

Appendix E Review of Air Release Models

NIOSH has studied exposure to solvents at a number of screen printing facilities over the past three decades. Some of the highest solvent concentrations were found in the screen washing area at Impressions Handprinters in Chicago, in June 1984 (NIOSH Health Hazard Evaluation Report 84-299-1543). The toluene concentrations in the screen-washing area during the ink removal process ranged from 181-727 ppm. These concentrations exceed the OSHA STEL for toluene (150 ppm). At other screen printing sites, NIOSH investigators observed similar concentrations of organic solvents in the air. NIOSH observed airborne toluene concentrations of 115-239 ppm during screen cleaning operations at the main U.S. Post Office in Chicago in July 1981 (NIOSH Health Hazard Evaluation Report 81-383-1151). NIOSH observed airborne cyclohexanone concentrations of 10-25 ppm during screen cleaning at Downing Displays in Cincinnati, Ohio (NIOSH Health Hazard Evaluation Report 82-330-1252). The CEB model predicts $C_p = 22$ ppm. NIOSH investigations are generally triggered by union or management concern about working conditions, and therefore NIOSH data generally reflects worst-case exposures. Thus, it appears that use of the "typical case" parameters in the CEB model provides estimates of occupational exposure which are high, but within the range of the observed data. Use of the "worst-case" parameters in the CEB model generates estimates which are an order of magnitude greater than the field data.

SAIC reviewed the theoretical basis for CEB's air release model and compared it to other mass transfer relationships in order to determine whether it might be possible to obtain even better agreement with the NIOSH data, especially for the worst-case ventilation scenario. SAIC also reviewed the results of Pace Laboratories' experimental measurements of liquid volatilization, which were performed for CEB. These measurements mainly relate to high-vapor pressure compounds evaporating under turbulent airflow conditions. For practical reasons, Pace was unable to run the apparatus at airspeeds less than 100 ft. min^{-1} , and therefore could not obtain correlations specific to the laminar flow regime.

SAIC identified two problems that may cause eqs. (1) and (2) to overestimate airborne concentrations. The first is that CEB's default assumptions for Q , the volumetric air flow rate, may be inconsistent. CEB uses $v_z = 100 \text{ ft. min}^{-1}$ in eq. (1). An air velocity of 100 ft. min^{-1} through a screen cleaning room 8 ft wide x 10 ft long x 10 ft high would imply $Q = 8,000 \text{ ft}^3 \text{ min}^{-1}$. The actual flowrate would be lower than this, since the maximum velocity would not be reached in the corners of the room nor immediately adjacent to the walls. However, CEB uses a typical air flow rate of $Q = 3,000 \text{ ft}^3 \text{ min}^{-1}$, which may be too low. Changing Q to $8,000 \text{ ft}^3 \text{ min}^{-1}$ would reduce the predicted airborne concentrations in Example 1 by a factor of 2.3, bringing the exposure estimates down to about 560 mg. m^{-3} . The second source of possible error identified by SAIC in the standard CEB approach seems to lie in the theoretical basis of eq. (1).

The derivation of eq. (1) is given in Appendix K of the CEB Manual for the Preparation of Engineering Assessments. The following general equation governs all mass transfer processes in unreacting systems:

$$\rho \frac{\partial c}{\partial t} = -\mathbf{v} \cdot \nabla c + D_{ab} \nabla^2 c$$

where

c	=	Concentration, mol.m ⁻³
t	=	Time, s
\mathbf{v}	=	Velocity vector, m.s ⁻¹
D_{ab}	=	Diffusivity in air, m ² .s ⁻¹
ρ	=	Air density, kg.m ⁻³

For steady, unidirectional flow of air over a pool of liquid as shown in Figure 1, this can be simplified to:

$$v_z \frac{\partial c}{\partial x} = D_{ab} \frac{\partial^2 c}{\partial x^2}$$

where

v_z	=	Velocity in the z direction, m.s ⁻¹
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If v_z is assumed not to vary with height above the liquid pool, this equation can be solved analytically to yield eq. (1). However, this assumption is flawed. Because of viscous drag, a laminar boundary layer develops when air begins to flow over a flat surface. This is illustrated in Figure 2. The velocity varies vertically within this layer from zero at the surface to the undisturbed flow velocity at the edge of the layer. The boundary layer construct is an approximation to the truth, originally developed to simplify the analysis of airflow close to and far from the surface of airfoils. However, the results of a boundary layer analysis can be made as accurate as required. The flow regime within the layer is characterized by a boundary-layer Reynolds number, Re_x , computed as follows:

$$Re = \frac{\rho v z}{\mu}$$

where

Re_x	=	Reynolds number, dimensionless
ρ	=	Air density, kg.m ⁻³
z	=	Length along surface from leading edge, m
μ	=	Air viscosity, kg.m ⁻¹ .s ⁻¹

If the value of Re_x is less than about 10⁵, the flow in the layer will be laminar. Above this value, the flow will become turbulent. For the case of a 100 ft.min⁻¹ air stream flowing over a 2127 in² silk screen, the Reynolds number is about 4,000 and the flow regime is laminar. If a chemical is diffusing from the surface of the liquid pool, a concentration profile will develop that has the same shape as the velocity profile within the boundary layer. However, the diffusive boundary layer is thinner than the velocity boundary layer, meaning that, if one moves vertically away from the pool surface, the concentration will be found to reach zero before the air velocity has quite reached its free stream value. The thicknesses of the flow and mass transfer boundary layers are related by the Schmidt number, Sc :

$$Sc = \frac{\mu}{\rho D_{ab}}$$

which is the ratio of the diffusion rates for mass and momentum. The mass transfer boundary layer is thinner than the velocity boundary layer by a factor of $Sc^{1/3}$. The rate of mass transfer can be expressed in terms of another dimensionless group, the Sherwood number:

$$Sh = \frac{Fz}{cD_{ab}}$$

where:

- Sh = Sherwood number, dimensionless
 F = Mass flux, $\text{mol.m}^{-2}.\text{s}^{-1}$
 c = Concentration at the pool surface, mol.m^{-3}

Both experimentally and theoretically, these three dimensionless groups are found to be related as follows for the case of laminar flow over a surface (R.E. Treybal, *Mass-Transfer Operations*, 3rd ed., p.66; J.M. Coulson, *Chemical Engineering*, vol.1, 3rd ed., p.332):

$$\frac{Sh}{Re_x Sc^{1/3}} = \frac{0.332}{\sqrt{Re_x}}$$

This equation is analogous to the following equation for heat transfer:

$$\frac{N}{Re_x Pr^{1/3}} = \frac{0.332}{\sqrt{Re_x}}$$

where:

- Nu = Nusselt number, dimensionless heat transfer coefficient
 Pr = Prandtl number, ratio of heat and momentum diffusivities

The latter equation can be tested very simply by placing thermocouples in the airflow over a heated plate, thus providing additional validation for eq. (A-6). Equation (A-6) should work best for low rates of volatilization, where the mass flux does not affect the airflow and the latent heat of vaporization does not cause appreciable temperature changes in the liquid or air. This corresponds to the case of a low-vapor pressure chemical, which is often the case of greatest interest to CEB. According to eq. (A-6), the mass flux varies from place to place along the pool. The average value is:

$$\frac{N}{Re_x Pr^{1/3}} = \frac{0.664}{\sqrt{Re_x}}$$

In deriving Eq. (1), the author states that an analogy may be drawn to a derivation in §17.5 of Bird, Stewart, and Lightfoot's *Transport Phenomena*. However, in that example, the

chemical is being absorbed from the air into the boundary layer. The velocity at the outside edge of the boundary layer, where most of the absorption occurs, is practically the same as the free stream velocity. In the present case, most of the concentration gradient lies within a thin layer right next to the surface of the liquid pool, where the air velocity is very much lower than the free stream velocity.

Example 1. Estimate the vapor generation rate and worker exposure during removal of ink from a printing screen using 100% toluene. The worker cleans screens for 1 hour each day in a room with a ventilation rate of $3,000 \text{ ft}^3 \cdot \text{min}^{-1}$. The screen area is $2,217 \text{ in}^2$. Assume a mixing factor of $k = 0.5$.

Toluene has the following physical properties:

Molecular weight: $92.14 \text{ g} \cdot \text{mol}^{-1}$
 Vapor pressure: 28 mmHg at $25 \text{ }^\circ\text{C}$
 Diffusion coefficient: $0.076 \text{ cm}^2 \cdot \text{sec}^{-1}$

Using these values in eq. (1) gives:

Generation rate G : $0.28 \text{ g} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$
 Airborne concentration: 141 ppm (C_v)
 $534 \text{ mg} \cdot \text{m}^{-3}$ (C_m)
 Exposure over 1 hour: 667 mg

If the CEB worst-case parameters are used in eq. (2), i.e., a mixing factor of $k = 0.1$ and a ventilation rate of $500 \text{ ft}^3 \cdot \text{min}^{-1}$, then the estimated airborne concentration is $C_v = 4,216 \text{ ppm}$. Exposures and volatilization rates are calculated by multiplying the pure-component values from Table 1 by the mole fraction of that component in the liquid phase. A typical screen has an area of $2127 \text{ in}^2 = 1.37 \text{ m}^2$. Each worker cleans screens for 1 hour per day. Amounts released should be checked against amount used to ensure mass balance.

Example 2. Recalculate the vapor generation rate and worker exposure for Example 1 using the laminar boundary-layer model.

The results are:

$Re_x = 3662$
 $Sc = 21.35$
 $Sh = 111.5$

The concentration at the pool surface can be estimated from the vapor pressure of toluene, which is 28 mmHg :

$$c = \frac{28}{760} \times \frac{1}{24.45} \times 92.14$$

giving $c = 0.139 \text{ kg} \cdot \text{m}^{-3}$. Substituting into the expression for Sh gives

$$F = 0.0995 \text{ g} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$$

Using this vapor generation rate and an air flow rate of $8,000 \text{ ft}^3 \cdot \text{min}^{-1}$ gives:

$$\begin{aligned} C_v &= 19 \text{ ppm} \\ C_m &= 71 \text{ mg.m}^{-3} \end{aligned}$$

resulting in a total worker exposure of 88 mg.

If the calculations are repeated with the air velocity set to $v = 6.25 \text{ ft.min}^{-1}$, corresponding to a volumetric flowrate into an $8 \times 10 \times 10 \text{ ft}$ room of $500 \text{ ft}^3.\text{min}^{-1}$, the results are:

$$\begin{aligned} C_v &= 379 \text{ ppm} \\ C_m &= 1428 \text{ mg.m}^{-3} \end{aligned}$$

and the total worker exposure is 1785 mg.day^{-1} inhaled. This result more closely approximates the highest concentrations found by NIOSH in the field.

The CEB model was compared to the results of the PACE experiments and found to be in moderately good agreement. This is not surprising, because most of the PACE data was collected in the turbulent flow mode. In turbulent boundary layers, the velocity is almost equal to the free stream value everywhere except in a very thin layer adjacent to the pool surface. In this case the assumptions used in deriving eq. (1) are correct. In laminar boundary layers, this is not the case, and eq. (A-7) should, in principle, provide a better representation of the physical situation.