

## Direct Measurement of Henry's Constant for *S*-Ethyl *N,N*-Di-*n*-propylthiocarbamate

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Many pesticides are susceptible to volatilization, which may result in decreased pest control and off-site deposition that may cause adverse environmental impacts. Prediction of such losses requires knowledge of pesticide partition coefficients, including Henry's constant ( $H_c$ ); however accurate data are lacking. In this experiment, the batch air stripping technique was used to determine  $H_c$  for EPTC (*S*-ethyl *N,N*-di-*n*-propylthiocarbamate). At 25 °C, measured  $H_c$  in pure water was 0.0107, 11 times greater than indirectly estimated values reported in the literature. The measured heat of volatilization for EPTC, used to describe the temperature dependence of  $H_c$ , was 37.12 kJ mol<sup>-1</sup>.  $H_c$  measured with soil extract was 7 times greater than that measured in pure water, presumably due to effects of dissolved salts and organic acids.

**Keywords:** EPTC; Henry's law constant; volatilization; soil solution

### INTRODUCTION

Movement of pesticides in the environment has become a major concern as their usage in agriculture has increased. Liquid-phase movement into ground and surface waters has received most of the attention, but gas-phase transport can also be an important pathway for loss of some agricultural pesticides. This can result in diminished efficiency and off-site pollution.

Prediction of movement in either the liquid or gas phase requires knowledge of how the chemical partitions between gas, liquid, and sorbed phases. The relationship between liquid- and gas-phase concentrations is described by Henry's law, eq 1, where  $P_i$  is the partial

$$P_i = H_c x_i \quad (1)$$

pressure of component  $i$  in the gas phase,  $H_c$  is the Henry's constant for solute  $i$ , and  $x_i$  is the mole fraction of component  $i$  in the liquid. We experimentally determined  $H_c$  for the chemical EPTC, a preemergent herbicide of the carbamothioate family that is widely used on several crops, most predominantly corn (*Zea mays* L.). It is the most heavily used herbicide in Minnesota (Gianessi and Puffer, 1991), and it is one of the most volatile herbicides in use today.

Henry's constant is related to the heat of volatilization,  $\Delta H_{\text{vol}}^{\text{P}}$ , via the van't Hoff equation:

$$H_c = \exp\left(-\frac{\Delta H_{\text{vol}}^{\text{P}}}{RT} + C\right) \quad (2)$$

where  $R$  is the universal gas constant,  $T$  is the temperature in kelvin, and  $C$  is a constant. Thus,  $H_c$  is temperature dependent, an important consideration for pesticides applied to bare soil surfaces that may be subject to diurnal temperature variations as great as 40 °C. In principle it is sufficient to measure  $H_c$  at a

single temperature if  $\Delta H_{\text{vol}}^{\text{P}}$  can be computed from tabled values of the heats of solution,  $\Delta H_{\text{sol}}^{\text{P}}$ , and vaporization,  $\Delta H_{\text{vap}}^{\text{P}}$ :

$$\Delta H_{\text{vol}}^{\text{P}} = \Delta H_{\text{vap}}^{\text{P}} - \Delta H_{\text{sol}}^{\text{P}} \quad (3)$$

In practice,  $\Delta H_{\text{sol}}^{\text{P}}$  and  $\Delta H_{\text{vap}}^{\text{P}}$  for pesticides are often known only to within an order of magnitude, if at all. Hence, it is useful to measure  $H_c$  at several temperatures to allow explicit solution of eq 2. Unfortunately, measured  $H_c$  values for pesticides are rare, so indirect estimates are often used for modeling purposes. The most common approach is to simply divide the saturation vapor pressure of the compound by its solubility (Suntio et al., 1988)

$$H_c = P_i^{\text{s}}/C_i^{\text{s}} \quad (4)$$

However, this assumes a single  $H_c$  value is valid over the entire range from infinite dilution to the solubility limit, which has not been demonstrated. A more practical problem with this approach is the lack of reliable, reproducible vapor pressure data for pesticides. As an example, reported saturation vapor pressures for EPTC at 25 °C range from 3.20 Pa (Wauchope et al., 1992) to 66.7 Pa (Spencer, 1976). A comprehensive list of saturation vapor pressure and solubility values can be found in Breiter (1995).

As an alternative to indirect estimation, there are a number of methods that have been used to directly measure  $H_c$ . These include both static and dynamic equilibration methods. Static equilibration (McAullife, 1971; Gossett, 1987; Robbins et al., 1993) is based upon the chemical equilibrium (i.e. partitioning) of a compound between a volume of water and the gas above it, in a sealed container. This technique is only sensitive for compounds with relatively high  $H_c$  ( $H_c > 0.1$ ) (Fendinger and Glotfelty, 1988; Betterton, 1992).

Dynamic equilibration methods (Fendinger and Glotfelty, 1988; Fendinger et al., 1989; Mackay et al., 1979)

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are based upon the measurement of relative changes in concentration within one phase, while effecting a near-equilibrium exchange with the other phase. These are more sensitive than static equilibration methods because the measurement is based upon a relative concentration change in the more easily measured phase, typically the liquid phase (Fendinger and Glotfelty, 1988).

Mackay et al. (1979) introduced a dynamic equilibration technique known as the batch air stripping or gas purging method. With this technique, the removal of the solute from an aqueous solution by a purge gas over a finite time is measured. The total mass of the solute,  $M$ , over this time period can be expressed as

$$M = \int_0^t F(t) dt + V_l C_l \quad (5)$$

where  $F(t)$  is the flux at time  $t$  of the solute from the solution,  $C_l$  is the concentration of the solute in the liquid phase at time  $t$ , and  $V_l$  is the volume of the liquid phase. Taking the derivative of eq 5 with respect to  $t$ , an expression for  $F(t)$  is obtained,

$$F(t) = -V_l(dC_l/dt) \quad (6)$$

$F(t)$  can also be expressed in terms of the gas phase as

$$F(t) = C_g f_g \quad (7)$$

where  $C_g$  is the concentration of solute in the gas phase and  $f_g$  is the flow rate of the purge gas ( $\text{m}^3 \text{min}^{-1}$ ). Incorporating the universal gas law,

$$C_g = P_g/RT \quad (8)$$

Equation 7 can be rewritten as

$$F(t) = P_g f_g/RT \quad (9)$$

Recalling that

$$P_g = H_c C_l \quad (10)$$

$F(t)$  can be expressed as

$$F(t) = H_c C_l f_g/RT \quad (11)$$

This eliminates the need for a measurement of  $P_g$ , so only the liquid-phase concentration needs to be measured. Equating eqs 6 and 11 and integrating with respect to  $t$ ,

$$\int_{C_0}^{C_l} \frac{dC_l}{C_l} = -\frac{H_c f_g}{V_l RT} \int_0^t dt \quad (12)$$

gives the final form of the equation as found in Mackay et al. (1979):

$$\ln(C_l/C_0) = -(H_c f_g/V_l RT)t \quad (13)$$

Unless the column is infinitely large or the amount of sample removed is infinitely small, the volume of the liquid phase will not remain constant, so eq 13 is not valid. Therefore, Gossett (1983) modified eq 13 to account for this volume loss by measuring the volume of the liquid phase during the  $i$ th time interval,  $V_i$ . Using eq 14,

$$\ln\left(\frac{C_i}{C_0}\right) = -\left(\frac{H_c f_g}{RT}\right) \sum_{j=1}^i \left(\frac{\Delta t_j}{V_j}\right) \quad (14)$$

where  $\Delta t_i$  is the amount of time of the  $i$ th interval (min);  $H_c$  can then be calculated from the slope of a graph of  $\ln(C_i/C_0)$  versus  $\sum(\Delta t_i/V_i)$

$$H_c = -\frac{(\text{slope})RT}{f_g} \quad (15)$$

and a dimensionless  $H_c$  can be calculated from the following expression

$$H_c = -\frac{\text{slope}}{f_g} \quad (16)$$

Equation 13 can also be derived from the basic mass transfer equations of the Lewis and Whitman (1924) two-film theory. This derivation can be found in Munz (1985).

While the effect of temperature on  $H_c$  is well-documented, the effect of soil components (soluble salts and organic matter) in solution is poorly understood. As a general rule gases are less soluble, i.e., higher  $H_c$ , in aqueous solutions of electrolytes (Glasstone, 1940). This is commonly known as the salting-out effect. This effect has been attributed to the congregation of dipolar molecules of a polarizable solvent around the ions of the added electrolyte. The resultant effective Henry's law constant,  $H_c^*$ , is given by

$$H_c^* = \gamma^* H_c \quad (17)$$

where  $\gamma^*$  is an activity coefficient. The effect of soluble salts on  $\gamma^*$  can be determined from the following equation

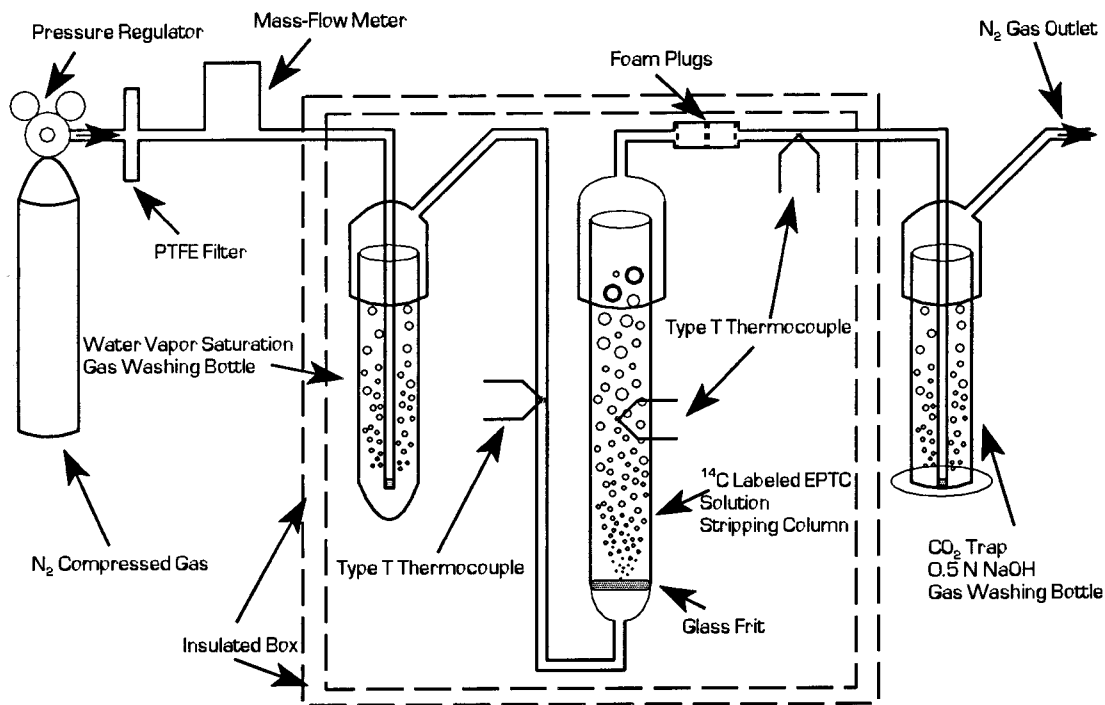
$$\log(\gamma^*) = \sum_{q=1}^Q h_q I_q \quad (18)$$

where  $h_q$  is the Setchenow constant (Setchenow, 1892) attributable to electrolyte species  $q$ ,  $I_q$  is the ionic strength attributable to electrolyte species  $q$ , and  $Q$  is the number of soluble salts present. In practice, the lack of reliable and reproducible values of  $h_q$  for electrolytes found in soil solution and the lack of information concerning the effect of organic matter preclude use of eqs 17 and 18 for estimating  $H_c$ .

## MATERIALS AND METHODS

The experimental apparatus used in this work is shown in Figure 1. The system consists of a nitrogen cylinder, particle filter, mass flow meter, gas washing bottle, a stripping vessel, and a  $\text{CO}_2$  trap. All tubing is Teflon with Swagelok fittings. EPTC is removed from the liquid phase by nitrogen gas bubbles, and the concentration of EPTC in the liquid phase is measured periodically to determine the loss of pesticide to the gas phase. EPTC lost in this way is sorbed onto foam plugs, which are subsequently analyzed to allow for mass balance.

A 1.00 L stock solution of EPTC (99.0% pure; Chem Service, West Chester, PA), having a concentration of  $5.00 \text{ mg L}^{-1}$ , was prepared using deionized water. Then 1.00 mL of solution was removed and replaced with 1.00 mL of  $^{14}\text{C}$ -carbonyl-labeled EPTC ( $8.25 \text{ mg L}^{-1}$  and  $16.13 \text{ MBq L}^{-1}$ ) to create a  $16.13 \text{ kBq L}^{-1}$  solution. These experimental solutions were tightly covered and stored at  $4^\circ\text{C}$  when not in use. A 0.50 N NaOH solution was prepared by adding 45.0 g of NaOH pellets (98.5%



**Figure 1.** Apparatus for measurement of  $H_c$  of EPTC. Nitrogen gas bubbled through the solution becomes saturated with respect to EPTC, in the process decreasing the liquid-phase concentration. Nitrogen gas flows from the left side of the diagram to the right side of the diagram.

pure; Fisher Chemical, Fisher Scientific, Lawn Park, NJ) to 2.25 L of deionized water.

The column was filled with 120 mL of the EPTC solution and allowed to thermally equilibrate overnight prior to the start of each experimental run. Nitrogen gas,  $N_2$ , used to remove EPTC from liquid solution at a flow rate of 100–200  $mL\ min^{-1}$ , was filtered through a PTFE filter (ACRO 50, 1.0  $\mu m$ , Gelman Sciences, Ann Arbor, MI). The gas flow rate was measured using an Omega FMA-217 mass flow meter (Omega Engineering, Inc., Stamford, CT). The  $N_2$  gas was saturated with water and brought to temperature equilibrium by passing it through a gas washing bottle filled with distilled, deionized water and then introduced into the stripping column through a glass frit to purge the EPTC solution. This column, 45 cm long with an inner diameter of 2 cm, has a sampling port located 2 cm above the glass frit. A glass column was used since EPTC does not adsorb to glass (Sharom and Soloman, 1981). After exiting the column,  $N_2$  gas in equilibrium with EPTC was passed through two expanded polyether foam plugs (Indenti-Plugs, Jaece Industries, Inc., North Tonawanda, NY) and a  $CO_2$  trap. The  $CO_2$  trap, a 250 mL gas washing bottle filled with 250.0 mL of 0.50 N NaOH, was used to trap  $^{14}C$  which might have mineralized from EPTC.

To determine the change in concentration of EPTC in the liquid phase at time  $t$ , at least 2 mL of solution was taken every 3–15 min, depending on the temperature. Temperature and  $H_c$  are directly proportional, so at higher temperatures EPTC is removed more rapidly, necessitating shorter sampling intervals. Before each sample was collected, approximately 0.5 mL of solution was collected into a waste vial to clear the sampling port of the previous sample solution. At the conclusion of each experiment, 2.00 mL of each sample was transferred by pipet into 7 mL scintillation vials containing 5.0 mL of Ecolite scintillation cocktail (Research Products Division, ICN Biomedicals, Costa Mesa, CA). Concentrations in disintegrations per minute, DPM, were counted using a Packard Tri-Carb 1500 scintillation counter with DPM option (Packard Instrument Co., Meriden, CT). Each sample was counted for 10 min. A 1.00 mL aliquot of the NaOH solution was transferred to a 7 mL scintillation vial containing 5.0 mL of scintillation cocktail and counted as previously discussed.

To determine the effects of ionic strength and organic matter on  $H_c$ , EPTC was added to a soil solution from the upper 2 cm

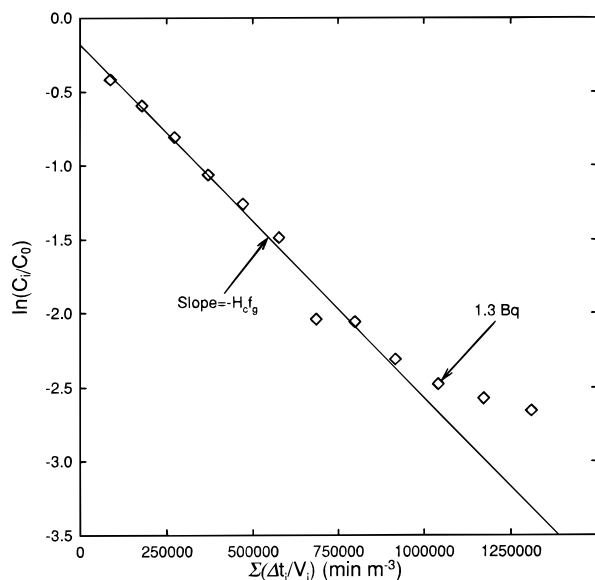
**Table 1.** Total Alkalinity ( $HCO_3^-$ ), Nitrate Concentration ( $NO_3^-$ ), pH, Ionic Strength ( $I$ ), EC Corrected to 25 °C, and Organic Carbon for Soil Extracts of Varying Gravimetric Water Content ( $w$ )

| $w$   | $HCO_3^-$ ,<br>$mol\ L^{-1}$ | $NO_3^-$ ,<br>$mol\ L^{-1}$ | pH    | $I$ , $mol(+)$<br>$L^{-1}$ | $EC_{25\ ^\circ C}$ ,<br>$dS\ m^{-1}$ | organic C,<br>$mg\ L^{-1}$ |
|-------|------------------------------|-----------------------------|-------|----------------------------|---------------------------------------|----------------------------|
| 0.512 | 51.14                        | 53.1                        | 7.420 | 0.00930                    | 0.5807                                | 227.6                      |
| 0.247 | 102.0                        | 108.2                       | 7.178 | 0.0204                     | 1.284                                 | 425.2                      |
| 0.124 | 204.0                        | 215.3                       | 6.906 | 0.0391                     | 2.329                                 | 874.0                      |
| 0.062 | 405.5                        | 427.4                       | 6.960 | 0.0777                     | 4.449                                 | 1787                       |

of a Waukegan silt loam (fine-silty over sandy or sandy skeletal, mixed, mesic Typic Hapludoll) that has an organic carbon content of approximately 2.4%. The soil was oven-dried at 35 °C to allow precise determination of the gravimetric water content,  $w$ , of the saturated paste to be created. The saturated paste was made using the procedure of Rhodes (1982), except that the paste was allowed to stand at least 30 min to allow the soil solution to reach equilibrium with the soil colloids. A 500.0 mL soil extract of a saturated paste having a  $w = 0.519$  was stored in an amber bottle at 4 °C. The rest of the soil extract was heated to evaporate the water until the equivalent of a saturated paste having a  $w = 0.247$  was reached. Again 500.0 mL of soil solution were stored in an amber bottle at 4 °C.

Organic and inorganic C in solution were measured, in milligrams per liter, with a Dohrmann DC-80 carbon analyzer (Xertex Corp., Santa Clara, CA). Total soil ion concentrations were measured with an ARL Model 3560 ICP-AES with simultaneous detection (Fissons, Danver, MA) using plant and water standards, and the  $NO_3^-$  concentration, in moles per liter, was measured with an Alpkem Rapid Flow Analyzer (Perstorp, Silver Spring, MD) set to measure the  $NO_3^-$  concentration using a cadmium coil for reduction to  $NO_2^-$  and a directly proportional color reagent at the Research Analytical Laboratory of the University of Minnesota. Solution pH was determined using an Orion Research Digital Ionalyzer (Model 601A). The free ion concentration was calculated from the above data using the SPECIES program of Barak (1990). The results for each of the solutions are found in Table 1.

A 0.40 L aliquot of a 5.00  $mg\ L^{-1}$  EPTC soil solution was prepared, using the extract of a soil paste having a  $w = 0.247$ .



**Figure 2.** Scatter plot of  $\ln(C_i/C_0)$  as a function of  $\Sigma(\Delta t_i/V_i)$ . This experiment yielded a  $H_c$  of 0.0125, determined using the slope, at 27.76 °C with a flow rate of 191.0 mL  $\text{min}^{-1}$ .

This soil solution was spiked with  $^{14}\text{C}$  by removing 80.0  $\mu\text{L}$  of solution and replacing it with 80.0  $\mu\text{L}$  of  $^{14}\text{C}$ -carbonyl-labeled EPTC solution (49.03  $\text{mg L}^{-1}$  and 95.8  $\text{MBq L}^{-1}$ ) creating a 19.2  $\text{kBq L}^{-1}$  solution. The column was filled with 90 mL of this EPTC soil solution and allowed to temperature equilibrate overnight.

The experimental temperature was about 28 °C. The flow rate was set at about 100  $\text{mL min}^{-1}$ . To determine the concentration of EPTC left in the liquid phase at time  $t$ , at least 1 mL of solution was taken every 3 min. At the conclusion of each experiment, 1.00 mL of each of the samples was transferred, by pipet, into 7 mL scintillation vials containing 5.0 mL of Ecolite scintillation cocktail. The other experimental steps were executed as previously discussed.

To prevent loss of EPTC and to allow mass balance, two expanded polyether foam plugs were placed on the outlet side of the stripping column. After each experimental run, the first plug was cut into four equal pieces. Each piece was placed into its own 20 mL scintillation vial and sealed. The second plug was cut into three equal pieces and stored the same way. To determine the amount of EPTC transferred to the instruments used in handling the foam plugs, they were wiped down with a Kimwipe (Kimberly-Clark Corp., Neenah, WI) and methanol, and the Kimwipe was placed in a 20 mL scintillation vial for analysis. The EPTC recovered on each piece of foam plug was determined using a Packard Tri-Carb B306 oxidizer (Packard Instrument Co.). The scintillation cocktail was made up of 6 mL of Packard Carbo-Sorb  $\text{CO}_2$  absorber for scintillation cocktail (Canberra) and 14 mL of Packard Permafluor V complete scintillation cocktail (Canberra). The concentration of  $^{14}\text{C}$  in all of these vials was measured using a scintillation counter, as previously discussed.

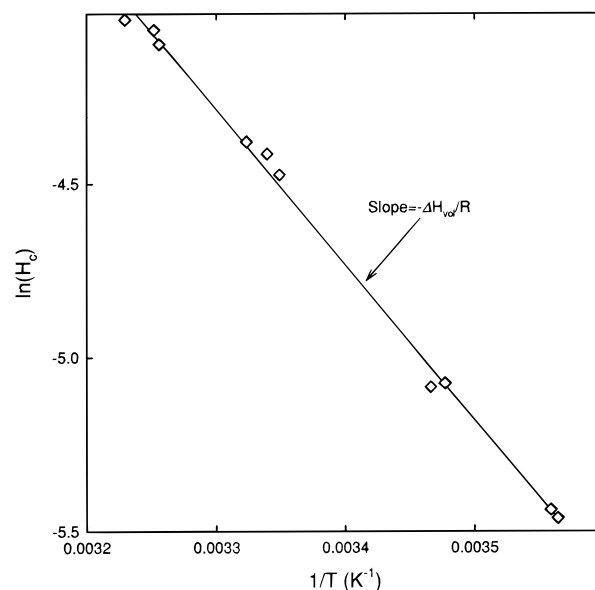
## RESULTS AND DISCUSSION

**Calculation of  $H_c$ .** An example of the procedure for calculating  $H_c$  is shown in Figure 2. The data shown were obtained at a temperature of 27.76 °C, found in Table 2, and they are typical of most runs.  $H_c$  was calculated using the slope of a plot of  $\ln(C_i/C_0)$  as a function of  $\Sigma(\Delta t_i/V_i)$  (eq 14). Samples (data points) having radioactivity < 1.7 Bq ( $2 \times$  background) were not used in the calculation of  $H_c$ .

**Temperature Dependence of  $H_c$  in Deionized Water.** The temperature,  $T$  (°C), and  $H_c$  values for each experimental run are listed in Table 2. The inverse of

**Table 2.**  $H_c$  and the  $r^2$ -Value of the Regression Line Used To Calculate  $H_c$ , also Flow Rate, Average Purge Height, Percent of Mineralized Carbon (% $\text{CO}_2$ ), and Mass Balance for Experiments Conducted Using Deionized Water over a Range of Temperatures

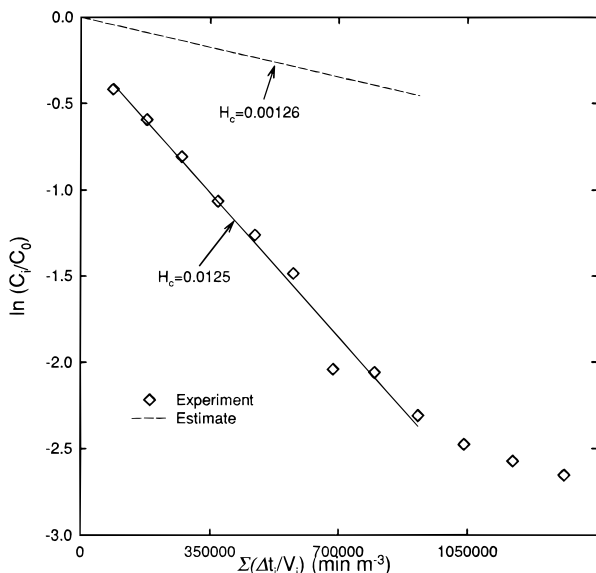
| temp, °C     | $H_c$    | $r^2$ | flow rate, $\text{mL min}^{-1}$ | purge height, cm | % $\text{CO}_2$ | mass balance, % |
|--------------|----------|-------|---------------------------------|------------------|-----------------|-----------------|
| 7.46 ± 0.30  | 0.004 24 | 0.990 | 172.7 ± 5.2                     | 27.26            | 0.117           | 78.34           |
| 7.89 ± 0.04  | 0.004 34 | 0.994 | 174.5 ± 2.3                     | 26.58            | 0.569           | 92.64           |
| 14.43 ± 0.14 | 0.006 25 | 0.984 | 216.0 ± 9.1                     | 22.56            | 0.0044          | 75.78           |
| 15.34 ± 0.04 | 0.006 19 | 0.992 | 188.5 ± 5.4                     | 25.34            | 0.0             | 85.57           |
| 25.47 ± 0.41 | 0.011 4  | 0.970 | 185.9 ± 4.9                     | 25.73            | 0.0             | 25.21           |
| 26.32 ± 0.45 | 0.012 1  | 0.980 | 221.0 ± 3.7                     | 26.59            | 0.231           | 31.81           |
| 27.76 ± 0.05 | 0.012 5  | 0.983 | 191.0 ± 22.4                    | 25.28            | 0.658           | 73.54           |
| 34.00 ± 0.24 | 0.016 6  | 0.998 | 100.8 ± 2.6                     | 25.03            | 1.730           | 100.99          |
| 34.39 ± 0.09 | 0.017 3  | 0.987 | 110.2 ± 5.8                     | 27.18            | 0.960           | 101.72          |
| 36.49 ± 0.14 | 0.017 8  | 0.998 | 179.5 ± 8.2                     | 29.04            | 0.0             | 94.70           |



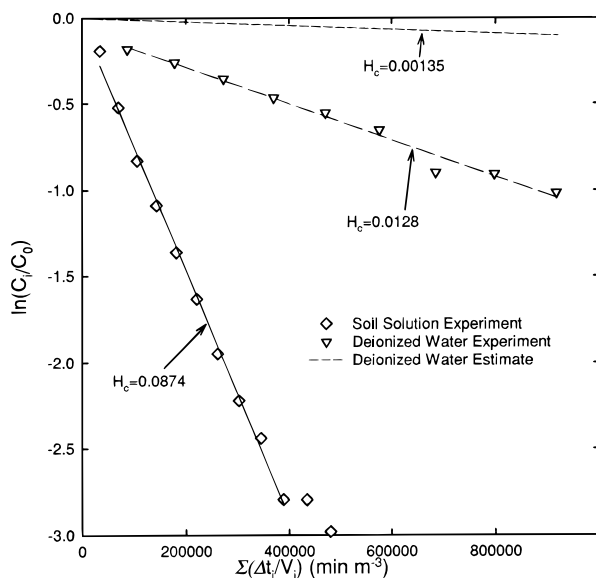
**Figure 3.** Determination of  $\Delta H_{\text{vol}}^{\circ}$  for EPTC using the slope.

the absolute temperature,  $1/T$  ( $\text{K}^{-1}$ ), and the natural log of  $H_c$ ,  $\ln(H_c)$ , values are plotted in Figure 3. The slope of this plot is  $-\Delta H_{\text{vol}}^{\circ}/R$ , where  $\Delta H_{\text{vol}}^{\circ}$  is the heat of volatilization and  $R$  is the universal gas constant. The data yield an estimated  $\Delta H_{\text{vol}}^{\circ} = 37.12 \text{ kJ mol}^{-1}$  for EPTC. Using this value in the van't Hoff equation for equilibrium dependencies produces an estimated  $H_c$  at standard temperature (25 °C) of 0.0107. This is more than 11 times greater than the indirect estimate of  $H_c$ , 0.000 950, produced by dividing the accepted saturation vapor pressure of 4.67 Pa (Patchett et al., 1964) by the reported solubility of 375  $\text{mg L}^{-1}$  (Freed et al., 1962), at 25 °C, as shown in Figure 4. Cliath (1978), using a diffusion cell, also measured a value for  $H_c$  that was much higher than the indirect estimate. In general it should be preferable to use measured values for  $H_c$  rather than estimates. Baker et al. (1996) found better agreement between modeled and measured EPTC volatilization for the first day if a number similar in value to the one found in this paper or Cliath (1978) was used for  $H_c$  instead of an estimated value.

The mean standard error of temperature for all experimental runs was 0.24 °C, and the average purge height for all of the temperature dependence runs was  $26.06 \pm 1.72 \text{ cm}$ , safely above the minimum height requirement for equilibrium (Breiter, 1995). The mean recovery percentage of EPTC (amount sorbed on plug/amount lost from solution  $\times 100$ ) was  $87.91 \pm 11.22$ . It



**Figure 4.** Comparison of experimental and estimated  $H_c$  values for EPTC in deionized water. The temperature and flow rate of the experiment were 27.82 °C and 191.0 mL min<sup>-1</sup>, respectively. A saturated vapor pressure of 5.87 Pa (Patchett et al., 1964) and a solubility of 352.4 mg L<sup>-1</sup> (Freed et al., 1962) were used to estimate  $H_c$  at 27.82 °C.



**Figure 5.** Comparison of experimental  $H_c$  for EPTC in soil solution and experimental and estimated  $H_c$  values for EPTC in deionized water. The temperature and flow rate of the experiments were 28.52 °C and 82.1.0 mL min<sup>-1</sup>, respectively. A saturated vapor pressure of 6.21 Pa (Patchett et al., 1964) and a solubility of 347.1 mg L<sup>-1</sup> (Freed et al., 1962) were used to estimate  $H_c$  at 28.52 °C in deionized water.

is worth noting that in two preliminary runs where Tygon tubing was used rather than Teflon, the recovery percentages were only 25.21 and 31.81%, indicating considerable sorption of EPTC on the Tygon.

**$H_c$  in Soil Solution.** The effect of the soil environment was examined by measuring the  $H_c$  of the pesticide EPTC in a soil extract from a saturated paste having a known gravimetric water content, ionic strength, and organic C concentration. A plot of  $\log(C_i/C_0)$  as a function of  $\Sigma(\Delta t_i/V_i)$ , Figure 5, demonstrates the effect of the soil solution's ionic strength and organic matter on  $H_c$ . This experiment was conducted at two temperatures for a soil extract having a  $w$  value of 0.247, and

**Table 3.**  $H_c$  and the  $r^2$ -Value of the Regression Line Used To Calculate  $H_c$ , also Flow Rate, Average Purge Height, Percent of Mineralized Carbon (%CO<sub>2</sub>), and Mass Balance for Experiments Conducted Using Soil Solutions over a Range of Temperatures

| temp, °C     | flow rate, mL min <sup>-1</sup> | $H_c$  | $r^2$ | purge height, cm | % CO <sub>2</sub> | mass balance, % |
|--------------|---------------------------------|--------|-------|------------------|-------------------|-----------------|
| 26.88 ± 0.05 | 123.1 ± 3.7                     | 0.0826 | 0.999 | 20.33            | 0.16              | 90.92           |
| 28.52 ± 0.02 | 82.1 ± 3.0                      | 0.0874 | 0.997 | 19.93            | 0.36              | 87.43           |

the results are given in Table 3. These values are about 7 times greater than the  $H_c$  values for EPTC at comparable temperatures in deionized water and about 70 times greater than the  $H_c$  values obtained indirectly using saturated vapor pressure and solubility data.

Both Gosset et al. (1985) and Click (1993) demonstrated that the  $H_c^*$  for a compound in a solvent having an ion concentration of 1 mol(+) L<sup>-1</sup> can be up to 50% higher than its  $H_c$  in deionized water, depending upon the salt in solution. However, since the soil solution in this experiment had only 0.0204 mol(+) L<sup>-1</sup>, the ionic strength should have had little impact upon the effective  $H_c$ . There is a possibility that the polarity of EPTC is such that even the low concentration of salts found are enough to raise the fugacity higher than expected. The presence of organic matter in the soil solution might also have played a role. Nicholson et al. (1984) concluded that humic acids had little effect upon  $H_c$ ; however, the highest concentration they examined contained only 17 mg L<sup>-1</sup> of total organic carbon while the solution used in this experiment contained 425.2 mg L<sup>-1</sup>. The exact mechanism of the increase is unknown; however, it may include effects due to interactions of increased salt and organic matter concentrations.

## CONCLUSIONS

We used the batch air stripping method to directly measure  $H_c$  for EPTC, a common herbicide. The value obtained in deionized water was approximately 11 times greater than accepted estimates calculated by dividing the reported saturation vapor pressure by the reported solubility, indicating the need to accurately measure  $H_c$  rather than estimate it. In soil solution the discrepancy was far larger; in this case the measured  $H_c$  was about 7 times larger than the value measured in deionized water and nearly 80 times the indirect estimate. The reason for this is not known and provides motivation for further study.

## ABBREVIATIONS USED

$H_c$ , Henry's law constant; EPTC, *S*-ethyl *N,N*-di-*n*-propylthiocarbamate;  $\Delta H_{vol}^P$ , heat of volatilization (kJ mol<sup>-1</sup>);  $\Delta H_{sol}^P$ , heat of solution (kJ mol<sup>-1</sup>);  $\Delta H_{vap}^P$ , heat of vaporization (kJ mol<sup>-1</sup>);  $C_i$ , concentration of the liquid phase at time  $t$ ;  $C_b$ , concentration of the liquid phase during the  $i$ th time interval;  $C_0$ , initial concentration of the liquid phase;  $H_c^*$ , effective Henry's law constant;  $h_q$ , Setchenow constant attributable to the electrolyte species  $q$ ; NaOH, sodium hydroxide; N<sub>2</sub>, molecular nitrogen.

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