southwest winds, no sources of aerosol are located upwind of the measuring site. Although these data are consistent with the conclusion (1) that aerosol transport of heavy CHC is a mesoscale rather than a global phenomenon, it cannot resolve the relative importance of dry deposition and rain scavenging for any location other than La Jolla: A 50 cm yr^{-1} rainfall containing 10×10^{-12} g ml^{-1} would contribute only 5 g km^{-2} yr^{-1}, whereas dry deposition is responsible for a PCB flux at La Jolla based on average measured fluxes during October and February 1972, of 180 g km^{-2} yr^{-1}.

We can write Raoult's law for sparingly soluble compounds as $P/C = P_o/C_o$ where P is the vapor pressure of the compound over a solution of concentration C, and P_o and C_o are the vapor pressure of pure compound and its solubility in water, respectively. DDT has a solubility of 2×10^{-9} g ml^{-1} and a vapor pressure of 10^{-6} mm Hg (17) which is equivalent to 2×10^{-5} g m^{-3} if the vapor behaves as a perfect gas. Consider a concentration of 10 ml m^{-3} of rain falling continuously at a flux of 1 l. m^{-2} h^{-1} (360 in./year) through a 1-km deep stratum of atmosphere containing DDT vapor. For this situation, if equilibrium partitioning between phases occurs, Raoult's law predicts that one 10^3 part of the total DDT be present in the liquid and that the time constant for removal of DDT vapor from the atmosphere by rain is 10^4 h.

The flux of particulate material onto the glass plates averaged 10^5 times the CHC flux, but no correlation was found between CHC and particulate fluxes. Bidleman and Olney (18) observed that a negligible fraction of airborne CHC was captured on a glass fiber filter capable of removing 98% of particulates having diameters greater than 0.03 μm. This is an indication that airborne CHC exists primarily in the vapor state. However, high PCB fluxes were strongly correlated with smoggy conditions and the deposition of black-colored particles. Chlorinated pesticide fluxes reached their maximum levels on days when brown-colored particles were deposited. In urban areas, CHC could well be more strongly associated with the surfaces of soot particles (19) than with the more hydrophylic particles found at remote locations.

From measured collision (target) efficiencies (20) for rain drops falling through clouds of smaller particles and from experimental raindrop size distributions, Chamberlain (21) has calculated washout coefficients from which the time required to diminish the concentration of particulates in the air to one-half the original concentration can be found. For 2.0-μm diam particles with density 2.0 in rain falling at 1 mm h^{-1}, this half-life is 1.9 h. A 1-μm diam particle under similar conditions has a half-life of about 20 h. Most atmospheric aerosols have size distributions which account for only a small percentage of total surface area on particles larger than 1 μm [5% for Los Angeles aerosol (8)]. In his conclusion to the chapter on precipitation scavenging in "Meteorology and Atomic Energy" ($22, 23$), R. J. Engelmann states, "In the case of particles smaller than 1 micron, it is generally agreed that washout by rain is insignificant."

The times required for washout by rain of CHC in the vapor state or adsorbed on submicron particles are as long or longer than the time attributable to the process of dry deposition. Since precipitation occurs only a fraction of the time (1.8% in Southern California) and since dry deposition takes place continually (even during precipitation), then dry deposition is the major mechanism for transfer of heavy chlorinated hydrocarbons from the atmosphere.

Conclusions

The half-life in the troposphere of aerosol, high-boiling chlorinated hydrocarbons released near the surface is about 5 h. This corresponds to a downwind distance at which the quantity of material remaining in the plume is reduced by one-half of less than 100 km. Consequently, the atmosphere cannot be considered to be a large reservoir for these pollutants. The source strength for emission of aerosol PCB (54% chlorine mixture only) of metropolitan Los Angeles is calculated to be 20 metric tons/year (based on February 1972 deposition flux and wind data) and 30 metric tons/year (using October 1972 data). Inspection of theoretical isopleths (Figure 1) calculated with a two-dimensional aerosol transport and irreversible deposition model from single-point wind data indicates that about 30% of the emitted PCB is deposited in the Pacific Ocean in the Gulf of Santa Catalina.

Dry deposition accounts for the majority of CHC fallout. Measurements of CHC concentration in rainwater have been reported which were made with a receptor left out for weeks or months (24). These measurements are likely to be biased by the dry deposition which would also fall on the collecting surface. In fact, Tarrant and Tatton (4) found that the influx of organochlorine pesticides in rain fall was not sufficient to account for the observed increase with time of the concentration of these compounds in untreated soil plots. These rainfall concentrations are crucial because they have been used along with the questionable assumption that aerosol CHC is uniformly distributed over the globe to predict the flux of CHC into the world's oceans (3).

Land areas are good absorbers of aerosol CHC. Except for agricultural soils subject to heavy pesticide application, land areas are capable of adsorbing a great deal more airborne CHC before the rate of secondary emission balances the deposition flux. This conclusion, of course, holds only for compounds with low (10^{-4}–10^{-5} mm Hg or less) vapor pressures. Low boiling compounds are likely to have much longer residence times in the atmosphere, be dispersed over much wider areas, and find their way more rapidly to the oceans. A half-life of hours or a few days for CHC in the troposphere would lead to severe local contamination of land areas ($\sim$100-km radius about the source) before atmospheric transport could be expected to produce serious contamination on a global scale. On the other hand, a pollutant entrained in an ocean current could easily have started its journey from an urban area as an aerosol. Global transport via ocean currents is the most logical explanation for the presence of most of the heavy CHC which has been detected in the ocean at places remote from known sources of contamination.

An annotated listing of the computer program in Fortran that was developed for the computations of deposition fluxes from a plume of superposed Gaussian puffs and an additional figure have been deposited with the ACS Microfilm Depository Service.

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