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Relationship Between the Evaporation Rate and Vapor Pressure of Moderately and Highly Volatile Chemicals

Ian van Wesenbeeck · Jeffrey Driver ·
John Ross

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Abstract Volatilization of chemicals can be an important form of dissipation in the environment. Rates of evaporative losses from plant and soil surfaces are useful for estimating the potential for food-related dietary residues and operator and bystander exposure, and can be used as source functions for screening models that predict off-site movement of volatile materials. A regression of evaporation on vapor pressure from three datasets containing 82 pesticidal active ingredients and co-formulants, ranging in vapor pressure from 0.0001 to >30,000 Pa was developed for this purpose with a regression correlation coefficient of 0.98.

Keywords Vapor pressure · Evaporation · Pesticide · Co-formulant

The evaporation rates of active and inert ingredients in agricultural products and residential consumer products are required in order to estimate exposures for the purpose of human dietary and residential risk assessment. The evaporation rate of an ingredient can be used to estimate the exposure of by-standers and can also be used to estimate the amount of residual material remaining on plants or other surfaces for the purpose of human or non-target species risk assessments. In the case of pest control products, inert ingredients are defined as components of the product that do not provide activity against a particular pest, but are required in the formulation as a carrier, solvent, surfactant, de-foaming agent, etc.

The evaporative flux of pesticides has been measured in the field using direct measurement techniques such as the aerodynamic method (Parmele et al. 1972; Majewski et al. 1989; Ross et al. 1990) or dynamic flux chambers (Gao et al. 1997; Yates 2006). Generally these studies involve significant logistical efforts and are costly to perform. Numerous researchers, however, have suggested that volatile losses from soil, crops, and aqueous systems can be estimated from physico-chemical parameters (Hamaker 1972; Burkhard and Guth 1981; Smit et al. 1998). Guth et al. (2004) reported the results of more than 190 experiments, which were carried out with 80 different crop protection chemicals under controlled conditions (laboratory and/or greenhouse). Their data analysis showed that physico-chemical parameters, such as vapor pressure (VP), Henry's law constant, water/air and soil/air distribution coefficients can be used to make reasonable predictions of volatile losses from crop and soil surfaces, and that VP was the best predictor of losses from soil and crops. Woodrow et al. (1997) developed a simple method for predicting pesticide emissions using correlations with VP. Using correlations of VP and measured emission rates from non-reactive surfaces (glass, plastic, and plants), Woodrow et al. (2001) developed a regression equation that predicts the emission rate (g m^{-2} h^{-1}) of a volatile chemical. Laboratory methods to determine the evaporation of liquids include the American Society for Testing and Materials (ASTM) method D3539-87 (ASTM 1987). Briefly, this

I. van Wesenbeeck (✉)
DowAgroSciences, LLC, 9330 Zionsville Road, Indianapolis,
IN 46268, USA
e-mail: ijvanwesenbeeck@dow.com

J. Driver
Infoscientific.com, Inc., 10009 Wisakon Trail, Manassas,
VA 20111, USA

J. Ross
Infoscientific.com, Inc., 5233 Marimoore Way, Carmichael,
CA 95608, USA

method enables the determination of evaporation loss relative to a standard (n-butyl acetate), and the time to 90% evaporation loss.

Materials and Methods

The ASTM method D3539-87 was conducted on a thin-film evaporometer and has been applied to a wide range of volatile liquids, including paints, solvents, and thinners, and insecticide spray-based oils (ASTM 1987). Basically the method involves adding a known volume of liquid on a known area of filter paper that was suspended from a balance in a cabinet. Dried air (0% relative humidity) at 25°C was passed through the cabinet at a known rate (approx 20 L/min). The change in weight of the filter paper was plotted against time so that a flux or a time to 90% evaporation can be determined. Typically the result was compared to the time for 90% evaporation of n-butyl acetate which was used as a standard. An ER can be calculated as (ASTM 1987):

$$\mathrm{ER} = \frac{(\mathrm{C} * \mathrm{D})}{(\mathrm{A} - \mathrm{B})}, \tag{1}$$

where ER = evaporation rate (g $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$);

$$\mathrm{C} = \frac{0.70 * 0.80}{128} = 0.00438\,\mathrm{mL\,cm}^{-2};$$

0.70 mL is the specimen size, 0.8 is the increment between 10% and 90% evaporation points, and 128 cm^2 is the total evaporating surface of a 90 mm diameter filter paper, D = specific gravity at 25°C, A = 90% evaporation time (s), and B = 10% evaporation time (s).

The ASTM method contains evaporometer results for over 50 compounds. The evaporometer data from 52 of these compounds were used in this analysis. The compounds chosen were based on the availability of vapor pressure (VP) data in the open literature (e.g., Material Safety Data Sheets, MSDS's). Since the ASTM method tests the evaporation under conditions of 0% relative humidity (RH), the results were corrected to account for an atmospheric condition of 50% RH. This value was chosen since the majority of the Guth volatility studies were conducted in the 30%–50% humidity range.

The relative humidity of the Woodrow experiments was not reported, but likely the experiments were conducted at ambient RH, and thus greater than 0%. Correction of the ER for RH was conducted using the CHEMCOMP program (proprietary software, service mark of the Dow Chemical Company, Guthrie 1988; Kalina 1987). The software program, developed for the paint and coatings industry, uses the latent heat of vaporization, vapor pressure, and molecular weight for a chemical and then calculates the % evaporation as a function of time at the temperature and relative humidity specified by the user, and thus the parameters A and B are easily obtainable for the purpose of a flux or emission rate calculation. On average the ASTM ERs were reduced by 12% when re-calculated with 50% RH. The vapor pressures and evaporation data for 52 products tested using the ASTM Evaporometer method constitute one dataset in this study. The natural log transformed (Ln) ER was linearly regressed against Ln VP.

Woodrow et al. (1997, 2001) developed a regression equation relating the emission rate (i.e., evaporative loss) of a compound from soil, water, or plant surfaces, to the VP of the compound. This was based on the fact that the volatility of an inert or active ingredient was defined primarily by its VP. Vapor pressure can be regarded as the underlying driving force leading to the emissions of residues deposited on plant surfaces (Woodrow et al. 2001) and furthermore can be assumed to act alone for a brief period after application so that residues volatilize from an essentially non-interactive surface (Woodrow et al. 1997). Woodrow further concluded that estimated evaporative fluxes did not vary significantly if measured literature values or modeled VPs were used. The regression equation for plant surfaces was based on 12 compounds (Beacon oil, Chevron oil, dodecane, n-octanol, tridiphane, trifluralin, pendimethalin, isooctyl 2,4-D, diazonin, toxaphene, dieldrin, and *p*,*p*′-DDT) exhibiting a range of VP from 6.6×10^{-4} to 200 Pa. Woodrow et al. (2001) found that their estimated fluxes were able to predict downwind concentrations of volatile pesticides quite well, suggesting confidence in the calculated emission rates. The compounds used in the Woodrow et al. study (not including *p*,*p*′-DDT) were used as a second dataset in this study. The Ln ER was linearly regressed against Ln VP (MINITAB v 12.21, State College, PA), resulting in a similar regression equation to that reported by Woodrow et al. (2001).

Guth et al. (2004) summarized volatilization data from 123 soil and 71 crop studies with 80 agricultural compounds conducted according to the Biologische Bundesanstalt fur Land Forstwirtschaft (Federal Biological Research Center for Agriculture and Forestry, BBA) guideline. Percent loss values observed during 24 h after application are reported for 123 soil and 71 crop volatility studies. They observed that generally, volatile losses from crop surfaces were found to be greater than from soil surfaces under comparable experimental conditions. Guth et al. (2004) reported mass loss of material in the first 24 h after application, but did not report actual emission or evaporation rates for their test compounds.

The actual compound names are not given in the Guth publication. Although all the compounds studied by Guth et al. (2004) were pesticides, the most volatile of which had a VP < 0.1 Pa, losses from crop surfaces within 24 h of application were as high as 80%. Guth et al. (2004) also conclude that volatilization of compounds with VPs $< 1 \times 10^{-4}$ Pa are unlikely to evaporate significantly in a 24-h-period, thus only compounds with VPs $> 1 \times 10^{-4}$ Pa were used in this analysis (n = 25). Since Guth et al. (2004) reported the percentage of applied material lost from foliage surfaces in a 24-h-period after application, an average ER over the 24-h-period was calculated as follows:

$$\mathrm{ER}\left(\mu\,\mathrm{g\,m^{-2}\,h^{-1}}\right) = \frac{\%\text{ mass lost in 24 h} * \text{application rate}\left(\mu\mathrm{g\,ha^{-1}}\right)}{10{,}000\,\mathrm{m^2\,ha^{-1}} * 24\,\mathrm{h}} \quad (2)$$

The Guth dataset also contained VP values (at either 20 or 25°C) for each compound which were Ln transformed and regressed with the calculated Ln transformed ERs similar to the other datasets. An analysis was conducted to determine if the three individual regression equations were co-linear (i.e., the same line). The co-linearity of the three separate regression lines was evaluated in a pooled data regression by assigning dummy variables ‘Za’ and ‘Zb’ to the ‘experiment type’ (i.e., for Woodrow, Za = 1 and Zb = 0, for Guth, Za = 0 and Zb = 1, and for ASTM, Za = 0 and Zb = 0) and evaluating the statistical significance of those interaction terms in the regression.

Results and Discussion

The objective of this study was to examine the relationships between the ER and VP of three independent datasets, the data presented by Guth et al. (2004), Woodrow et al. (1997, 2001), and data from selected compounds for which ASTM evaporometer data exists. The three datasets represent compounds that vary widely in their range of VP. The study by Guth et al. (2004) examined only pesticidal active ingredients and thus VP ranged from 8.7×10^{-10} to 1.7×10^{-2} Pa in their study. Guth observed that compounds with VP $< 1 \times 10^{-4}$ Pa did not significantly volatilize from plant surfaces in a 24-h-period and thus they were not included in this analysis. The compounds listed in the ASTM method include many solvents and other volatile compounds with VP ranging from 1 to >30,000 Pa (at 25°C). The Woodrow study, although it examined only 12 compounds, considered both pesticidal and non-pesticidal products with VPs ranging from 4.4×10^{-5} to 200 Pa. Given the widely differing ranges of compound VPs in the three datasets, a second objective of this study was to determine if the three datasets can be statistically combined into a single dataset to obtain a regression equation relating VP and ER.

The linear regression of the Ln (ER) on Ln (VP) for the ASTM data (n = 52) resulted in the following regression equation:

$$\mathrm{Ln}\,[\mathrm{ER}] = 12.7 + 0.865\,\mathrm{Ln}\,(\mathrm{VP}) \qquad \left(r^2 = 0.93\right) \quad (3)$$

A linear regression of Ln (ER) versus Ln (VP) for the crop data for pesticides with VPs greater than 1×10^{-4} Pa in Guth et al. (2004) results in the following regression equation (n = 25):

$$\mathrm{Ln}\,[\mathrm{ER}] = 12.0 + 0.899\,\mathrm{Ln}\,(\mathrm{VP}) \qquad \left(r^2 = 0.44\right) \quad (4)$$

The co-efficients in both the above relationships are remarkably similar considering the high VPs in the ASTM dataset and the relatively lower VPs in the Guth dataset, with no overlap in VP’s between the two datasets. The regression equation given by Woodrow et al. (2001), where the VPs ranged from 6.6×10^{-4} to 2×10^{2} Pa is as follows:

$$\mathrm{Ln}\,[\mathrm{ER}] = 11.81 + 0.8596 * \mathrm{Ln}\,(\mathrm{VP}) \qquad \left(r^2 = 0.99\right) \quad (5)$$

Once again, the regression co-efficients are remarkably similar to both the Guth and ASTM datasets. The data from Guth et al. (2004), Woodrow et al. (1997), and the ASTM (1987) method can be combined to develop a single regression equation relating VP and ER as shown below:

$$\mathrm{Ln}\,[\mathrm{ER}] = 12.2 + 0.933\,\mathrm{Ln}\,(\mathrm{VP}) \qquad \left(r^2 = 0.98\right) \quad (6)$$

The co-linearity of the three separate regression lines can be evaluated in pooled data regression by assigning dummy variables ‘Za’ and ‘Zb’ to the ‘experiment type’ (i.e., for Woodrow, Za = 1 and Zb = 0, for Guth, Za = 0 and Zb = 1, and for ASTM, Za = 0 and Zb = 0) and evaluating the statistical significance of those interaction terms in the regression. The resulting regression equation (n = 89) is:

$$\mathrm{Ln}\,[\mathrm{ER}] = 12.7 + 0.865\,\mathrm{Ln}\,(\mathrm{VP}) - 0.754\,\mathrm{Za} - 0.937\,\mathrm{Zb} + 0.034\,\mathrm{VP} * \mathrm{Za} + 0.0141\,\mathrm{VP} * \mathrm{ZB} \quad (7)$$

The *p*-statistic for all the dummy variables and interaction terms (Za, Zb, VP * Za, and Vp * Zb) are $p > 0.1$ indicating they are not statistically significant. Thus the null hypothesis, that the lines are co-linear, cannot be rejected, and Eq. 6 can be used as a regression for all of the data. Figure 1 shows the regression (Eq. 6) with the 95% prediction bands which predict the confidence limits for an individual estimate.

Limitations of the method include variability in the relative humidity of the experiments which were used to obtain the regression. Although humidity affects ER (e.g., a 12% reduction on average for the 52 ASTM compounds when corrected for 50% RH) it would only be critical to correct for this in a higher tier assessment. Also, although

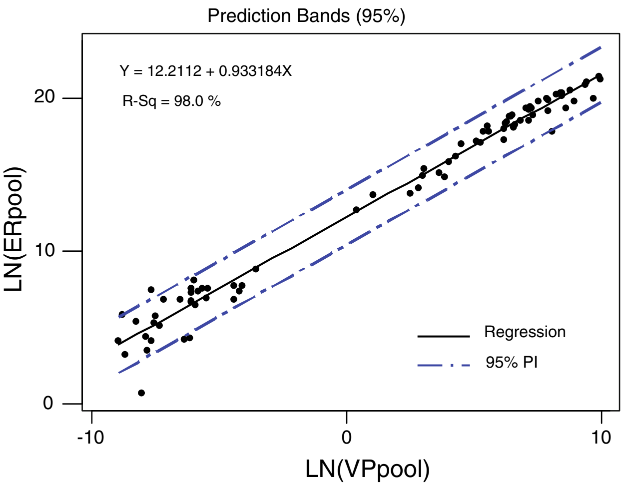

Fig. 1 Regression of pooled data from Guth, ASTM, and Woodrow showing 95% prediction bands

the assumption was that volatility acts alone for a short period of time after contact and thus there was no interaction with the surface, this may not be the case for all compounds used in the analysis. Degradation, sorption, and other potential dissipation processes are not taken into account, and thus the ER of lower VP compounds may be overpredicted with this equation, necessitating accounting for the impact of these processes for these compounds. The effect of mixtures was not taken into account, and compounds are assumed to act independently, although it is well known that co-volatilization can increase ER (Lalah et al. 1996), while increased solute concentration can decrease ER. It should be noted, however, that the compounds used in the Guth et al. study were formulated products and thus the ERs estimated from that study include the effect of co-formulants, which could explain the lower R^2 in the VP/ER relationship in that study. Estimates of ER based on VP using this regression approach can have up to an order of magnitude error, thus these estimates should be used primarily for screening purposes. Higher tier assessments would require actual ER measurements in the matrix of interest, including the effect of degradation, co-volatilization, and sorption processes.

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