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MEMORANDUM

TO: John H. Ross, Senior Toxicologist
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FROM: Michael H. Dong, Staff Toxicologist **[Original signed by M Dong]**
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DATE: July 16, 1998

SUBJECT: REVIEW OF U.S. EPA'S SWIMODEL VALIDATION REPORT

The above draft report (EPA Contract No.68-W6-0030; Work Assignment No. 2-2, dated June 1998) represents a very comprehensive work in terms of model validation and in light of the limited data available. The Swimmer Exposure Assessment Model (SWIMODEL) was developed by U.S. EPA for use to estimate human exposures to toxic contaminants present in swimming pools. Following are the specific observations and comments on this report. Of these comments, the last one should be given special consideration during the draft's revision.

1. Versar, Inc., the contract company that was tasked to assist in the validation of this model, used the PBPK (physiologically-based pharmacokinetic) model rather intelligently. In this study, a two-step validation approach was used. First, available biomonitoring data from the literature were used to validate a PBPK model constructed for swimmer exposure to chloroform. Second, the dose rates and values from all six routes of entry that were estimated by SWIMDOEL were compared with those simulated by the PBPK model. The literature data used by Versar were extensive.

2. The dose values calculated by SWIMODEL exceeded those simulated by the PBPK model, but not more than by a factor of two.

3. As anticipated previously and was substantiated in this validation report, only minimal exposure (~ 5% of the total) would result via other routes (ingestion, aural, buccal/sublingual, orbital/nasal, etc.). At least for chloroform, the inhalation exposure pathway was found to be more important at higher ventilation rates associated with exercise, despite the observation that the dermal exposure pathway typically dominated the dose rates estimated by SWIMODEL.

4. Like many other exposure models, SWIMODEL calculates inhalation exposure from multiplying ambient concentration in air (C_{vp}) by inhalation rate. Where air concentrations from direct monitoring are not available or attainable, the model suggests that they be estimated by using either the Henry's law or the Raoult's law method. Versar's validation study showed that when compared to available literature data, the Henry's law method *over*estimated the ambient chloroform levels by 1 to 2 orders of magnitude, and that the Raoult's law method *under*estimated the chloroform levels by 1 to 2 orders of magnitude.

5. The Henry's law equation describes the ambient air concentration as the product of water concentration (C_w) and the unitless Henry's law constant (K_{aw}):

   $C_{vp} = C_w \times K_{aw}$.

   Versar used a K_{aw} of 0.2 to calculate the ambient chloroform air levels present inside indoor swimming pools. This unitless constant is consistent with those compiled by Verschueren (1996) and by Sander (1996). The reason for the overestimation is simply the fact that the constant used in the validation study was from C_{vp} based on laboratory observations whereas the literature C_{vp} values were measured in settings where the air exchange rates were relatively high. The overestimation may be warranted for exposure screening purposes.

6. According to the model, the Raoult's law equation likewise describes the ambient air concentration as the product of water concentration and a complex factor (F) which itself is a function of several constants and variables:

   $C_{vp} = C_w \times F$,

   where F is primarily a function of vapor pressure and temperature.

   For all practical purposes, this Raoult's law estimation equation is *useless* in that its underestimation of the ambient chloroform air levels was found to be nearly 2 orders of magnitude. The ambient air level estimated by this equation would almost certainly be underestimated by 1 or 2 orders of magnitude regardless of what the *practical* water concentration or the *practical* vapor pressure might be; that is, F is basically a constant since its vapor pressure- and temperature-dependent value will have no major impact on the prediction outcome.

7. Equations 10 and 11 in the validation report (p.25) showed that the ambient chloroform levels predicted by the Henry's law method and by the Raoult's law method differed by about 1,000-fold (by 863-fold, to be exact). However, the discussion on thermodynamic basis by Suntio *et al*. (1988) suggests that both estimation equations and the underlying parameters are interrelated. According to Suntio *et al*.,

   $P^o = (K_{aw} \text{ x } RT)/v$,

   where P^o is the vapor pressure of the pure chemical in liquid state (as discussed on p.24 of the validation report), *R* is the gas constant, *T* is the absolute temperature at which the vapor pressure is measured, and *v* is the molar volume of the solution having the typical value of $18 \text{ x } 10^{-6} \text{ m}^3/\text{mol}$ (i.e., that of water).

   In the validation study, the P^o value used by Versar was 243 mmHg, or 32,400 Pa. Yet from the above Suntio equation, the P^o value should have been $2.8 \text{ x } 10^7$ Pa [= (0.2) x (8.314 Pa m^3/mol K) x (303 K)/18 x 10^{-6} m^3/mol]. The value for the K_{aw}-based P^o is exactly 864 times greater than the value used by Versar.

   In short, if the K_{aw}-based P^o value (which ironically does not seem to be Raoult's law specific) were used in the Raoult's law equation, both the Henry's law method and the Raoult's law method would yield the same estimate for the ambient air concentration C_{vp}.

References

Verschueren K (1996). *Handbook of Environmental Data on Organic Chemicals*. New York: John Wiley & Sons.

Sander R (1996). *Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, Version 2 (November 4, 1996)*. Centre for Atmospheric Chemistry, York University, North York, Ontario, M3J 1P3, Canada (e-mail: sander@turing.sci.yorku.ca). Report downloaded from http://www.science.yorku.ca/cac/people/sander/res/henry.html.

Suntio LR, Shiu WY, Mackay D, Seiber JN, Glotfelty D (1988). Critical Review of Henry's Law Constants. *Reviews of Environ. Contam. Toxicol*. 103:1-59.