CURRENT RESEARCH

Transport of Heavy Chlorinated Hydrocarbons in the Atmosphere

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■ Fluxes of aerosol polychlorinated biphenyl (PCB, chlorine mixture) ranging from 2×10^{-9} to 9 [illegible] 3×10^{-7} g m^{-2} day^{-1} were measured at [illegible], 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 [illegible] of aerosol PCB introduced into the troposphere to occur [illegible]

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% ar[illegible] 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 1.8×10^{-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 i[illegible]

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_2t, minus the concentration-dependent term describing the disappearance via the combined agencies of secondary emission and leaching downward, k_1C_2, to give $dC_2/dt = k_2t - k_1C_2$ which is solved by $C_2(t) = k_1^{-1}k_2t[1 - \exp(-k_1t)]$. With $k_2 = 6 \times 10^{-6}$ g m^{-2} yr^{-1} and $C_2(t = 30\ \text{yr}) = 1.8 \times 10^{-3}$ 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

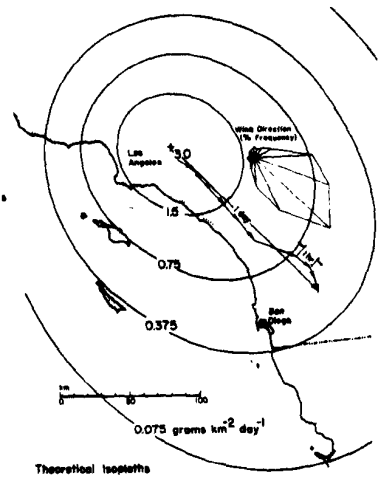
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Tarrant and Tatton (4) show that soil concentrations of CHC in areas not subject to direct application are *increasing* so that the assumption of a steady state cannot be made. Since the disappearance of CHC from soil is due to leaching as well as 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.



Theoretical Isopleths

Figure 1. Model parameters for calculation of this series of isopleths: deposition coefficient, $k = 0.146$ h^{-1}; exponential dispersion parameter, $n = 0.26$; 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

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 (≥ 10 μm) 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:

$$\chi_\omega = \int_0^\infty \chi(z)dz$$

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-

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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, $F = k\chi_{wi}$, 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 χ ($z = 10$ 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):

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

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

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

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).

Table I. Ground Level Concentration, $\chi(z = 10$ cm), Deposition Flux, and Deposition Velocity of Aerosol PCB Measured During Various Atmospheric Stability Conditions

Mo./day, 1972	Wind speed, m/s (stability)	Ground level concn, (g/m^2) $\times 10^{-9}$	Flux (g/m^2 h) $\times 10^{-7}$	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 $\sigma^2 = 2Kt$ (with K the Fickian eddy diffusivity), this Gaussian distribution (Equation 1) provides a solution to the gradient diffusion equation:

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

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

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

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

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.

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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

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

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

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

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

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

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: $u_i(\text{eff}) = \alpha u_i(\text{obs})$.

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 δ = (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_0 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-

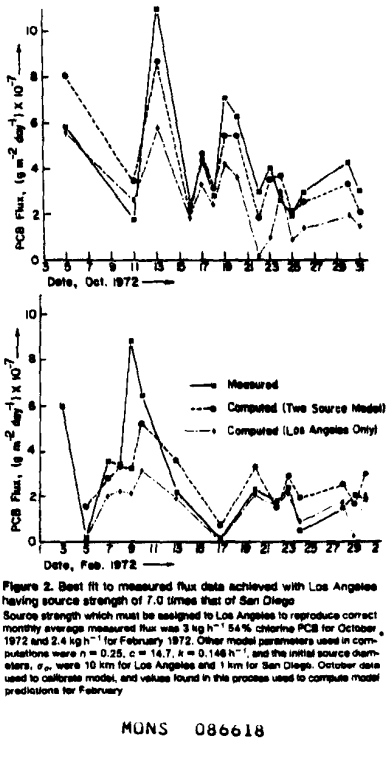


Figure 2. Best fit to measured flux data achieved with Los Angeles having source strength of 7.0 times that of San Diego

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 $n = 0.25$, $c = 14.7$, $k = 0.148$ h^{-1}, and the initial source diameters, σ_0, 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

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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 [redacted] 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 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.

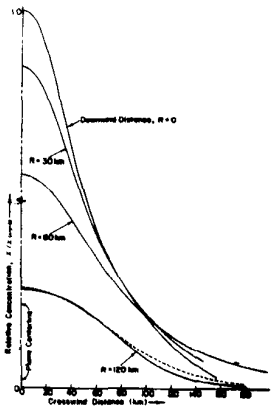


Figure 3. Predicted cross-wind plume dimensions at various distances from source

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 $\sigma = 60$ km

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}.

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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 10^3 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 [redacted] This corresponds to a downwind distance at which the quantity of material remaining in the plume is reduced by one-half of less th[redacted] calcu[redacted] PCB (54% [redacted] 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 (~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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Literature Cited

(1) McClure, V. E., LaGrange, J., *Bull. Environ. Contam. Toxicol.*, in press.
(2) Nash, R. G., Woolson, E. A., *Science*, 157, 924 (1967).
(3) Woodwell, G. M., Craig, P. P., Johnson, H. A., *ibid.*, 174, 1101 (1971).
(4) Tarrant, K. R., Tatton, J. O'G., *Nature*, 219, 725 (1968).
(5) Iallizer, N. F., Dumbauld, R. K., *Int. J. Air Water Pollut.*, 7, 999 (1963).
(6) Sehmel, G. A., *J. Colloid Interface Sci.*, 37, 891 (1971).
(7) Chamberlain, A. C., *Int. J. Air Water Pollut.*, 3, 63 (1960).
(8) Whitby, K. T., Husar, R. B., Liu, B.Y.H., *J. Colloid Interface Sci.*, 39, 177 (1972).
(9) (SSMO) "Summary of Synoptic Meterological Observations", Vol 7, p 461, U.S. Naval Weather Service Command, CFSTI, Springfield, Va., 1970.
(10) Sutton, G. A., *J. Colloid Interface Sci.*, 37, 891 (1971).
(11) Elliott, W. P., Engelman, R. J., Nickols, P. W., "Area Dosage Relationships and Time of Arrival in the Green Glow Program, Air Force Surveys in Geophysics No. 134," Report AFCRL-468, Air Force Cambridge Research Laboratories, 1961 (quoted in *ref. 22*, p 160).
(12) Heftar, J. L., *J. Appl. Meteorol.*, 4, 153 (1965).
(13) Young, D. R., McDermott, D. J., Heeson, T. C., "Southern California Coastal Water Research Project", Report TM 224, El Segundo, Calif., Nov. 1975.
(14) Meetham, A. R., *R. Meteorol. Soc., Q. J.*, 76, 359 (1950).

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(15) "Environmental Research, 5, #3, PCB Environmental Impact, A Review by the Panel on Hazardous Trace Substances", p 276, March 1972.
(16) Scura, E. D., McClure, V. E., *Mar. Chem.*, 3, 337 (1975).
(17) "Beilstein's Hanbuch für Organischen Chemie", Vol 5, Vierte Auflage, 1964.
(18) Bidleman, T. F., Olney, C. E., *Science*, 173, 516 (1974).
(19) Abbott, D. C., Harrison, R. B., Tatton, J. O'G., Thompson, J., *Nature*, 211, 259 (1966).
(20) Langmuir, I., *J. Meteorol.*, 5, 182 (1948).
(21) Chamberlain, A. C., "Aspects of Travel and Deposition of Aerosol and Vapor Clouds", British Report AERE-HP/R-1261, 1943.
(22) "Meteorology and Atomic Energy 1968", D. H. Slade, Ed., TID-24190, Clearinghouse for Federal Scientific & Technical Information, NBS, Springfield, Va., 1968.
(23) Engelman, R. J., Perkins, R. W., Hagen, D. I., Haller, W. A., "Washout Coefficients for Selected Gases and Particulates", Proc. 59th Annual Meeting Air Pollution Control Assoc., 1966.
(24) Wheatly, G. A., Hardman, J. A., *Nature*, 207, 468 (1965).

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Supplementary Material Available. *An annotated listing of the computer program in Fortran, wind direction and speed data, and an additional figure will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Operations Office, Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number ES&T-76-1223.*

PCB and PCT Contamination of the Environment near Sites of Manufacture and Use

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■ A survey was conducted to assess the degree of environmental contamination with polychlorinated biphenyls (PCB's) and polychlorinated terphenyls (PCT's) in the vicinity of the single U.S. manufacturing facility [redacted], and two users in the investment casting industry located in urban Chicago and suburban Detroit. PCB concentrations were found [redacted] near the manufacturer and 5.2 ppm [redacted] PCT's were detected as high as 13 ppm in the vicinity of one user facility. The distribution of PCB's and PCT's suggested a [redacted] mode of transport from the source. Analysis of wastewaters indicated the discharge of PCB's and PCT's in the μg/l. level.

Polychlorinated biphenyls (PCB's) have a basic chemical structure as shown in Figure 1. From 1 to 10 chlorine atoms may be attached to the structure, resulting in 210 possible isomers. PCB's have certain physical properties, including high heat capacity, chemical stability, and excellent dielectric properties which make them highly desirable for a number of industrial uses. Concern has been expressed in recent years over the widespread dispersion of PCB's in the environment. These compounds are suspected to have significant adverse effects on organisms at the top of the food web, including man. Biomagnification of this contaminant in natural predator–prey food chains has been documented by numerous studies. To complicate the problem, the rate of degradation of PCB's in the environment, particularly the higher substituted isomers, is apparently extremely slow. This situation allows for significant accumulation of these persistent chlorinated organic compounds in the environment. A thorough discussion of the problem and of the environmental data that are available has been presented by Selikoff (*1*) and the U.S. Government Interdepartmental Task Force (*2*).

Polychlorinated terphenyls (PCT's) have a similar but more limited industrial application. A generalized PCT structure is illustrated in Figure 1. There exists little information concerning PCT's in the environment. The environmental behavior of PCT's may be expected to be similar to that of PCB's.

The Monsanto Co. is the sole domestic producer of both PCB's and PCT's under the trade name of Aroclors. In response to the rising concern over PCB's in the environment, the Monsanto Co. has voluntarily taken two actions to reduce the environmental hazard. Beginning in 1970, the production of Aroclor was voluntarily reduced by the manufacturer, and supply was discontinued to those users who could not control release to the environment. Production of the more highly chlorine substituted Aroclor mixtures, including all PCT's, has since been curtailed or discontinued, and a lower substituted, refined mixture (Aroclor 1016) has been introduced. Some research indicates the lower substituted PCB isomers do not persist as long in the environment as the higher substituted isomers, and that they may be amenable to biological degradation, hence reducing the potential hazards to the environment. A recent public announcement by Monsanto Co. (January 1976) has indicated their intention to suspend all production of PCB's.

PCB's are presently employed in electrical capacitors, transformers, vacuum pumps, and gas-tranamission turbines (*3*). Both PCB's and PCT's are currently used in the investment casting industry as a major constituent of the wax material used. This material is fashioned into the shape to be cast. A refractory mold is then formed around the wax shape. The wax is melted and poured from the mold, leaving the mold prepared for casting of the shape in metal.

The investment casting industry has not been supplied by Monsanto Co. for several years. PCB's and PCT's have been imported from foreign sources to meet this demand. Hutzinger et al. (*3*) list the origin and trade name of foreign manufactured PCB mixtures.

Sampling and Analysis

A field sampling program was conducted in early 1975 under the direction of the Environmental Protection Agency to assess the effectiveness of voluntary controls by industry in eliminating the release of PCB's to the environment. Samples were taken in the vicinity of the domestic manufacturing facility and two PCB and PCT user facilities. The production facility is located in Sauget, Ill.; the user facilities are located in urban Chicago, Ill., and suburban Detroit, Mich.

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Surface soil samples were collected at each site from the [redacted] to a distance of approximately 2000 m in four directions, subject to the physical constraints encountered. At each soil sample point, five subsamples were collected within a radius of 10 m to a depth of 2.5 cm over a 100 cm^2 area. Vegetative matter was removed with forceps, and the five subsamples were composited and thoroughly mixed. This mode of sampling was designed to collect a homogeneous surface soil sample representative of the chosen sample point. Every attempt was made to select sample points where surface vegetation was sparse and where it appeared unlikely wind scour would be a major soil transport factor. Samples were placed in precleaned wide-mouth glass jars with aluminum foil-lined closures.

Water samples were taken in 1-l. glass containers, composited, and stored in 4-l. precleaned glass-stoppered reagent bottles. Soil samples were extracted in a soxhlet apparatus with 1:1 nanograde hexane/acetone, dried with sodium sulfate, and concentrated on a Kuderna-Danish apparatus. The procedure follows that prescribed by the EPA (*4*). Water samples were triple extracted with 15% nanograde ethyl ether in hexane, dried with sodium sulfate, and concentrated on a Kuderna-Danish apparatus as described in EPA recommended procedures (*5*). Both soil and water sample extracts were cleaned on a silica gel column, to remove interfering pesticides, using the method of Snyder and Reinert (*6*) followed by a sulfuric acid cleanup as described by Murphy (*7*).

All analyses were conducted by electron capture gas chromatography using a Varian 2760 instrument. A 1.8-m, 3-mm i.d., glass column packed with 1.5/1.95% OV-17/QF-1 on a chrom W-HP, 80/100 mesh support at 200 °C was used for PCB analysis. A 3% SP-2401 glass column of length 1.1 m and i.d. 3 mm was operated at 220 °C for analysis of PCT's. Mass spectrographic confirmation was obtained for selected samples. Quantitation of the PCB and PCT present was conducted by electronic integration of the area of all peaks matching the most closely related Aroclor standard.

Results and Discussion

PCB's were detected in soil samples from all three locations surveyed. The gas chromatographic elution patterns most closely matched those of Aroclor 1242 and Aroclor 1260. Decachlorobiphenyl was present in samples taken at two of the three sites. PCT's were detected in soils at the urban Chicago location and in sediments at the suburban Detroit location.

Manufacturing Facility. Aroclors have been produced by Monsanto Co. at [redacted], site since prior to 1957. PCB mixtures ranging from 16 to 68% chlorine have been produced over the years. Production of the higher percent chlorine mixtures has been voluntarily reduced since 1970, and lower substituted isomers have been introduced. Polychlorinated terphenyls and chlorinated benzenes have also been produced at this facility. Terphenyl production was suspended in 1971 (*8*). The company operates a liquid injection incinerator to dispose of in-house liquid wastes and contaminated PCB's. The environs of the facility are dedicated predominately to heavy industrial use with a limited amount of residential housing.

The results of the analysis of soil samples taken in the vicinity of this manufacturing facility are summarized in Table I. Aroclor 1242 was present in approximately one-half of the samples. [redacted] Aroclor 1260 was present in all samples. Concentrations ranged from 0.03 to 9.6 ppm. Decachlorobiphenyl was also detected in all samples at a concentration ranging from 0.049 to 2.4 ppm. Total PCB concentrations of 0.15–20.7 ppm on a dry weight basis were detected within a

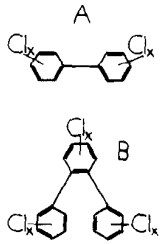


Figure 1. Basic chemical structure of (A) polychlorinated biphenyls (PCB's) and (B) polychlorinated terphenyls (PCT's)

Table I. Results of Analysis of Soil Samples Taken in Vicinity of Monsanto Co. Krumrich Production Facility in Sauget, Ill.

Direction from facility	Distance from facility, m	ppm			
		Aroclor 1242	Aroclor 1260	Decachloro-biphenyl	Total PCB
SE	250	6.1	9.6	2.4	[redacted]1
NE	450	0.68	0.31	0.38	1.37
SE	600	3.0	2.9	1.3	7.2
SW	600	<0.01	0.65	0.12	0.77
NW	600	10	9.6	1.1	[redacted]7
NE	620	<0.01	1.4	0.90	2.3
NE	700	<0.01	0.12	0.61	0.73
NW	850	<0.01	0.03	0.40	0.43
NE	950	<0.01	0.05	0.097	0.13
SW	950	0.45	0.28	0.081	0.81
SE	1000	<0.01	0.20	0.27	0.47
SE	1050	0.82	1.3	1.6	3.72
NW	1100	0.46	0.39	0.12	0.97
SW	1250	<0.01	0.10	0.049	0.15
SW	[redacted]	<0.01	0.26	0.081	0.34

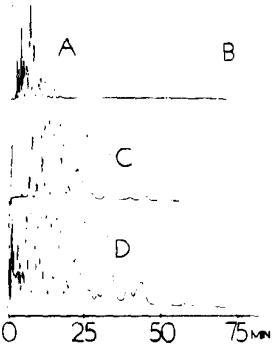


Figure 2. Typical chromatograms of standard Aroclors, decachlorobiphenyl, and soil sample taken in vicinity of Monsanto Co., Sauget, Ill.

(A) Aroclor 1242, (B) decachlorobiphenyl, (C) Aroclor 1260, (D) soil extract

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1450-m radius of the facility. No PCT was present in soils from this location.

A typical chromatogram of a soil sample taken in the vicinity of the Monsanto facility is shown in Figure 2 along with the chromatogram of several other PCB's run under the same instrument conditions. This particular soil sample contains 11 ppm Aroclor 1242, 9.3 ppm Aroclor 1260, and 1.0 ppm decachlorobiphenyl. Lighter chlorinated Aroclor mixtures are likely present as well. The instrument conditions employed, however, do not give adequate separation of these mixtures to permit accurate quantification. The presence of decachlorobiphenyl at the concentrations observed is interesting. Decachlorobiphenyl has been reported as a component of only one Aroclor mixture (Aroclor 1268). Whether it may be a component of any of the terphenyl mixtures produced or a by-product is not known.

Referring again to Table I, the higher PCB concentrations are apparently at points closer to the facility with concentrations generally [redacted]. This distribution suggests [redacted] of the PCB's, including decachlorobiphenyl, from the manufacturing facility, with subsequent deposition onto the surrounding landscape.

A 24-h composite sample from the influent and the effluent of the Sauget village sewage treatment plant taken on February 17–18, 1975, was provided by plant personnel. The Monsanto Co. uses this facility jointly with the village. Analysis (μg/l.) of these samples was as follows:

	Aroclor 1242	Aroclor 1260	Decachlorobiphenyl
Influent	6.8	8.7	<0.01
Effluent	4.5	4.7	<0.01

The treatment plant effects a [redacted] Aroclor 1242 and [redacted] No decachlorobiphenyl was detected [redacted] Ill. Prior to 1972, Aroclors 5442, 5460, and 6090 were purchased and used by this industry in the compounding of investment casting waxes. Subsequent to 1972, Fenclor DK and Aroclor 5460 have been in use. Aroclors 5442 and 5460 are terphenyl mixtures with 42 and 60% chlorine by weight, respectively. Aroclor 6090 is 90% terphenyl and 10% Aroclor 1221. Fenclor DK is a foreign-supplied PCB [redacted] Corp., Milan, Italy) consisting of nearly pure decachlorobiphenyl. The manufacturing facility is situated in an urban neighborhood. Residential housing, parks, and a hospital are located within a 3-km radius.

The analytical results for soil samples at this site are tabulated in Table II. Aroclor 1260 was present in all samples, ranging from a low value of 0.22 ppm to a high of 1.8 ppm. Decachlorobiphenyl was present in all but two samples with a maximum concentration of 3.6 ppm located 20 m from the facility. Total PCB concentrations ranged from 0.22 to 5.2 ppm. PCT's were also present in many of these soil samples. The gas chromatographic elution pattern closely matched that of Aroclor 5460. One PCT concentration as high as 13 ppm was measured.

Figure 3A demonstrates that Fenclor DK is nearly pure decachlorobiphenyl. One minor peak elutes just before the predominate decachlorobiphenyl peak. The retention of the minor contaminant peak is such that it may be expected to be an octachlorobiphenyl since it exhibits the same retention time as the latest eluting peak in a standard Aroclor 1260 mixture. It is apparent by comparison of peak retention times with the sample chromatogram, Figure 3C, that decachlorobiphenyl is present in the soil sampled. The measured concentration of decachlorobiphenyl in this particular sample was 1.2 ppm. The presence of decachlorobiphenyl in this sample has been confirmed by mass spectrometry.

The sample elution pattern also indicates the presence of Aroclor 1260 as can be seen by comparison with the Aroclor 1260 elution pattern, Figure 3B. The concentration of Aroclor 1260 in this sample is 0.53 ppm. There is no indication of degradation of the Aroclor 1260 since virtually all peaks in the sample chromatogram are present in the same relative proportion as in the standard. There are no significant, undefined peaks in the chromatogram following the acid cleanup procedure. Certain of the sample chromatograms indicate the presence of lower weight PCB's; however, the quantities present tend to be far less than either Aroclor 1260 or decachlorobiphenyl at this site.

Figure 4 is a gas chromatogram of a soil extract from this site showing the presence of various PCB's, decachlorobiphenyl, and PCT. The PCT present closely resembles the Aroclor 5460 shown.

There exists no apparent spatial pattern of Aroclor 1260 distribution over the study site. There is little evidence in the data to indicate the source of the Aroclor 1260 contamination

Table II. Results of Analysis of Soil Samples Taken in Vicinity of an Investment Casting Facility in Urban Chicago, Ill.

Direction from facility	Distance from facility, m	ppm			
		Aroclor 1260	Decachlorobiphenyl	Total PCB	Aroclor 5460
NE	20	0.40	1.2	1.6	3.2
SE	20	0.26	0.51	0.77	0.38
SW	20	1.5	0.75	2.25	4.2
NW	20	1.6	3.6	[redacted]	13
E	450	0.69	0.58	1.27	4.1
NE	600	0.34	0.19	0.53	0.25
SW	620	0.57	0.040	0.61	<0.17
NW	620	0.29	0.001	0.29	0.28
NE	1050	0.81	0.033	0.84	0.17
SW	1150	0.67	0.020	0.69	0.79
NW	1220	0.56	0.034	0.59	<0.17
NE	1500	0.24	0.053	0.29	<0.17
E	1620	0.22	<0.001	0.22	<0.17
NW	[redacted]	1.8	<0.001	1.8	0.23

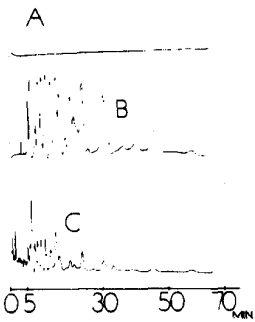


Figure 3. Typical chromatograms of standard PCB's and soil sample taken in vicinity of investment casting facility in Chicago, Ill. (A) Fenclor DK, (B) Aroclor 1260, (C) soil extract

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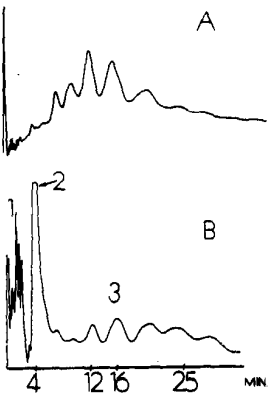


Figure 4. Chromatogram of Aroclor 5460 and soil sample taken in vicinity of investment casting facility in Chicago, Ill.
(A) Aroclor 5460, (B) soil extract showing presence of (1) PCB's, (2) decachlorobiphenyl, and (3) PCT's

Table III. Results of Analysis of Soil Samples Taken in Vicinity of Investment Casting Facility in Suburban Detroit, Mich.

Direction from facility	Distance from facility, m	ppm Aroclor 1260	ppm Aroclor 5460
SE	60	0.04	<0.17
NW	60	0.12	<0.17
NW	60	0.07	0.64
NW	200	<0.01	<0.17
SE	520	0.05	<0.17
NW	800	<0.01	<0.17
NE	900	0.14	<0.17
SE	900	0.06	<0.17
NW	1000	0.12	<0.17
SW	1050	0.03	<0.17
SW	1050	<0.01	<0.17
NW	1350	0.03	<0.17
SE	1500	0.04	<0.17
E	1650	18[a]	<0.17
NE	2100	<0.01	<0.17
SW	2100	0.02	<0.17

[a] Aroclor 1242.

is the facility surveyed. Aroclor 1260 has not, in fact, been reported to have been used by this company.

The spatial distribution of both decachlorobiphenyl and PCT do indicate higher soil-borne concentrations near the investment casting facility with generally decreasing levels at increased distances. There exists a strong statistical correlation among the data for decachlorobiphanyl and the PCT (Aroclor 5460) and little correlation between Aroclor 1260 and decachlorobiphenyl or the PCT.

Again, as at the production facility, the spatial distribution of the PCB and the PCT present is indicative of airborne transport. The Aroclor 1260 detected is apparently not from the source surveyed, whereas decachlorobiphenyl and PCT are likely from this user. It is somewhat surprising to see evidence of significant airborne transport of the higher substituted and less volatile PCB isomers and of PCT. That the gas chromatographic elution pattern shows little evidence of either selective emission or selective transport of the more volatile isomers would indicate the source of the airborne contamination is at such a temperature that the entire PCB or PCT mixture is in the [redacted] the point of emission.

Investment Casting Facility, Troy, Mich. This facility is located in a small industrial park in suburban Detroit, Mich. Surroundings consist principally of other small industries and residential areas. It has been reported that this company [redacted] used in the casting process from the company located in Chicago which is discussed above. The analytical results of soil samples taken at this location are summarized in Table III.

Aroclor 1260 is detectable in most of the soil samples. Decachlorobiphenyl is absent in the soils. PCT's are present in one sample taken 60 m northwest of the user. No spatial distribution pattern of PCB or PCT is evident. The one observed concentration of 18 ppm Aroclor 1242 appears to be anomalously high. Replicate analysis, however, yielded similar values for this sample. Aroclor 1242 was not detected in any other soil samples from this area.

A drainage ditch passes adjacent to the north boundary of the industrial park in which the facility is located. The drainage ditch serves to remove stormwater runoff in the vicinity and receives discharged cooling water from several local small industries including the one surveyed.

Analyses of cooling water at the point of discharge, of water and sediments within the drainage ditch, and of water and sludge deposits within the sanitary sewer system serving the area are reported in Table IV. It is apparent from these data that discharged cooling waters and waters in the drainage ditch at the time of sampling were free of both PCB's and PCT's. Bottom sediments within the drainage ditch, however, contained significant concentrations of Aroclor 1242, Aroclor 1260, decachlorobiphenyl, and Aroclor 5460. The source of this contamination of ditch sediments may be attributed to

Table IV. Results of Analysis of Various Samples Taken in Vicinity of Investment Casting Facility in Suburban Detroit, Mich.

Sample	Aroclor 1242	Aroclor 1260	Decachlorobiphenyl	Aroclor 5460
Cooling water discharge	<0.1 μg/l.	<0.1 μg/l.	<0.01 μg/l.	<0.1 μg/l.
Drainage water	<0.1 μg/l.	<0.1 μg/l.	<0.01 μg/l.	<0.1 μg/l.
Drainage water	<0.1 μg/l.	<0.1 μg/l.	<0.01 μg/l.	<0.1 μg/l.
Ditch sediment	2.3 ppm	6.7 ppm	0.09 ppm	6.7 ppm
Ditch sediment	9.4 ppm	8.9 ppm	0.11 ppm	5.1 ppm
Sanitary sewer water 1530, 2/22/75	<0.1 μg/l.	<0.1 μg/l.	<0.01 μg/l.	<0.1 μg/l.
Sanitary sewer water 1615, 2/22/75	<0.1 μg/l.	<0.1 μg/l.	<0.01 μg/l.	<0.1 μg/l.
Sanitary sewer water 1145, 2/23/75	<0.1 μg/l.	7.0 μg/l.	4.1 μg/l.	7.5 μg/l.
Sanitary sewer sludge deposits	<0.01 ppm	0.11 ppm	0.034 ppm	5.0 ppm

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wastewater discharges, sometime previous to the time of sampling, or to surface runoff in the vicinity.

Water and bottom sludge samples were taken from the sanitary sewer system serving the industrial park. Grab samples of the water were taken three times from a manhole access. As shown in Table IV, PCB's and PCT's were not detected in waters sampled at 1530 and 1815, but when sampled at 1145 the following day, PCB's and PCT's were present at a concentration of 11.1 and 7.5 μg/l., respectively. Sludge deposits within the sewer contained 0.14 ppm PCB and 5.0 ppm PCT on a dry weight basis. It appears that intermittent discharge of both PCB and PCT to the sanitary sewer system is occurring.

Conclusions

PCB[illegible] to the environment has occurred near the domestic production facility and two user facilities. The spatial distribution of soil contamination suggests [illegible] transport of the contaminant from the manufacturer and one of the two users surveyed. At the manufacturing site, Aroclor 1260 and decachlorobiphenyl were distributed in such a manner as to indicate the production facility to be the source. In urban Chicago, decachlorobiphenyl and PCT contamination appears to be superimposed on a rather random background of Aroclor 1260 contamination in such a manner to suggest the investment casting facility is the source of the decachlorobiphenyl and the PCT, but not the Aroclor 1260. In suburban Detroit, the background soil level of Aroclor 1260 shows no distribution pattern that would indicate the source to be the facility surveyed.

Influent and effluent wastewater samples from Sauget, Ill., attest to the removal, albeit incomplete, of PCB in the biological waste treatment system. Water and sediment samples from the suburban Detroit location indicate PCB and PCT discharges or contaminated runoff into surface drainageways sometime in the past. Discharges to the sanitary sewer system are apparently continuing.

Voluntary control on the release of PCB's and PCT's to the environment by industrial sources cannot be considered entirely effective. It is not possible to determine from soil contamination levels at the manufacturing site, whether or not the contamination has occurred since voluntary controls have been instituted (ca. 1970). At the urban Chicago location, however, it appears soil contamination has occurred since 1972 when Fenclor DK came into use. Contamination of wastewaters is still evident.

Literature Cited

(1) Selikoff, I. J., Ed., *Environ. Res.*, **5**, 3 (1972).
(2) U.S. Government Interdepartmental Task Force on PCB's, "PCB's and the Environment", NTIS Document COM-72-10419, 1972.
(3) Hutzinger, O., Safe, S., Zitko, V., "The Chemistry of PCB's", CRC Press, Cleveland, Ohio, 1974.
(4) Environmental Protection Agency, "Analysis of Pesticide Residues in Human and Environmental Samples", Pesticides and Toxic Substances Effects Laboratory, Research Triangle Park, N.C., 1974.
(5) Environmental Protection Agency, "Method for Polychlorinated Biphenyls (PCB's) in Industrial Effluents", NERC, Cincinnati, Ohio, 1973.
(6) Snyder, D., Reinert, R., *Bull. Environ. Contam. Toxicol.*, **6**, 5 (1971).
(7) Murphy, P. G., *J. Assoc. Off. Anal. Chem.*, **55**, 6 (1972).
(8) Papageorge, W. B., Monsanto Industrial Chemicals Co., St. Louis, Mo., private communication, 1975.

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Use of Permeation Tubes for Calibration of Vinyl Chloride Analyses

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■ A study was conducted to determine the performance of vinyl chloride permeation tubes when used to prepare low-level gaseous calibration standards which are convenient for the analysis of samples in the gas or liquid phase. Permeation rates were determined gravimetrically at three temperatures including extended periods at 25 °C. The rates at 25 °C for FEP and TFE Teflon tubes (0.250 in. o.d. × 0.030 in. wall thickness) were, respectively, 0.259 and 1.98 μg/cm min, and the activation energies of permeation were determined to be 15.0 and 11.9 kcal/g mol. Gas samples prepared in a flow dilution system containing a permeation tube were used to calibrate a gas chromatograph equipped with a gas sampling valve. Calibration data, accuracy, and limit of detection are presented. Although the permeation tubes were convenient, periodic weighing is recommended for highest accuracy since slightly decreasing rates were observed in four tubes and some polymerization of the reservoir liquid occurred in one tube.

Recent recognition of the carcinogenic hazards associated with vinyl chloride exposure generated the need to monitor low levels in work areas and ambient air. The federal Occupational Safety and Health Administration set an occupational exposure limit of 1 ppm for an 8-h time-weighted average with a ceiling of 5 ppm for a period not exceeding 15 min (*1*). An "action level" of 0.5 ppm and above was established for employers for implementing certain required control procedures. Because of important economic and legal implications, accurate analysis of airborne vinyl chloride is essential.

The Environmental Protection Agency recently published a tentative method of analysis for ambient air concentrations (*2*), similar to that recommended by the National Institute for Occupational Safety and Health for occupational areas (*3*). Both methods were based on adsorption of vinyl chloride on charcoal and desorption into carbon disulfide followed by gas chromatographic determination using a flame ionization detector. The accuracy of the method was thus dependent upon

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the accuracy of the standards as well as the sampling procedures. Calibration standards were prepared by gravimetric and volumetric procedures. Gravimetric techniques were used to determine the weight of vinyl chloride absorbed when it was bubbled through toluene; aliquots of this solution were diluted with carbon disulfide. Standards were also prepared volumetrically using measured volumes of the vinyl chloride gas which were injected directly into carbon disulfide. Both of these methods were inconvenient and were subject to errors from evaporation.

Permeation tubes are useful in preparing continuous, low-level concentrations of a variety of compounds including SO_2, NO_2, H_2S, Cl_2, NH_3, propane, and other hydrocarbons (*4–6*). Tube behavior with each individual compound must be determined experimentally since a stable permeation rate cannot be achieved if the tubing is affected by the permeant gas or if the contents polymerize, decompose, or react with the dilution air. The purpose of this work was to evaluate permeation tubes for preparing accurate gaseous vinyl chloride standards.

Experimental

Permeation tubes were prepared from 0.250 in. o.d. × 0.030 in. wall thickness tubing of both FEP (fluorinated ethylene propylene copolymer) and TFE (tetrafluoroethylene polymer) Teflon. A long-lived tube was constructed by attaching a TFE Teflon tube to an 8-ml stainless steel bottle. The tubes were constructed and filled, and the ends plugged with a Teflon rod secured with Swagelok ferrules in the manner previously described (*5*). The vinyl chloride was purified by passage through a cold trap to remove traces of phenol which are sometimes added to the cylinder gas as stabilizers. The tubes after standing in the hood for approximately 2.5 days were maintained at a constant temperature under a continuous flow of dry, purified air. Two sets of permeation tubes were studied.

Permeation rates from the first set of tubes were determined gravimetrically over periods up to 8 months, during which the tubes were held at three temperatures in a cyclical pattern as shown in Table I. Several weighings were made at each temperature, as noted, and the slopes of plots of weights vs. age were used to determine the rates. Least-squares plots of the data are shown in Figure 1, which is an Arrhenius-type plot. The abscissa scale is not linear but is proportional to the negative reciprocal of absolute temperature, and the ordinate is a logarithmic scale of permeation rates. The rates at 25 °C for FEP and TFE Teflon were, respectively, 0.259 and 1.96 μg/cm min, and from the slopes, the activation energies of permeation were calculated to be 15.0 and 11.9 kcal/g mol. The higher rate for TFE Teflon was more convenient for instrument calibration. The observed permeation rates were corrected to 25 °C by means of the Arrhenius equation and are given in the last column of Table I. These corrected rates were plotted against the final ages, and a line was fitted to the data for each tube by the method of least squares. The rates for the FEP Teflon tube (I) were essentially constant. Those for TFE showed very slight downward trends of 0.14 and 0.03%/day of the initial rates for the 20-cm tube (II) and the 11-cm tube with a stainless steel reservoir (III), respectively.

The monomeric liquid vinyl chloride appeared stable in the first set of permeation tubes which were exposed to flows of dry dilution air for periods as long as eight months. A stable permeation rate was maintained when the tube was kept at a constant temperature. For greatest accuracy, it was found desirable after a temperature cycle to determine the new permeation rate. The relative standard deviations of the

Table I. Permeation Rates of Vinyl Chloride Through Teflon Tubing (0.250 in. o.d. × 0.030 in. Wall Thickness)

Mean [a] temp, °C	Heating period, days	Final age, days	No. of weighings	% Rel SD of slope [b]	Permeation rate, μg/cm min	
					Obsd	Corr [c] to 25 °C
I. FEP Teflon (14-cm effective length)						
25.0	16.1	21	9	0.35	0.244	0.244
30.0	12.7	34	8	0.11	0.373	0.246
25.0	13.0	47	10	0.16	0.256	0.256
35.0	7.1	54	6	0.14	0.593	0.261
30.0	25.9	80	11	0.08	0.399	0.263
25.0	26.6	107	8	0.07	0.265	0.265
35.0	4.8	115	6	0.09	0.597	0.262
25.0	6.9	123	8	0.26	0.266	0.266
25.0	37.2	160	2	...	0.262	0.262
25.0	38.0	198	2	...	0.265	0.265
25.0	36.7	235	2	1.1	0.257	0.257
II. TFE Teflon (20-cm effective length)						
30.0	6.8	12	7	0.042	2.786	1.987
25.0	13.0	25	10	0.10	1.999	1.999
35.0	8.1	33	6	0.26	3.710	1.934
30.0	5.8	39	7	0.21	2.671	1.918
III. TFE Teflon (11-cm effective length with 8-ml stainless steel reservoir)						
25.0	10.1	13	9	0.11	2.018	2.018
35.0	7.1	20	5	0.09	3.968	2.064
30.0	25.9	46	11	0.31	2.817	2.023
25.0	26.6	73	8	0.05	1.994	1.994
35.0	4.8	78	6	0.26	3.762	1.962
25.0	6.9	84	8	0.25	2.004	2.004
25.0	37.2	122	2	...	1.987	1.987
25.0	38.0	160	2	...	1.975	1.975
25.0	36.7	196	2	1.8	1.915	1.915

[a] Thermostatic control ±0.02 °C. [b] Coefficient of variation × 100. [c] By means of Arrhenius equation.

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