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September 25, 1984

Mr. Raymond A. Freeman
Mr. Jerry M. Schroy
MONSANTO COMPANY
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166

Dear Sirs:

When Dr. Farmer returned from his meeting with you last week, he gave me a copy of several draft publications which you have written concerning the mathematical simulation of dioxin volatilization.

I must confess that all of us (Spencer, Farmer and myself) were astonished to find that a compound with the physical-chemical characteristics of dioxin would volatilize to the extent predicted in your model. We therefore undertook to check the model assumptions, equations, and also reran isothermal simulations on our screening models.

I am afraid that I at least have become convinced that you have made a huge error in the formulation of your equations, which has the effect of allowing the chemical to diffuse in the vapor phase without a reduction in mobility due to adsorption. By sorting through your publications, I believe I have found the place in the derivation where this error occurred. My line of reasoning is as follows:

In the paper "Environmental mobility of dioxin" the Theory section begins on page 10 with a continuity equation for the gaseous concentration which is equivalent to the following:

$$\frac{\partial}{\partial t}\left[\varepsilon C_a + C_d\right] = \varepsilon h D_{ab} \frac{\partial^2 C_a}{\partial z^2} \qquad (1)$$

which is identical to your equation (1) where the expression for R in equation (2) is plugged into equation (1) and R_1 is deleted as it was in your paper.

(continued)

e quantity in brackets represents the total concentration of dioxin in
ss per volume of soil. The equation states that the time rate of
ange of this material is entirely due to the gradient of the vapor
ux which is essentially correct. There is a small error at this point
the formulation of the paper in that h is set equal to τ/ϵ and τ is
signed a value of 2. If τ is considered to be a tortuosity it should
duce the available vapor space compared to air. In fact, we use the
llington-Quirk model for the combined terms

$$\epsilon h\, D_{ab} = D_g^{soil} = \frac{a^{10/3}}{\epsilon^2} D_{ab} \qquad (2)$$

ere a is air content. This has the effect of reducing the gaseous
ffusion coefficients significantly compared to its value in free air,
rticularly when the soil is moist. Your model, if formulated with the
rameter values that are indicated in the back of the paper, would
tually increase this over its value in free space which is not
rrect.

wever, the principal error in the model formulation occurs when you
·gin with a rate limited expression for the concentration of chemical
the adsorbed phase

$$\frac{\partial}{\partial t} C_d = \alpha (C_a - K' C_d) \qquad (3)$$

ıere my parameters α and K' have replaced many of the symbols in your
ıper. Although you do not state it explicitly in your other paper, in
ıe paper "Modeling the tranport of 2,3,7,8-TCDD..." you state at the
ɔttom of page 5 that the vapor phase transport is so rapid that it
ways equilibrates with the adsorbed phase from which you set equation
3) equal to 0. However, this is equivalent to the assumption that

$$C_a = K' C_d \qquad (4)$$

ıd hence, that

$$\frac{\partial C_d}{\partial t} = \frac{1}{K'} \frac{\partial C_a}{\partial t} \qquad (5)$$

ıus, equation (1) should be modified by plugging in equation (5) and
ɔt by dropping the term involving C_d. Thus, instead of the equation at
ıe bottom of page 5 of the second paper, the equation should read

$$\frac{\partial C_a}{\partial t} = \frac{h D_{ab}}{(\epsilon + 1/K')} \frac{\partial^2 C_a}{\partial z^2} \equiv D_E \frac{\partial^2 C_a}{\partial z^2} \qquad (6)$$

(continued)

I don't know the status of this paper or of your work published in other areas. I do believe, however, that the information available for dioxin is so scarce that papers such as you have presented would have a significant influence on the thinking of scientists and non-scientists alike. I will be happy to talk with you in further detail about this if you are either uncertain about my reasoning or in disagreement with it. I would hope that we could resolve this before any mistaken information reaches the open literature.

Sincerely,

William A. Jury

William A. Jury
Professor of Soil Physics

WAJ:dem
cc: W. F. Spencer
W. J. Farmer