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OFFICE OF
RESEARCH AND DEVELOPMENT

SUBJECT: Estimation of Ambient Air Concentration at the Contaminated Harbor

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TO: Frank Ciavattieri
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Region I



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As we discussed in our meeting in March, please find enclosed a copy of a methodology which can be used to estimate ambient air concentrations at the harbor site where sediments are contaminated by organics. The methodology is based on the information currently available in the literature. Since we have not received the most recent monitoring data, a comparison between the predicted and measured values has not been made. When we receive the ambient air monitoring data from the New Bedford Harbor site, we will then be able to validate the models contained in the methodology.

To facilitate the use of the methodology, a brief illustrative problem dealing with PCB-contaminated sediments has been included. After the methodology is reviewed by your office and/or your contractor, we will be glad to discuss any questions you might have. You may wish to then incorporate the procedure as part of the risk assessment for the air pathway to assess both the no action alternative and future remedial actions. For any further information, you may contact Seong T. Hwang at FTS-475-8919 or myself at FTS-382-2588.

Attachment

cc: Seong T. Hwang (RD-689)
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Estimation of Ambient Air Quality Impacted by Emissions
from Sediment-Contaminated Water Body

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The sediment contaminated by organic compounds in the bottom of a water body including lake, river, estuary or harbor could be a source of ambient air contamination. The contaminant in sediment will slowly diffuse into the water body contaminating the water. Once the contaminant is in the water, the mass transfer process occurs causing the water-phase contaminant to volatilize into the atmosphere. The overall process of volatilization involves the three phases of mass transfer from sediment to water and then eventually to the atmosphere.

The rate of volatilization will be affected by various chemical and physical parameters which are site-specific and chemical-specific. Some of these parameters are vapor pressure, Henry's law constant, diffusion coefficients, thickness of diffusional resistance in sediment, and mass transfer coefficients. The contaminant emitted into the atmosphere will be dispersed by the winds and eventually reach the receptor population downwind of the water body. This writeup will present 1) a method of estimating the emission rate of the contaminant from a water body which is contaminated by bottom sediments because of transfer of the contaminant from the sediment to the water body; and 2) methods of estimating the ambient air concentrations being impacted by the emissions.

The two-resistance theory under the assumption of a steady-state emission rate provides the following formula for the emission rate:

$$q = \frac{k_e}{K_d} C_e \quad (1)$$

where q = the flux rate, $g/cm^2 \cdot s$; k_e = sediment-side mass transfer coefficient, cm/s ; K_d = partition coefficient between sediment and water, L/Kg ; and C_e = contaminant concentration in sediment, g/g . For derivation of this simplified equation, see the attachment.

The estimated emission rate can be substituted into dispersion equations for predicting the ambient air concentrations at a receptor location above the water surface or beyond the downwind edge of the water body. Different dispersion formula apply for the two situations. These dispersion equations are as follows.

1) Above the water surface

$$C = \sqrt{2 \pi} \frac{q \cdot x}{\sigma_z \bar{u}} \left[1 - \operatorname{erf} \left(\frac{z}{\sqrt{2} \sigma_z} \right) \right] \quad (2)$$

where C = ambient air concentration, g/cm^3 ; x = distance from the upwind edge of the contaminated water body, cm ; σ_z = standard deviation in the vertical direction, cm ; \bar{u} = wind speed, cm/s ; and z = the receptor height, cm .

2) Beyond the downwind edge of the contaminated water body. The ambient concentration at a receptor location beyond the boundary can not be estimated by Eq. (2) applicable for on-site concentrations. The ambient air concentration off-site of the water body can be estimated from

$$C = \frac{q \cdot a}{\sqrt{2 \pi} \bar{u} \sigma_z} e^{-\frac{1}{2} \left(\frac{z}{\sigma_z} \right)^2} \left[\operatorname{erf} \left(\frac{y + \frac{b}{2}}{\sqrt{2} \sigma_y} \right) - \operatorname{erf} \left(\frac{y - \frac{b}{2}}{\sqrt{2} \sigma_y} \right) \right]$$

where a = equivalent length of the contaminated water body parallel to the

wind direction, cm; b = equivalent length of the contaminated water body perpendicular to the wind direction, cm; y = distance measured perpendicular to the wind direction from the center line of the winds, cm; and σ_y = standard deviation in the lateral direction, cm.

The attachment also provides the derivation for the short-range dispersion equations. A paper presenting these equations is in press for publication in a peer-reviewed journal. No experimental data are available at present to validate these models.

It is recommended to use the following relationships for estimating lateral and vertical standard deviations:

° For stability C

$$\sigma_y = 0.35 x^{0.894}$$

$$\sigma_z = 0.17 x^{0.911}$$

where x is given in cm, and σ_y is also given in cm.

° For stability D

$$\sigma_y = 0.23 x^{0.894}$$

$$\sigma_z = 0.78 x^{0.725}$$

Example Calculation

Harbor water is contaminated by sediment containing 1000 ppm of PCBs. Henry's law constant for PCBs - 1254 is given as $8.37 \times 10^{-3} \text{ atm/m}^3 \text{ g mol}$ ($0.343 \text{ g/cm}^3 \text{ air/g/cm}^3 \text{ H}_2\text{O}$). The sediment side mass transfer coefficient is

$$k_e = 1 \times 10^{-6} \text{ cm}^2/\text{s} (0.5)^{4/3}/10 \text{ cm} \cong 4 \times 10^{-8} \text{ cm/s.}$$

where it is assumed that the porosity of sediment is 0.5 and the sediment thickness retarding the transfer of PCBs from sediment to water is 10 cm.

From Thibodeaux's Chemodynamics, the individual mass transfer coefficients can be obtained as follows:

° Air-side mass transfer coefficient

$$k_g = 3000 \text{ cm/hr} \left(\frac{18}{328.4} \right)^{1/2} = 692 \text{ cm/gr} \cong 0.2 \text{ cm/s}$$

where the molecular weight of Aroclor - 1254, 328.4, is used to correct the mass transfer coefficient from the value reported for water molecules.

° Water-side mass transfer coefficient

$$\begin{aligned} k_L &= 3 \text{ cm/hr} \left(\frac{44}{328.4} \right)^{1/2} \\ &= 1.1 \text{ cm/hr} \\ &\cong 0.0003 \text{ cm/s} \end{aligned}$$

The application of two-resistance theory will provide the overall mass transfer coefficient, K_{oL}

$$\frac{1}{K_{oL}} = \frac{1}{0.0003} + \frac{1}{(0.343)(0.2)}$$

or $K_{oL} = 0.0003 \text{ cm/s}$.

Assuming that the partition coefficient between sediment and water, K_d , is 1000 L/Kg. One can estimate the emission rate from the sediment-contaminated water body

$$q = 4 \times 10^{-8} \text{ cm/s} (1000 \times 10^{-6} \text{ g/g}) / 1000 \text{ cm}^3/\text{g} = 4 \times 10^{-14} \text{ g/cm}^2 \cdot \text{s}$$

The ambient air concentration at a point 2 m above the water surface located 800 m downwind from the upwind edge of the contaminated water body will be estimated under the assumption of stability D, and a wind speed of 470 cm/s.

$$\sigma_y = 0.23 (80000)^{0.894} = 5560 \text{ cm}$$

$$\sigma_z = 0.78 (80000)^{0.725} = 2800 \text{ cm}$$

Eq. (2) is used to estimate the concentration.

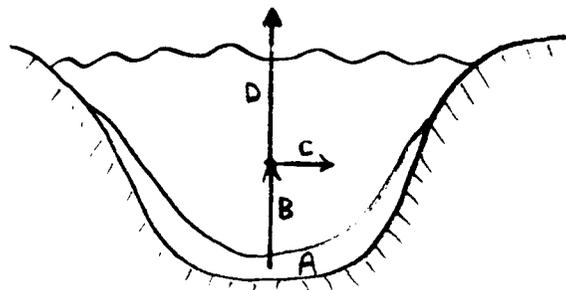
$$C = \frac{4 \times 10^{-14} (80000)}{\sqrt{2\pi} \cdot 2800 (470)} \left[1 - \operatorname{erf} \left(\frac{200}{\sqrt{2} \cdot 2800} \right) \right]$$

$$= 5.8 \times 10^{-15} \text{ g/cm}^3$$

$$= 0.006 \text{ ug/m}^3$$

Appendix A

Derivation of Steady-State Model Relating the Sediment and Water Concentration



The steady-state model assumes that the rate of mass transfer across sediment water interface is equal to the rate of escape by volatilization across the air-water interphase under the assumption of negligible disappearance by reaction in the water body.

A = B at sediment/water interface.

B = C + D

B: rate at which the contaminant leaves sediment/water interface

C: reaction

D: escaping rate by volatilization.

Nomenclature: C_e = conc. in sediment, mg/kg

k_w = water-side mass transfer coeff. above sed., cm/hr

K_{oL} = overall mass-transfer coefficient based on water side for air-water interface, cm/hr

k = reaction rate constant in water column, hr⁻¹

k_e = sediment side mass-transfer coeff., cm/hr

K_d = partition coefficient between sed. and water, L/Kg

C_w = conc. in water, mg/L.

A = mass transfer area, cm²

Subscript i = interface

V = volume of water body, cm³

h = V/A, cm

The rate of transfer across the sediment/water interface can be expressed by

$$k_e [C_e/K_d - C_w] A = k_w [C_{wi} - C_w] A$$

$$\frac{k_e C_e}{K_d} - k_e C_{wi} = k_w C_{wi} - k_w C_w$$

$$C_{wi} = [k_e \frac{C_e}{K_d} + C_w k_w] / (k_w + k_e) \quad (A-1)$$

Equation (A-1) provides the concentration at the sediment/water interface.

For $B = D + C$, the mass balance can be written as

$$k_w (C_{wi} - C_w) A = K_{oL} (C_w - o) A + k V C_w$$

or

$$C_{wi} = C_w [k_w + K_{oL} + h k] / k_w \quad (A-2)$$

Equate Eqs. (A-1) and (A-2) and solve for C_e .

$$\frac{\frac{k_e C_e}{K_d} + C_w k_w}{k_w + k_e} = \frac{C_w [k_w + K_{oL} + h k]}{k_w}$$

$$C_e = \frac{C_w [\quad]}{k_w} - C_w k_w \frac{K_d}{k_e}$$

or

$$C_w = \frac{1}{K_d} \frac{k_w k_e C_e}{(k_w + k_{oL} + h k) (k_w + k_e) - k_w^2} \quad (A-3)$$

Equation (A-3) is a desired result relating the sediment and water concentration under the steady-state condition.

Equation (A-3) can be further simplified by expanding its numerator, comparing the magnitude of each terms and ignoring the small terms. Then Equation (A-3) can be rewritten as

$$C_w = \frac{k_e}{K_{OL}} \frac{1}{K_d} C_e \quad (A-4)$$

The rate of atmospheric emissions from the contaminated water due to the release of contaminant in sediment into the water can be estimated from

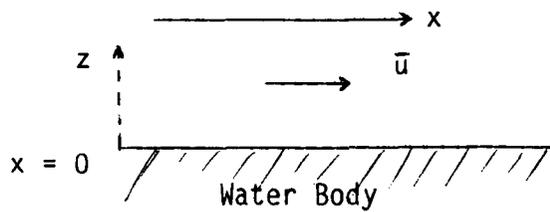
$$\begin{aligned} q &= K_{OL} C_w = K_{OL} \frac{k_e}{K_{OL}} \frac{1}{K_d} C_e \\ &= \frac{k_e}{K_d} C_e \end{aligned} \quad (A-5)$$

where the sediment-side mass transfer coefficient can be estimated from

$$k_e = D_w E^{4/3} / r \quad \text{cm/S} \quad (A-6)$$

with D_w = diffusion coefficient of contaminant in water, cm^2/S , E = porosity of the sediment, and r = thickness of the sediment, cm . (Use about 10 cm for default sediment thickness).

For a large water body, it can be shown that the ambient air concentration at a location above the water body under the turbulent atmospheric conditions can be represented by the following partial differential equation (Hwang: Environmental Progress, Vol 2, 1983, p. 81)



$$\frac{\partial c}{\partial t} = D_z \frac{\partial^2 c}{\partial z^2} \quad (1)$$

where $t = x / \bar{u}$

x : Distance from the upwind edge of the contaminated water body
 \bar{u} : Average wind speed
 c : Ambient air concentration
 D_z : Diffusion coefficient

Equation (1) should be solved with the following boundary conditions:

- 1) B.C. $c(t, \infty) = 0$
- 2) B.C. $c(0, z) = 0$
- 3) B.C. $D_z \frac{\partial c}{\partial z} = q$ at $z = 0$ at any t

where q = flux in mass per unit square area per unit time

Equation (1) can be conveniently solved with the following change of variables:

$$\eta = \left(\frac{1}{4 D_z t} \right)^{1/2} z \quad (2)$$

Then
$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial \eta} \frac{\partial \eta}{\partial t} \quad (3)$$

and

$$\begin{aligned} \frac{\partial^2 c}{\partial z^2} &= \frac{\partial}{\partial z} \left(\frac{\partial c}{\partial n} \cdot \frac{\partial n}{\partial z} \right) \\ &= \frac{\partial n}{\partial z} \frac{\partial}{\partial n} \left(\frac{\partial c}{\partial n} \cdot \frac{\partial n}{\partial z} \right) \\ &= \frac{\partial n}{\partial z} \left(\frac{\partial^2 c}{\partial n^2} \cdot \frac{\partial n}{\partial z} \right) \end{aligned} \quad (4)$$

Since

$$\frac{\partial n}{\partial z} = \left(\frac{1}{4D_z t} \right)^{1/2} \quad (5)$$

and

$$\frac{\partial n}{\partial t} = - \frac{1}{2t} \left(\frac{1}{4D_z t} \right)^{1/2} z \quad (6)$$

Substitution of Equations (5) and (6) into Equations (4) and (3), respectively, yields

$$\frac{\partial c}{\partial t} = - \frac{1}{2t} \left(\frac{1}{4D_z t} \right)^{1/2} z \frac{\partial c}{\partial n} \quad (7)$$

and

$$\frac{\partial^2 c}{\partial z^2} = \left(\frac{1}{4D_z t} \right) \frac{\partial^2 c}{\partial n^2} \quad (8)$$

Substitution of Equations (7) and (8) into Equation (1) and rearrangement give

$$-2 n \frac{dc}{dn} = \frac{d^2 c}{dn^2} \quad (9)$$

Also the boundary conditions change to

- 1) B.C. $c = 0$ at $n = \infty$
- 2) B.C. $c = 0$ at $n = \infty$
- 3) B.C. $D \frac{\partial c}{\partial z} = q$ at $n = 0$

The boundary conditions (1) and (2) are identical after the change of variables.

If we let $p = \frac{dc}{dn}$, then Equation (9) can be simplified to

$$-2 n p = \frac{dp}{dn} \quad (10)$$

Upon integrating Equation (10), one gets

$$p = Ae^{-n^2} \quad (11)$$

or $\frac{dc}{dn} = Ae^{-n^2} \quad (12)$

The boundary conditions (1) and (2) can be applied to Equation (12) as follows:

$$\int_c^0 dc = A \int_n^\infty e^{-n^2} dn \quad (13)$$

Equation (13) upon integration becomes

$$C = A \frac{\sqrt{\pi}}{2} (\operatorname{erf}(n) - 1) \quad (14)$$

To apply the boundary conditions (3), Equation (14) can be differentiated as follows:

$$\begin{aligned} \frac{\partial c}{\partial z} &= A \frac{\sqrt{\pi}}{2} \frac{2 \operatorname{erf}(\eta)}{\partial \eta} \frac{\partial \eta}{\partial z} \\ &= A \frac{\sqrt{\pi}}{2} \frac{2}{\sqrt{\pi}} e^{-\eta^2} \left(\frac{1}{4D_z t} \right)^{1/2} \end{aligned} \quad (15)$$

Applying the boundary condition (3), we get

$$\begin{aligned} -D_z \left. \frac{\partial c}{\partial z} \right|_{z=0} &= -D_z A E^{-0} \left(\frac{1}{4D_z t} \right)^{1/2} \\ &= q \end{aligned}$$

Hence, the integration coefficient A becomes

$$A = - \frac{q}{D_z} (4D_z t)^{1/2} \quad (16)$$

Substitution of Equation (16) into Equation (14) yields

$$C = - \frac{q}{D_z} (4D_z t)^{1/2} \frac{\sqrt{\pi}}{2} (\operatorname{erf}(\eta) - 1) \quad (17)$$

Now we make use of the expression for the diffusion coefficient related by

$$D_z = \sigma_z^2 \bar{u} / 2 x \quad (18)$$

where z = standard deviation in the vertical direction.

Substitution of Equation (18) into Equation (17) yields

$$C = \sqrt{2 \pi} \frac{q x}{z \bar{u}} \left[1 - \operatorname{erf} \left(\frac{z}{\sqrt{2} \sigma_z} \right) \right] \quad (19)$$