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Determination of vapor pressure-temperature relationships of current–use pesticides and transformation products

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Sub-cooled liquid vapor pressures (P_L^0) of current–use organochlorine and organophosphate pesticides (chlorothalonil, chlorpyrifos methyl, diazinon, fipronil) and selected transformation products (chlorpyrifos oxon, heptachlor epoxide, oxychlordane, 3,5,6-trichloro-2-pyridinol) were determined at multiple temperatures using the gas chromatography retention time technique. Results were utilized to determine vapor pressure-temperature relationships and to calculate enthalpies of vaporization (ΔH_{vap}). While results for chlorothalonil and diazinon were comparable with published values, the measured value for fipronil (1.82×10^{-6} Pa) is almost an order of magnitude higher than the reported literature value (3.7×10^{-7} Pa). The availability of vapor pressure temperature relationships for these chemicals will aid in pesticide risk assessment development and improve the effectiveness of mitigation and remediation efforts.

Keywords: Vapor pressure; temperature; pesticides; transformation.

Introduction

Pesticides are among the most widely used chemical compounds. In the United States alone, more than \$11 billion annually are spent on pesticides[1] and 400 million kilograms of active ingredients are purchased each year for agricultural use.[2] Although pesticides essential for crop protection, exposure to wildlife, sensitive plant species and humans is of concern since many can be carcinogenic, neurotoxic, cholinesterase inhibitors, endocrine disruptors, developmental and reproductive toxins.[3−10] Furthermore, such exposure is not limited to locations around application sites as some pesticides may travel long distances after application via atmospheric transport[11,12] and affect biota in remote regions.

Knowledge of accurate physical and chemical properties is a requirement for accurate and reliable environmental fate and risk assessments. Vapor pressure (VP) is among the most important physical properties as it plays an important role in governing the gas-phase concentration of pesticides and their tendency for long range transport. Vapor pressure is highly dependent on temperature, hence, spatial latitude, longitude and seasonal conditions greatly influence compound phase distribution and transport. The sub-cooled liquid vapor pressure (which does not include the lattice energy present in the solid phase) is more relevant to the low level concentration conditions present in the environment. The sub-cooled liquid vapor pressure has been successfully used to predict the vapor-particle partitioning of organochlorine compounds in the atmosphere.[13−15]

Another important physical property in assessing pesticide fate is the air-water partition coefficient or Henry's Law constant (HLC). This temperature-dependent constant is useful in estimating the volatilization potential of a chemical from surface water to the atmosphere.[16] When coupled with atmospheric concentration data and rainfall information, HLC may also be used to estimate the wet deposition of pesticides. HLC is often estimated using vapor pressure and aqueous solubility. While solubility values as a function of temperature and other basic physical properties (such as melting and boiling points) are readily available for many compounds, vapor pressure data for most semi-volatile organic compounds are scarce. VP values are typically available at only one temperature (20 or 25°C), and extrapolation over the ambient temperature range may be inaccurate.

The lack of vapor pressure values at over a range of temperatures results in inaccurate estimations of HLC values. Hence, there is a need to experimentally determine vapor pressures and their temperature dependence.

The objective of this study was to determine the vapor pressure-temperature relationships for some commonly used pesticides and selected transformation products. The knowledge of these relationships enabled the determination of the enthalpies of vaporization (ΔH_{vap}) values thereby facilitating the calculation of vapor pressure across a large temperature range. The gas chromatographic retention time technique[17] was utilized to determine the sub-cooled liquid vapor pressures. This technique is better suited for low volatility compounds when compared with other traditional methods such as manometric determination and the determination of boiling points at reduced pressure. The advantage of this technique over other methods (like gas saturation, gas effusion) lies in speed, smaller sample size, purity and stability.[18] Furthermore, as this method measures sub-cooled liquid vapor pressure, it allows accurate measurements above and below the compound's melting point. This technique has been used for several organic compounds of environmental interest, with good results, including organophosphate pesticides[18], napthalenes and organochlorines.[19,20]

The results from this study contribute to the small body of vapor pressure-temperature relationship data available for some commonly used pesticides and will enhance the capability to accurately determine the phase distribution of these chemicals in the environment. For this study, eight test compounds were selected. The eight test compounds may be categorized as current-use pesticides (CUPs) or transformation products of important pesticides (Table 1). The pesticides are organochlorines (OCs) and organophosphates (OPs), which are historically among the most commonly used groups of pesticides. As of 2001, OPs formed 70% of the insecticide market in the U.S.[1] Chlorothalonil is the only fungicide included while the remaining analytes are insecticides or their products. Fipronil is a relatively new insecticide (U.S. registration in 1996[3]). All the CUPs are registered for use in U.S. and (except for chlorpyrifos methyl) in Canada. Among the parent compounds, only chlorpyrifos is registered for use and the use of chlordane and heptachlor (known carcinogens) has been banned in U.S. and Canada. Chlorothalonil, diazinon and chlorpyrifos are intensively used in the agricultural as well as the industrial/commercial sector.[1] None of the transformation products are registered for use (neither U.S. nor Canada), yet they have been detected in the environment.[21−23]

Materials and methods

All the compounds in this study were obtained from Accu-Standard (New Haven, CT), Chem Service (West Chester, PA), Dow Elanco (now Dow Agrosciences, Indianapolis, IN), Velsicol Chemical Corporation (Rosemont, IL) and Riedel-de Haen (Seelze, Germany). The purities were in the range of 98–100%. Acetone and acetonitrile (Chromatographic Grade, Fisher Scientific, Fair Lawn, New Jersey) were the solvents used and the concentrations utilized in the experiments were low (0.07–0.13 $\mu g/\mu L$).

Briefly, the gas chromatographic retention time method involves the determination of retention times for the test, reference and standard compounds under isothermal conditions. After many runs over a range of temperatures, the retention time data is then analyzed to obtain values for vapor pressure and enthalpy of vaporization. Vapor pressures of the seven pesticide standard compounds (Table 1) and at different temperatures for the reference compound (p,p′-DDT) are available with great accuracy.[19,20]

A Hewlett Packard gas chromatograph (5890 Series II) with a flame ionization detector (FID) was used for analysis. The column used was DB-1MS, 1.0 m length × 0.25 mm i.d. and 0.25 μm film thickness. The split ratio was 20:1. The carrier gas was helium and the flow rate ranged from 1.5–4 mL/min. The injector and detector temperatures were 280 and 300°C, respectively. A series of seven isothermal runs in the temperature range of 100–130°C were made for all compounds (up to 150°C for fipronil and heptachlor epoxide). The retention times at every temperature were collected and analyzed. For selected compounds and selected temperatures, duplicate runs were conducted and GC retention times were not significantly different (less than 0.02 min.)

The correlation between relative retention times (V_r) and enthalpies of vaporization (ΔH_{vap}) is expressed as:

$$Ln\left[\frac{V_{r,1}}{V_{r,2}}\right] = \left[1 - \left(\frac{\Delta H_{vap,1}}{\Delta H_{vap,2}}\right)\right]LnP^0_{L,2} - c \qquad (1)$$

where, 1 and 2 refer to the test and reference compounds, and c is a constant. $P^0_{L,2}$, the liquid-phase saturation vapor pressure of the reference compound (p,p′-DDT) at temperature T (K), was determined using Equation 2[21]:

$$\log P_L = 12.48 - \frac{4695}{T} \qquad (2)$$

The vapor pressure of a test compound was then computed using the ratio of enthalpies and c (from Equation 1):

$$Ln\left(P^0_{L1}\right)_{GC} = \left(\frac{\Delta H_{vap,1}}{\Delta H_{vap,2}}\right)LnP^0_{L,2} + c \qquad (3)$$

where, $(P^0_{L1})_{GC}$ is the value obtained by the retention time data.

The correlation between the experimental and literature values for the standards (Eq. 4) was used to correct for the experimental inequalities for the test compounds by:

$$\log P^0_L = m \log P^0_{GC} + c \qquad (4)$$

Table 1. Compound type, registration status and chemical information on test, reference and standard analytes.

Compound	Compound type	Registered for use in U.S.	CAS #	Chemical formula	Chemical name
Test					
Chlorothalonil	OC fungicide	Yes	1897-45-6	$C_8Cl_4N_2$	Tetrachloroisophthalonitrile
Chlorpyrifos methyl	OP insecticide	Yes	5598-13-0	$C_7H_7Cl_3NO_3PS$	O,O-dimethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate
Diazinon	OP insecticide	Yes	333-41-5	$C_{12}H_{21}N_2O_3PS$	Diethyl 2-isopropyl-4-methyl-6-pyrimidinyl phosphorothioate
Fipronil	Phenylpyrazole insecticide	Yes	120068-37-3	$Cl_2H_4Cl_2F_6N_4OS$	5-amino-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(1R,S)-(trifluoromethyl)sulfinyl]-
Heptachlor epoxide	Transformation product (parent: heptachlor)	No	1024-57-3	$C_{10}H_5Cl_7O$	1, 4, 5, 6, 7, 8, 8-heptachloro-2, 3-epoxy-3a, 4, 7, 7a-tetrahydro-4, 7-methanoidan
Oxychlordane	Transformation product (parent: chlordane)	No	27304-13-8	$C_{10}H_4Cl_8O$	2,3,4,5,6,6a,7,7-octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2H-indeno
Chlorpyrifos oxon	Transformation product (parent: chlorpyrifos)	No	5598-15-2	$C_9H_{11}Cl_3NO_4P$	3,5,6-trichloro-2-pyridyl diethyl phosphate
TCP	Transformation product (parent: chlorpyrifos)	No	6515-38-4	$C_5H_2Cl_3NO$	3,5,6-trichloro-2-pyridinol
Reference					
p,p′- DDT	OC insecticide	Banned	50-29-3	$C_{14}H_9Cl_5$	1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane
Standards					
$\alpha-$HCH	OC insecticide	Banned	319-84-6	$C_6H_6Cl_6$	1,2,3,4,5,6- hexachlorocyclohexane (α-isomer)
$\alpha-$chlordane	OC insecticide	Banned	5103-71-9	$C_{10}H_6Cl_8$	1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene
$\beta-$chlordane	OC insecticide	Banned	5103-74-2	$C_{10}H_6Cl_8$	1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene
Cis-nonachlor	OC insecticide	Banned	5103-73-1	$C_{10}H_5Cl_9$	1,2,3,4,5,6,7,8,8-nonachloro-2,3,3a,4,7,7a-hexahydro-
Trans-nonachlor	OC insecticide	Banned	39765-80-5	$C_{10}H_5Cl_9$	1,2,3,4,5,6,7,8,8-nonachloro-2,3,3a,4,7,7a-hexahydro-
Heptachlor	OC insecticide	Banned	76-44-8	$C_{10}H_5Cl_7$	1, 4, 5, 6, 7, 8, 8-heptachloro-3a, 4, 7, 7a-tetrahydor-4, 7-methanoindene
Chlorpyrifos	OP insecticide	Yes	2921-88-2	$C_9H_{11}Cl_3NO_3PS$	O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) ester

Temperature dependence of vapor pressure was determined using the Clausius-Clapeyron equation:

$$\log P_L = A_L + \frac{B_L}{T} \qquad (5)$$

where, $B_L = -\Delta H_{vap}/R$ and was used to obtain the enthalpy of vaporization (ΔH_{vap}).

Results and discussion

In order to validate the accuracy and dependability of our experimental design, vapor pressures for standard compounds were determined and compared to literature values. An excellent correlation was observed between the experimental (P^0_{GC}) and reported literature vapor pressure values for the standard compounds (Fig. 1). From this correlation (using the average of three reliable literature values of vapor pressure), the parameters for the conversion of P^0_{GC} to P^0_L (Equation 4) are determined as: m = 0.962 and c = -0.046 ($r^2 = 0.992$, standard error = 0.066).
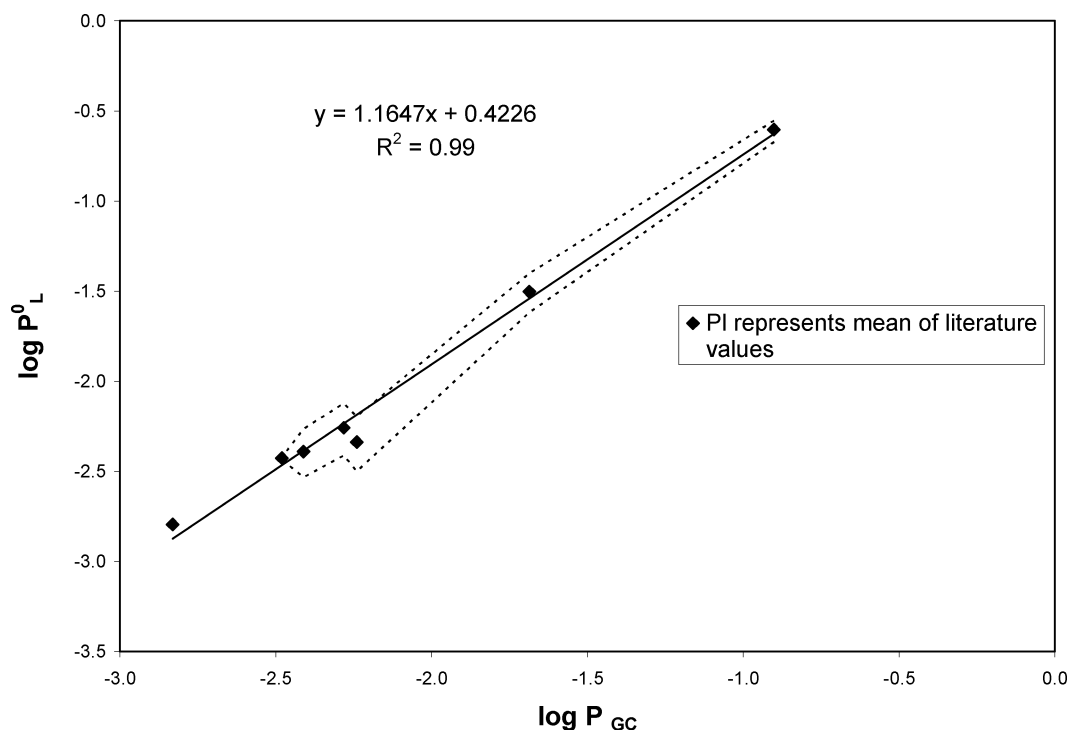
Fig. 1. Correlation between experimental and literature values of the standard compounds.

Vapor pressure at standard temperature

To enable comparison of literature VP values (available mostly at 25°C) and measured values (this study), VP results at 25°C were calculated using the Clausius-Clapeyron equation (Table 2). The measured vapor pressures of the test compounds varied greatly, spanning three orders of magnitude. The variation among the values for OPs was greater than among the OC pesticides.

The available literature values for chlorothalonil are the most widespread among our group. The measured value from this study (5.3×10^{-5} Pa) falls on the lower end of the literature value range and is about 30% lower than the value selected by Mackay et al. 1997 [24] (7.6×10^{-5} Pa). The

experimental value for the OP insecticide, diazinon (5.9×10^{-3} Pa), agrees well with the reported literature values ($8.7 \times 10^{-3} - 1.13 \times 10^{-2}$ Pa). Diazinon has the highest VP in the group and is, therefore, the analyte most likely to volatilize from the point of application in the absence of other competing loss processes.

In contrast, fipronil has the lowest reported vapor pressure of all the test compounds (3.7×10^{-7} Pa); however, the measured value (1.9×10^{-6} Pa) is almost an order of magnitude higher than the reported literature value. Current estimates regarding the fate of fipronil indicate that it does not readily volatilize and, except for loss through drift during spray applications, it is not likely to be found in the air. [3] However, results from this study suggest that

Table 2. Comparison experimental and published values of sub-cooled liquid vapor pressure values (Pa) @ 25°C

Compound name	Experimental P_L^o (Pa) @ 25° C (this study)	Published range of P_L^o (Pa) @ 25°C	Selected literature value (Pa)
Chlorothalonil	5.3×10^{-5}	$7.6 \times 10^{-5} - 232$ [24]	7.6×10^{-5} [24]
Chlorpyrifos methyl	1.7×10^{-5}	3.0×10^{-3} [9]	3.0×10^{-3} [9]
Chlorpyrifos oxon	6.2×10^{-6}	na	
Diazinon	5.9×10^{-3}	$8.7 \times 10^{-3} - 1.13 \times 10^{-2}$ [24]	2.0×10^{-2} [19]
Fipronil	1.9×10^{-6}	3.7×10^{-7} [28]	3.7×10^{-7} [28]
Heptachlor epoxide	7.6×10^{-6}	$2.56 \times 10^{-3} - 9.97 \times 10^{-2}$ [24]	
Oxychlordane	7.3×10^{-6}	1.2×10^{-2} [25]	1.2×10^{-2} [25]
TCP	2.6×10^{-4}	na	

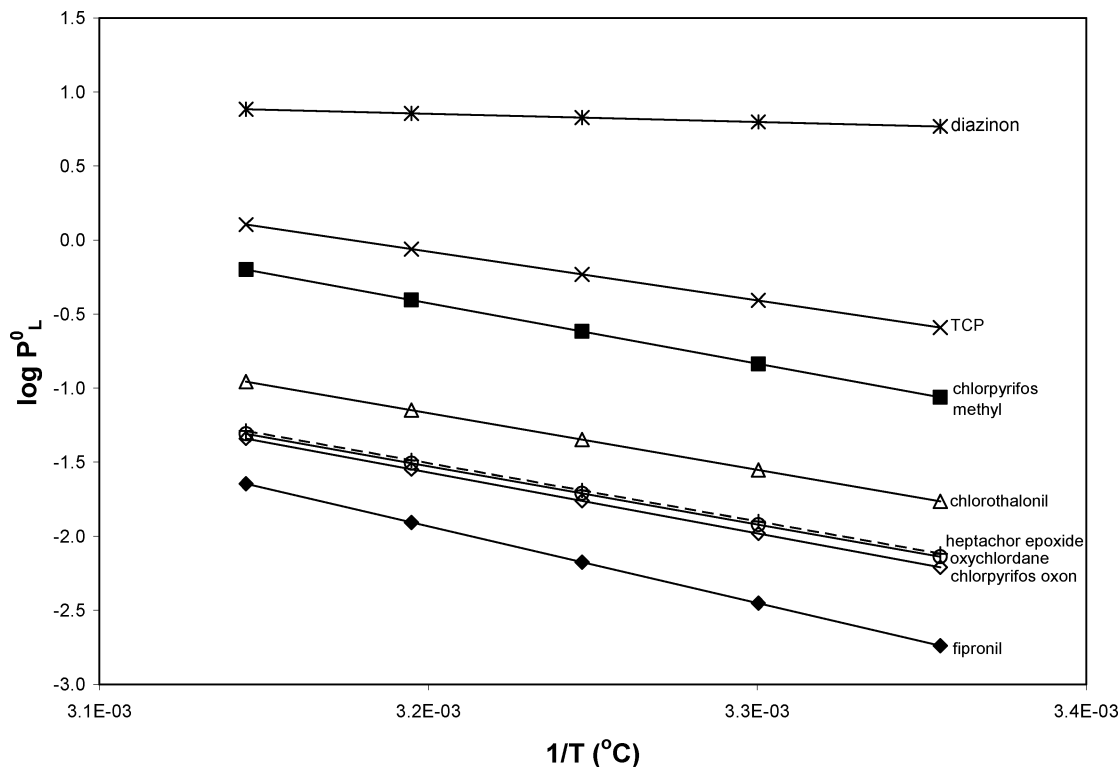TCP : 3,5,6-trichloro-2-pyridinol.
na: not available.

Fig. 2. Vapor pressure-temperature relationships for the chemicals under study.

it is more volatile and mobile than previously predicted. Alternatively, the measured value for chlorpyrifos methyl (1.7×10^{-5} Pa) is lower than literature values by a factor of 100 (3.0×10^{-3} Pa).[9] Its low volatility suggests a more likely presence in soils and water bodies. Besides hydrolysis, it also undergoes aerobic degradation in soil and one of the major metabolites is TCP.

The experimental values for the two OC transforms—heptachlor epoxide (7.6×10^{-6} Pa) and oxychlordane (7.3×10^{-6} Pa)—are three to four orders of magnitude lower than the available literature values. [25] The literature values are estimates and experimental measurements are not available. The results from this study support the requirement for direct measurements for a compound as has also been suggested by Paasivirta et al.[25] Vastly lower vapor pressure values indicate that these two compounds will be more persistent in soils and perhaps biota rather than the atmosphere. Both the compounds are very highly toxic to fish.[26] Heptachlor epoxide, the main heptachlor-related compound observed in the environment, bioconcentrates in aquatic organisms[6] and has been found in the fat of fish.[26] Parent pesticides of both these compounds are no longer registered in the United States. Heptachlor is also a major component of technical chlordane. The sources for these compounds, though not vast, still exist and studies on their occurrence and effects in aquatic environments remain important.

Literature vapor pressure values for the chlorpyrifos transforms, chlorpyrifos oxon and TCP, are not available.

Experimental results show that both the compounds are less volatile than the parent compound (3.35×10^{-3} Pa,[10]) and are, therefore, of greater concern in the water system. Chlorpyrifos is bioactivated in the liver to chlorpyrifos oxon which is then rapidly hydrolyzed to TCP. TCP is 100 times more volatile than the oxon (Table 2). The stability and volatility are likely reasons why TCP is the principal chlorpyrifos transformation product detected in the environment.[5] Chlorpyrifos oxon is a potent cholinesterase inhibitor[27], while TCP is not regarded as toxicologically important.

Vapor pressure variation with temperature

The vapor pressure-temperature relationship is different for each of the chemicals in our study (Fig. 2). The most valuable data generated in this study are the required coefficients, A_L and B_L, for the Clausius-Clapeyron equation (Eq. 5) (Table 3). The availability of these coefficients enables the calculation of vapor pressure at different ambient temperatures for each compound. For example, when the temperature increases from 20 to 40°C, the VP of chlorpyrifos oxon increases by an order of magnitude (3.6×10^{-3} to 2.8×10^{-2} Pa), while the increase for diazinon is much less (5.5-7.2 Pa). The vapor pressures of all compounds with higher values of the coefficient B_L (Table 3) rose by an order of magnitude with temperature change from 20 to 40°C. This shows their greater susceptibility to temperature changes and errors in environmental estimations are likely

Table 3. Parameters of the clausius-clapeyron equation and enthalpies of vaporization

Compound	B_L	A_L	ΔH_{vap} (kJ/mol)
Chlorothalonil	−3494	10.4	67
Chlorpyrifos methyl	−3826	11.1	73
Chlorpyrifos oxon	−4125	11.6	79
Diazinon	−549	2.6	11
Fipronil	−4431	12.2	85
Heptachlor epoxide	−3927	11.1	75
Oxychlordane	−3935	11.1	75
TCP	−3292	10.5	63

ΔH_{vap} = enthalpy of vaporization.

if temperature corrections are not incorporated. Heat of vaporization (ΔH_{vap}) is defined as the amount of heat (or energy) required per unit mass of a substance to completely vaporize the substance at its boiling point, and it reflects the ease of volatilization. In this respect, chlorpyrifos oxon is the most difficult to volatilize and diazinon the easiest in this group.

Conclusion

Results from these experiments reveal that some current-use pesticides have higher (fipronil) and some have lower (chlorpyrifos methyl) volatility than previously reported. Hence, model predictions of their phase distribution may provide quite different results from previous assessments. Experimental measurements are essential since literature values are mostly estimates and may vary widely. Vapor pressure values for most transformation products are not available at all and will have very different volatilities as compared to the parent compounds. Vapor pressures of more pesticides and their degradation/transformation/breakdown products, especially those which are most commonly used or are being newly introduced, should be experimentally determined and their relationship with temperature established to ensure realistic environmental distribution predictions.

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