

Henry's Law Constants for Pesticides Measured as a Function of Temperature and Salinity

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A wetted wall column device was used to determine air–water distribution coefficients [Henry's law constants (HLCs)] for pesticides: chlorpyrifos, trifluralin, endosulfans I and II, methyl parathion, metolachlor, and 2,4-D. The measured HLCs were all significantly higher than values calculated from published vapor pressure and solubilities except those for technical endosulfan and 2,4-D. With 2,4-D, however, the HLC was higher under acidic conditions. The effects of temperature and salinity were investigated using chlorpyrifos, trifluralin, and endosulfan I. Simulated seawater increased the HLCs from 1.5 to 2.4 times, which suggests a salting out effect. Natural water HLC values that were determined on Chesapeake Bay and Bering/Chukchi Sea water samples of microlayer and subsurface water were all lower than predicted values even after correction for temperature and salinity. Therefore, some as yet undefined factors in the aqueous phase appear to be responsible for these lowered HLCs. There was generally a linear increase in the log HLC versus increase in temperature for all of the pesticides in both distilled water and salt water except for trifluralin, which was curvilinear in simulated seawater.

Keywords: Henry's law constants; air–water partitioning; chlorpyrifos; trifluralin; endosulfan; methyl parathion; 2,4-D; metolachlor

INTRODUCTION

Knowledge of exact Henry's law constants (HLCs) for pesticides under environmentally representative conditions can be very important to understanding and predicting the fate of these chemicals in aquatic environments. HLCs essentially predict air–water partitioning as follows: $K_H = C_a/C_w$. This becomes a dimensionless ratio of the concentration of the chemical in the air C_a to the concentration of the chemical in the water C_w . These constants can be experimentally determined by measuring the respective concentrations in an equilibrated system. Several experimental methods have been devised for doing these measurements [Gossett, 1987 (bulk equilibration); Mackay et al., 1979 (gas sparging method); Fendinger and Glotfelty, 1988 [wetted wall column (WWC) method]; Schoene et al., 1984 (automated headspace–gas chromatography methods)].

Calculated HLC values are an indirect way to estimate air–water exchange of pesticides. Their accuracy depends on the accuracy of the respective vapor pressure and solubility values that are used to perform the calculations. For many compounds, these values are not precisely known, and this carries over to uncertainty about the HLC values determined from them. Therefore, the best approach for arriving at meaningful air–water distribution properties for pollutants is to make use of measured HLCs rather than calculated ones. It has also been shown that experimentally derived constants can be quite different from calculated values (Fendinger and Glotfelty, 1990).

It is generally accepted that both vapor pressure and solubility of pesticides vary in activity inversely as temperature changes; under ideal conditions, e.g. distilled water and in dilute solution, their log values should vary linearly with temperature as shown in the following equation (Schwarzenbach et al., 1993):

$$\ln K_H = -\left[\frac{\Delta H_{\text{vap}} - \Delta H_s^\circ}{R}\right]\frac{1}{T} + \text{constant}$$

ΔH_{vap} is the change in enthalpy for vapor pressure, ΔH_s° is the enthalpy change for solubility, and K_H is the term for the dimensionless Henry's law constant. Several methods have been suggested to correct HLCs for temperature (Hornbuckle et al., 1995; Thomas, 1990) and salinity (Gossett, 1987; Iwata et al., 1993). For PCBs, Ten Hulscher et al. (1992) derived a constant factor for temperature correction by determining HLC dependence for congeners from different homologue groups. Tataya et al. (1988) measured the temperature dependence of vapor pressure and solubility for PCBs in sea water and derived HLCs from these values, and Burkhard et al. (1985) have used several different methods to estimate representative HLC-determined temperature adjustments. Calculated slopes (A) for these curves [$\ln H = A(1/T) + B$] represent how sensitive the air–water partitioning process is to temperature changes. Kucklick et al. (1991) used a gas stripping method and found the slopes for α - and γ -hexachlorocyclohexane (HCH) to vary from -2382 (γ -HCH in distilled water) to -2969 (α -HCH in sea water). Typical values for these slopes can range from -1382 [calculated from data for benzo[ghi]perylene (ten Hulscher et al., (1992))] to a value as high as -7868 , which was used by Tataya et al. (1988) to represent PCBs as a class in his modeling studies. Also, separate values for slopes from -903 for methanethiol in artificial sea water to -2175 for diethyl sulfide in distilled water were reported for a

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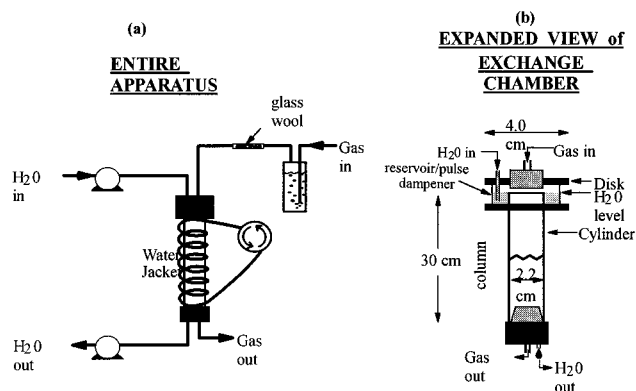


Figure 1. Wetted wall column (WWC) apparatus (Fendinger and Glotfelty, 1988): (a) schematic of entire apparatus showing water jacket for temperature control; (b) expanded view of exchange chamber.

group of organosulfur compound studied by Przyjazny et al. (1983). Sagebiel et al. (1992) carried out studies of HLCs for a group of phenols and the pesticide molinate using different temperatures and headspace methods. The slope for molinate from this work was -3024 (Staudinger and Roberts, 1996). Staudinger and Roberts (1996) summarized 123 experimental values where temperature effects on HLC were directly measured. Several groups of compounds (hydrocarbons, phenols, alcohols, pesticides, PCBs, etc.) were included and found to have slopes ranging from -1700 to -3300 .

To utilize HLCs in environmental modeling, it is essential to adjust the HLC values to represent the exact environmental conditions for the modeled area. In an ocean system, salinity has a significant impact on solubility. Temperature effects can also be very important. This has especially been noted for colder bodies of water, where gas transfer can be a significant input process (Lake Baikal, Iwata et al., 1995; Lake Superior, Hornbuckle et al., 1994; colder Northwest Territory lakes, Muir et al., 1990). Several recent publications have dealt with the question of salinity and temperature effect on HLCs that are used in environmental predictions. Kucklick et al. (1991) reported on the importance of temperature and salinity for explaining flux of hexachlorocyclohexane (HCHs) in natural environments. McConnell et al. (1993) and Hinckley et al. (1991) utilized these adjusted values to predict fluxes of HCHs, respectively, in the Great Lakes and Bering and Chukchi Seas.

HLC values were determined for several currently used pesticides under environmentally relevant conditions. Temperature and salinity were the major variables considered. The experimentally determined HLCs for natural waters and laboratory-derived waters were compared. Comparisons were made to examine the importance of some of the aqueous phase parameters (particularly salinity, total organic carbon, and suspended solids) to the air-water partitioning. The pesticides chosen for this study (trifluralin, chlorpyrifos, Thiodan, endosulfans I and II, metolachlor, methyl parathion, and 2,4-D) are heavily used in U.S. agriculture, their HLC values are easily measured by the WWC method (i.e. $HLC > 10^{-7}$, Fendinger and Glotfelty, 1988), and they are frequently measured in air and fog samples (Majewski and Capel, 1995).

APPROACH AND METHOD

Experimental Procedures. For determination of the HLC values, the modified WWC apparatus (Figure 1) of

Fendinger and Glotfelty (1988) was used. The HLCs were determined by separately equilibrating the chemicals (chlorpyrifos, trifluralin, Thiodan, endosulfans I and II, 2,4-D, metolachlor, and methyl parathion) in a thin liquid water film with a concurrent flow of air which passes down the center of the exchange column. The WWC device used in this study had a 30-cm length column, and the air flow rates were approximately 100 mL/min and the water flows rates 1–2 mL/min (Figure 1b). The original WWC apparatus of Fendinger and Glotfelty (1988) was modified to provide temperature control during the tests. The temperature was maintained by wrapping Tygon tubing around the glass exchange column (Figure 1a). Water was circulated through the tubing using a Neslab Model RT-210 constant-temperature bath at nominal settings of 4, 20, and 50 °C for most experiments. By indirect measure it was determined that these settings were effectively providing 8.3, 20, and 43.5 °C within the column. Breathing air was introduced to the column after it was saturated with distilled deionized water that had been maintained at the appropriate temperature for each test. The chemicals were generally added as aqueous solutions; however, the WWC method also allows addition of the chemicals in the gas phase. Aqueous phase additions are easier to manage because the concentrations are more predictable and easier to measure. Gas phase additions were carried out to verify that the air-water exchange values were independent of the mode of addition, i.e., that true steady state conditions were achieved in the exchange column. Several initial experiments were carried out to verify this fact. Although all of the HLCs derived from gas additions were slightly higher than those from the experiments run with a aqueous additions, the differences were never statistically significant ($p < 0.05$).

The aqueous solution phase concentrations were achieved by mixing the chemicals with the liquid solutions in 4-L completely filled bottles for a minimum of 1 day prior to each test. This allowed sufficient time for complete dissolution of the chemicals, which was verified by repeated sampling and analysis to ensure a constant concentration was maintained. The aqueous phase concentrations used for the equilibrium experiments with laboratory water were as follows: 0.51–8 ppb for trifluralin; 0.65–6.0 ppb for chlorpyrifos; 250 ppb for methyl parathion; 220 ppb for metolachlor; 40 ppb for 2,4-D; 0.051 ppb for Thiodan, 0.041–0.41 ppb for endosulfan I; and 0.045–0.45 ppb for endosulfan II. For the experiments with natural Arctic waters the concentrations were set to 5.3 ppb for trifluralin and 6.1 ppb for chlorpyrifos. For the Chesapeake Bay studies, 2.7 ppb of trifluralin, 3.1 ppb of chlorpyrifos, and 4.7 ppb of endosulfan I were used. The gas phase concentrations were established as follows: A glass wool plug (Figure 1b) was placed in the air line prior to entering the WWC chamber. This glass wool was dosed with the appropriate pesticide by adding it as a concentrated solution in organic solvents. The carrier solvent was allowed to evaporate before the experiments were begun. The levels that were added were operationally 10 times the amount needed to achieve the necessary aqueous phase concentration in the 4-L bottles. These were determined empirically, with the goal of matching aqueous phase effluent concentrations, so that direct comparisons with the aqueous phase additions could be made. Most of the individual wetted wall tests were carried out at least in triplicate.

Water collected from the WWC was passed through a 1-g Waters C₁₈ SepPak extraction cartridge, and the air was passed through 10 cm × 0.6 cm i.d. columns packed with Chromosorb 102 resin. The C₁₈ and Chromosorb columns were extracted by eluting with 10–20 mL of 1:1 acetone/hexane. Extracts were concentrated to appropriate volumes and analyzed by various detectors. The chlorinated pesticides, Thiodan and endosulfans I and II, and metolachlor were all analyzed on an HP Model 5989A gas chromatograph/mass spectrometer equipped with a 30-m, 0.25 i.d., DB-5 fused silica capillary column and detected by electron capture negative chemical ionization methods. The 2,4-D residues were extracted in the acid form and then derivatized to the ester by diazomethane reaction (EPA Standard Method 515.1; Graves, 1989). These extracts were then analyzed by electron capture gas chroma-

Table 1. Henry's Law Constant Values (and Selected Literature Values) for Several Pesticides As Determined by WWC Method at 20 °C in a 33.3% Solution of NaCl and Distilled Water

chemical	measured HLCs [(SE) (replicates)]		literature HLCs	
	salt water (33.3%)	distilled water	distilled water	citation
trifluralin	$6.18 (0.22) \times 10^{-3}$ (5)	$4.23 (0.15) \times 10^{-3}$ (8)	$2.4 (0.2) \times 10^{-3}$ (23 °C)	Fendinger et al. (1989)
chlorpyrifos	$2.02 (0.09) \times 10^{-4}$ (5)	$1.30 (0.13) \times 10^{-4}$ (8)	$1.7 (0.3) \times 10^{-4}$ (25 °C)	Fendinger and Glotfelty (1990)
thiodan (endo I + endo II)	$5.43 (0.42) \times 10^{-3}$ (5)	$2.65 (0.15) \times 10^{-3}$ (5)	1.2×10^{-3} (20 °C) Calcd ^a	Suntio et al. (1988)
endosulfan I (endo I)	$5.29 (0.23) \times 10^{-3}$ (5)	$2.72 (0.10) \times 10^{-3}$ (5)	2.74×10^{-4} (25 °C) Calcd	Cotham and Bidleman (1989)
endosulfan II (endo II)	$0.87 (0.24) \times 10^{-3}$ (5)	$3.6 (1.6) \times 10^{-4}$ (5)	2.53×10^{-5} (25 °C) Calcd	Cotham and Bidleman (1989)
metolachlor		$3.21 (0.16) \times 10^{-6}$ (3)	3.37×10^{-7} (25 °C) Calcd	Majewski and Capel (1995)
methyl parathion		$1.57 (0.48) \times 10^{-6}$ (3)	$2.5 (0.6) \times 10^{-6}$ (25 °C)	Fendinger and Glotfelty (1990)
2,4-D pH 1		$2.79 (0.79) \times 10^{-3}$ (3)	pH affect not studied	
2,4-D pH 7		3.5×10^{-4} (1)	2.26×10^{-4} (20 °C) Calcd	Suntio et al. (1988)

^a Calcd, calculated from water solubility and vapor pressure data.

tography after separation on a 30-m, 0.25 i.d., DB-608 capillary column. Chlorpyrifos and trifluralin were also quantitated by electron capture gas chromatography on a 30-m, 0.25 i.d., DB-1 capillary column. The Thiodan [technical mixture of 64–76% endosulfan I + 29–32% endosulfan II (Worthing and Walker, 1983)] was quantitated by summing the areas of its two peaks for endosulfans I and II. The individual isomers were quantitated using selective ion monitoring methods (m/z 372, 406, and 408). For total organic carbon (TOC) determinations, a Model 700 O-I Corp. TOC analyzer was used and the EPA Method 600/4-79-020 was employed. Salinities were determined under contract with the Chesapeake Biological Laboratory, Solomons, MD. Suspended solids were determined gravimetrically by filtration and distilled water rinsing of the filter to remove residual dissolved salt.

Natural water and surface microlayer samples were collected in the summer of 1993 from the Bering Sea (Anadyr Bay) and the Chukchi Sea (Kotzebue Sound) (Chernyak et al., 1996) and in the autumn of 1994 from the Chesapeake Bay (Pt. Lookout; Potomac River mouth, Solomons; Patuxent River mouth; and Sandy Point, MD—Baltimore harbor area). Subsurface whole-water samples from the Arctic were collected using a submersible pump [described in Chernyak et al. (1996)], and the Chesapeake Bay subsurface water samples were collected by immersing 4-L empty solvent jars below the water surface and allowing them to fill. Surface microlayer samples of 4–8 L were collected using a stainless steel mesh screen, and the Arctic ice was sampled as described in Chernyak et al. (1996). All of the Arctic water samples were preserved by addition of mercuric chloride to each bottle, and once returned to the laboratory, they were kept at 5 °C until the experiments were carried out. The average storage time for these samples was 4–6 months. The Chesapeake Bay samples were kept chilled at 5 °C until the tests were performed, which generally took place within 1–2 weeks after collection. All of the HLC experiments on natural waters were performed on unfiltered samples. To investigate the effect of salt concentrations on HLCs, a water solution of NaCl (33.3%) was used. Distilled deionized water was used as the laboratory water in all of these tests.

DATA

Experimental Data. Results of the WWC determinations of Henry's law constants for eight pesticides using a salt solution of 33.3% NaCl and distilled water at 20 °C are summarized in Table 1. These data are compared to selected literature values (for distilled water and temperatures between 20 and 25 °C) for these pesticides. Some of these literature data are WWC experimental results by Fendinger and associates (Fendinger et al., 1989; Fendinger and Glotfelty, 1990) for trifluralin, chlorpyrifos, and methyl parathion. Calculated values are listed for Thiodan [technical endosulfan (70:30 endosulfan I/endosulfan II)], metolachlor, and 2,4-D; these were all calculated according to the procedures discussed in Suntio et al. (1988). The experimental results for 2,4-D were determined under two different pH treatments to account for 2,4-D's low pK_a (~3.0; Howard et al., 1991). All of the measured HLC values for the salt water were significantly

different from those determined in the distilled water ($p < 0.05$).

Henry's law constants measured with the WWC device at 20 °C on natural water samples [Bering/Chukchi Sea (two locations combined as averages providing 8–10 replicates) and Chesapeake Bay (three locations with four replicates at each location)] are listed for three pesticides: trifluralin, chlorpyrifos, and endosulfan I (Table 2). Also listed for comparison to these values are the predicted HLCs (adjusted to the salinity measured at each site) for each compound. Salinity, total organic matter, and particulate concentrations are also presented. Each of the natural water samples consisted of a surface microlayer sample and a subsurface water sample collected from the same site. Tests of significance were carried out, and none of the paired sets of HLC values for microlayer and subsurface water samples were statistically significant from each other at the 0.05 probability level. Most of the measured HLC values for the Chesapeake Bay samples were lower than their salinity-adjusted estimated values; however, only the trifluralin values were significantly different (except the Sandy Point subsurface value) at the 0.05 probability level.

Results of the measurement of HLCs versus temperature for trifluralin and chlorpyrifos in several different water samples are graphically depicted in Figures 2–7, and the data for the results of the Arctic samples are provided in Table 3. Data in Table 3 list the average of each of the three to five replicate measurements of HLC which were carried out on each sample from one station in the Bering Sea (subsurface and microlayer sample), one in the Chukchi Sea (subsurface and microlayer sample), and a sample of melted Arctic ice. Results for three temperatures are listed: 8.3, 20, and 43.5 °C. Also listed are TOC values for each sample and the least-squares fit coefficient values, R^2 , for each series of data as they appeared when plotted as the log HLC versus temperature [$1/(T \text{ kelvin})$]. Baseline results for the laboratory waters are also graphically presented using this relationship for distilled water (Figures 2 and 3) and for 33.3% NaCl solutions (Figures 4 and 5) including their least-squares fit lines, linear fit equations, and R^2 values. The effect of variation in temperature on observed HLC for natural water samples from the Chukchi Sea is graphically compared with the salt water tests on each of the pesticides (Figures 4 and 5). Graphical comparisons of these two pesticides are presented for the microlayer and subsurface water sampling station in the Chukchi Sea (Figures 6 and 7). In these last two plots, the equation for the linear fit line for trifluralin and chlorpyrifos for the two lowest temperature measurements in the microlayer sample, 20 and 8.3 °C, is provided. Statistical tests for relative differences were performed on all of the data in Table 3. Each of the separate melted Arctic ice HLC values were significantly different ($p < 0.05$) from the corresponding HLC values measured for the same pesticide at that temperature. Tests of significance between the surface microlayer and subsurface water sample at each site and temperature were also performed. None of these paired sets of data were significantly different except for the lowest temperature for the trifluralin values for microlayer versus subsurface, Bering and Chukchi samples ($p = 0.05$) and at a probability level of

Table 2. Henry's Law Constants Determined at 20 °C for Surface Microlayer and Subsurface Water Collected from the Chesapeake Bay and Bering/Chukchi Seas^a

sampling location	sample type	salinity (‰)	TOC (ppm)	particulates (mg/L)	HLC × 10 ⁻³	
					measured	estimated (adjusted to salinity)
Trifluralin						
Pt. Lookout, MD	microlayer	17	0.4	30	4.58 ± 0.22	5.13 ± 0.18
	subsurface		1.0	16	4.53 ± 0.26	
Solomons, MD	microlayer	16	0.5	13	4.50 ± 0.22	5.08 ± 0.18
	subsurface		0.6	7	4.40 ± 0.18	
Sandy Point, MD	microlayer	12	0.6	6	4.35 ± 0.10	4.85 ± 0.17
	subsurface		0.6	320	4.13 ± 0.99	
Bering/Chukchi Sea	microlayer	32	3 to 46	NA ^b	5.10 ± 0.30 (10)	6.09 ± 0.22
	subsurface		2.2 to 3.3	NA	5.21 ± 0.44 (10)	
Chlorpyrifos						
Pt. Lookout, MD	microlayer	17	0.4	30	0.15 ± 0.03	0.16 ± 0.01
	subsurface		1.0	16	0.15 ± 0.02	
Solomons, MD	microlayer	16	0.5	13	0.14 ± 0.02	0.16 ± 0.01
	subsurface		0.6	7	0.16 ± 0.03	
Sandy Point, MD	microlayer	12	0.6	6	0.13 ± 0.04	0.15 ± 0.01
	subsurface		0.6	320	0.14 ± 0.01	
Bering/Chukchi Sea	microlayer	32	3 to 46	NA	0.15 ± 0.02 (8)	0.20 ± 0.02
	subsurface		2.2 to 3.3	NA	0.17 ± 0.01 (8)	
Endosulfan I						
Pt. Lookout, MD	microlayer	17	0.4	30	3.55 ± 0.31	3.82 ± 0.14
	subsurface		1.0	16	3.48 ± 0.22	
Solomons, MD	microlayer	16	0.5	13	3.60 ± 0.18	3.74 ± 0.14
	subsurface		0.6	7	3.30 ± 0.24	
Sandy Point, MD	microlayer	12	0.6	6	2.98 ± 0.33	3.46 ± 0.13
	subsurface		0.6	320	3.78 ± 0.64	

^a Shown also are the total organic carbon (TOC) content and particulate matter for each sample and the salinity-adjusted HLCs for each location. All measured HLC values represent averages of four replicates except were noted with numbers in parentheses. The plus and minus values are the standard errors of the means. ^b NA, not analyzed.

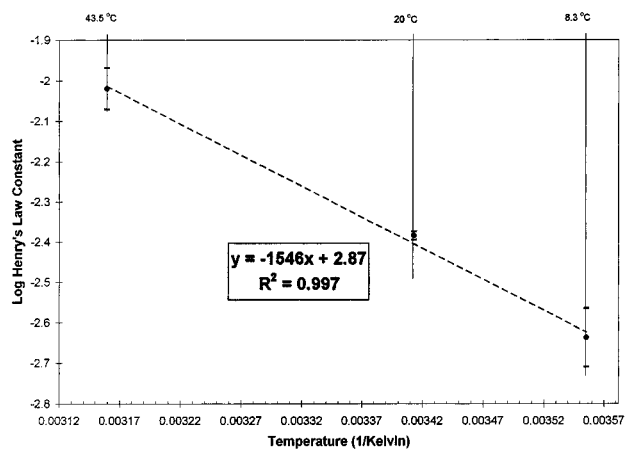


Figure 2. Variation of Henry's law constant for trifluralin with change in temperature using distilled water. Error bars represent the standard error about the mean. Equation for the relationship $\log H = A(1/T) + B$ is shown with the linear regression coefficient.

0.11 for the chlorpyrifos at 8.3 °C temperature (microlayer versus subsurface, Chukchi sample only).

DISCUSSION

Laboratory Water Experiments. It has already been demonstrated by other researchers that measured HLC values can significantly differ from calculated values for HLCs (Fendinger and Glotfelty, 1988; Fendinger et al., 1989; Yin and Hassett, 1986). The errors arising from calculated HLCs generally are much greater for the more insoluble compounds because of difficulties in making the solubility measurements (accounting for their increased sorption to particulate, dissolved organic matter interactions, sorption to surfaces of glassware, etc.). Our data also indicate that

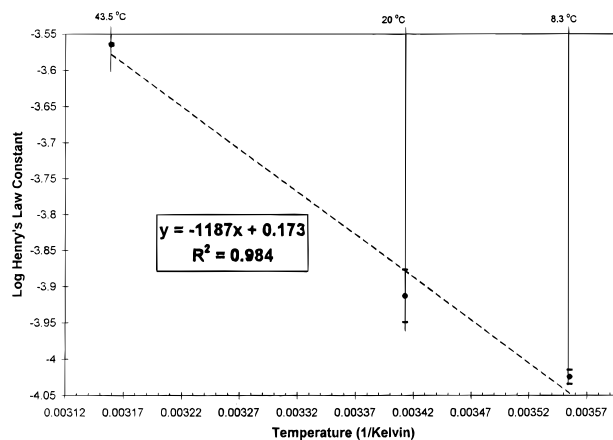


Figure 3. Variation of Henry's law constant for chlorpyrifos with change in temperature using distilled water. Error bars represent the standard error about the mean. Equation for the relationship $\log H = A(1/T) + B$ is shown with its linear regression coefficient.

wide differences from calculated HLCs can be observed; this was especially true for metolachlor, 3.21×10^{-6} (measured) versus 3.37×10^{-7} (calculated), and the two isomers of endosulfan. The agreement between the observed value for Thiodan (2.65×10^{-3}) versus that calculated (1.2×10^{-3}) is better; however, this agreement may be just fortuitous because Thiodan actually exists as two isomers (endosulfans I and II). Specific study of the HLCs for each of these isomers showed them to be quite different (5.29×10^{-3} for endosulfan I and 0.87×10^{-3} for endosulfan II). There was considerably more analytical uncertainty within the experimental values of the HLCs for the endosulfan II isomer [relative standard deviations (RSDs) of 0.27 and 0.44, respectively, for the salt water and distilled water values for endosulfan II versus 0.04 for both of these values

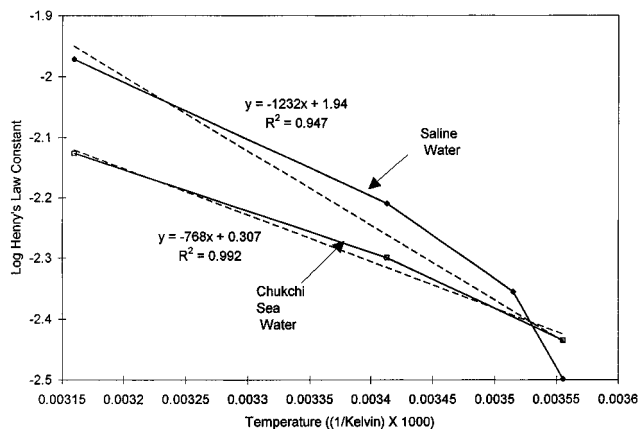


Figure 4. Comparison between the change in Henry's law constant with temperature for trifluralin using a salt water solution (33.3% NaCl) and an ocean water sample from the Chukchi Sea. Equations for the relationship $\log H = A(1/T) + B$ are shown with their linear regression coefficients.

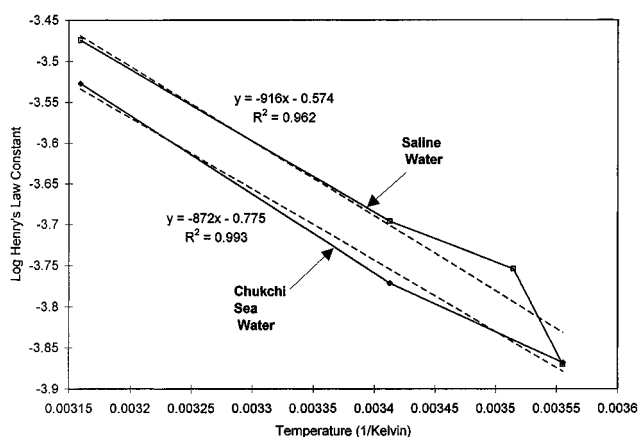


Figure 5. Comparison between the change in Henry's law constant with temperature for chlorpyrifos using a salt water solution (33.3% NaCl) and an ocean water sample from the Chukchi Sea. Equations for the relationship $\log H = A(1/T) + B$ are shown with their linear regression coefficients.

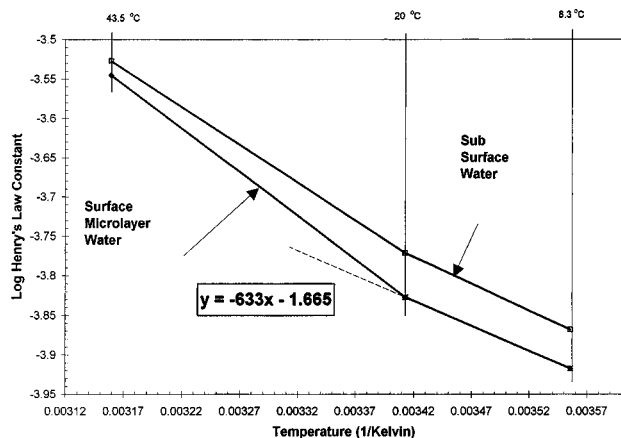


Figure 6. Comparison between the change in Henry's law constant for chlorpyrifos with temperature for an ocean water sample (subsurface water) and a surface microlayer sample from the same location in the Chukchi sea. Equation for the relationship $\log H = A(1/T) + B$ is shown for the microlayer.

for endosulfan I]. It was observed that endosulfan II appears to convert to endosulfan I during transfer across the air–water interface. This could account for the variability noted with the endosulfan II experimental data. Recent data have been obtained that provide a structural and thermodynamic basis for this conversion

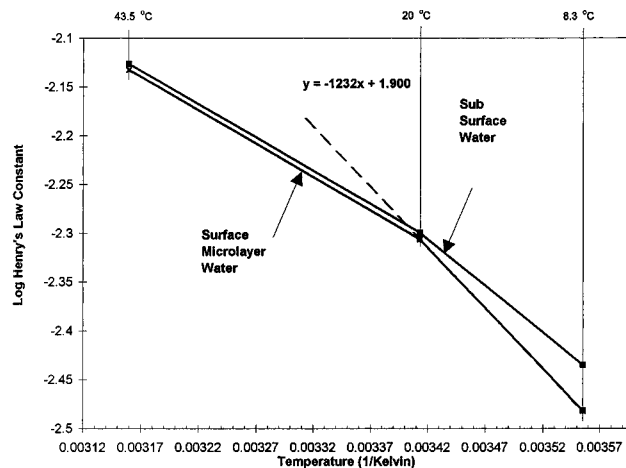


Figure 7. Comparison between the change in Henry's law constant for trifluralin with temperature for an ocean water sample (subsurface water) and a surface microlayer sample from the same location in the Chukchi sea. Equation for the relationship $\log H = A(1/T) + B$ is shown for the microlayer.

(Schmidt et al., 1997), and we have recently completed additional experiments that quantify this endosulfan II to endosulfan I conversion more precisely (Rice et al., 1997).

The experimental values for 2,4-D were carried out at pH 1 and 7. A pK_a range of 2.64–3.31 is reported for 2,4-D (Howard et al., 1991). The pH 1 conditions were used to see if the associated form of 2,4-D would have a higher HLC value than the disassociated form, which would be more abundant under neutral pH conditions. The hypothesis was found to be correct, e.g. the pH 1 HLCs for 2,4-D averaged 2.79×10^{-3} and the pH 7 determination was 3.5×10^{-4} . However, these values should be considered somewhat tentative at this time since only one determination was made at pH 7 and there was a great deal of uncertainty with the pH 1 values (RSD = 0.28). The agreement with the Suntio et al. (1988) calculated value for 2,4-D, however, was rather good, 3.5×10^{-4} (measured) versus 2.26×10^{-4} (calculated). It was assumed that calculated values of Suntio and associates were for neutral pH values.

The agreement of our WWC measurements versus earlier WWC determination made by Fendinger and associates was generally within expected experimental error, especially if a small temperature correction is used to adjust their values downward slightly. This, however, is not true for the respective trifluralin values, i.e. 4.23×10^{-3} versus the Fendinger et al. (1989) value of 2.4×10^{-3} . One possible explanation for these differences might be that we used concentrations ranging from 0.58 to 6 $\mu\text{g/L}$ or considerably less than the maximum solubility of trifluralin (500 $\mu\text{g/L}$; Suntio et al., 1988), while Fendinger and associates used values <50% of this maximum solubility (say 50–100 $\mu\text{g/L}$). We have also observed that trifluralin has a tendency to adsorb to surfaces, and differences in measured HLC values may be linked to the concentration differences noted above as well as surface sorption problems.

All of the HLC values for the salt solution were higher than their respective values in distilled water (Table 1). They varied by a factor of 1.5–2.4 depending on the compound. These results were similar to the range of 1.2–1.8 for data assembled by Schwarzenbach et al. (1993) for a group of organic compounds including PCBs and chloroform. This phenomenon is related to the "salting out" effect which impacts the water solubility

Table 3. Changes in Henry's Law Constants with Temperature Using Water Collected from the Arctic

source	water type ^b	TOC (ppm)	HLC ^a ± SE (replicates) at			linear fit log(HLC) vs temp (<i>R</i> ²)
			8.3 °C	20 °C	43.5 °C	
Trifluralin						
Bering	s surf	2.15	3.94 ± 0.15 (5)	5.39 ± 0.47 (5)	7.47 ± 0.23 (4)	0.989
	sml	3.14	3.53 ± 0.23 (5)	5.25 ± 0.31 (5)	7.45 ± 0.31 (4)	0.962
Chukchi	s surf	3.30	3.68 ± 0.19 (5)	5.03 ± 0.37 (5)	7.48 ± 0.17 (4)	0.992
	sml	45.5	3.30 ± 0.14 (5)	4.94 ± 0.21 (5)	7.37 ± 0.15 (4)	0.974
Arctic ice	surf	48.8	2.90 ± 0.22 (3)	4.08 ± 0.28 (3)	6.02 ± 0.83 (3)	0.985
Chlorpyrifos						
Bering	s surf	2.15	1.41 ± 0.33 (5)	1.70 ± 0.33 (5)	3.30 ± 0.11 (4)	0.978
	sml	3.14	1.18 ± 0.13 (5)	1.46 ± 0.15 (5)	3.03 ± 0.20 (4)	0.978
Chukchi	s surf	3.30	1.40 ± 0.20 (5)	1.74 ± 0.23 (5)	2.97 ± 0.11 (4)	0.993
	sml	45.5	1.22 ± 0.11 (5)	1.51 ± 0.11 (5)	2.85 ± 0.07 (4)	0.984
Arctic ice	surf	48.8	0.93 ± 0.08 (3)	1.10 ± 0.11 (3)	2.34 ± 0.20 (3)	0.966

^a For trifluralin, $\times 10^{-3}$; for chlorpyrifos, $\times 10^{-4}$. ^b Water types are as follows: s surf, subsurface; sml, surface microlayer; and surf, surface ice rather than deep ice.

and therefore the HLC value. Kucklick et al. (1991) compared artificial sea water and distilled water while studying the effect of temperature on the HLCs for α - and γ -hexachlorocyclohexane and observed similar effects. Gossett (1987) studied the relationship between ionic strength of KCl and HLCs for three low molecular weight chlorinated solvents (chloroform, tetrachloroethylene, and trichloroethylene) and verified the log relationship between HLC and salinity that was originally proposed by Setchenow (1889).

Natural Water Experiments. It is clear from the data in Table 2 that HLCs measured in natural water vary from determinations made in laboratory water. Even the highest salinity water from the Bering/Chukchi Sea (microlayer and subsurface water) had lower HLCs for trifluralin and chlorpyrifos than the laboratory-simulated sea water tests. Therefore, there appear to be other factors in the aqueous phase that favor retention of the pesticides in solution over loss to the vapor state. Several possibilities can be postulated. Dissolved organic matter is one likely factor since it was carefully excluded from the laboratory water experiments and it ranged from 2.15 to 3.3 mg/L for the subsurface water and from 3.1 to 46 mg/L for the microlayer samples. It has also been observed that ions (other than NaCl) which are natural to seawater can affect the activity coefficient of the solute; however, Schwarzenbach et al. (1993) pointed out that the effect was to increase this value (and increase the HLC), not to lower it as observed here. The ionization effects that were observed by Schwarzenbach were, however, shown to be compound dependent and there are no specific data to predict the effect of non-NaCl ions on the solubilities of trifluralin or chlorpyrifos. Suspended particulate material present in the natural water samples should act to increase the apparent solubilities of the compounds. Unfortunately, these measurements were only made for the Chesapeake Bay samples, and no obvious correlation between suspended matter and HLC was evident here.

For the Chesapeake Bay data in Table 2, it appears that there was a possible decrease in HLC related to the decrease in salinity. This trend was most evident for trifluralin. The equation for salting out [originally proposed by Setchenow (1889) in Schwarzenbach et al. (1993)] has the form, $\log \gamma = kI$ (γ is the symbol for the activity coefficient of the compound in water, k is the salting-out constant, and I is the molar concentrations of the respective salt) (Gossett, 1987). This log relationship can be represented as a similar log relationship of the HLC relative to the ionic strengths of solutions

tested here. The validity of this assumption is explicitly stated in the equation $K_H = \gamma_w V_w P^o$ (Schwarzenbach et al., 1993), where K_H is the dimensionless Henry's law constant, V_w is the molar volume of pure water, and P^o is the vapor pressure of the pure liquid. This equation states that HLCs are directly related to the activity coefficient of the compounds in water; therefore, they are interchangeable within the Setchenow equation as both are log related to the ion strength of the solution. By applying the linear equation relating log HLC and salt concentrations, HLCs for intermediate salinities were calculated using the observed zero and 33.3‰ salinity tests for the pesticides. Predicted values were closer to the observed values; however, all were slightly higher, e.g. for Pt. Lookout, MD, the HLC were 4.53×10^{-3} (observed) versus 5.13×10^{-3} (estimated) (Table 2). This again supports the possibility that there may be other unknown water parameters altering the HLC (generally lowering them) from values one would predict on the basis of simple NaCl ionic strength and temperature interactions.

Staudinger and Roberts (1996) discussed these "natural water matrix effects" in their recent review of HLC for environmental applications. Their conclusions were that these effects were minimal; however, most of the compounds they considered were more volatile and smaller molecular weight compounds such as benzene and toluene. The authors do, however, recognize that there can be multiple constituents in natural water that affect HLC values, i.e. pH, compound hydration, concentration, complex mixture effects, dissolved salts, suspended solids, DOM, and surfactants. The HLC values for endosulfan I in the Chesapeake Bay samples did not appear to follow any consistent trend. They did not consistently decrease with decreasing salinity, and the highest observed HLC for endosulfan I, 3.78×10^{-3} , was measured on the sample with the highest suspended solids concentration. This would suggest that the particulate matter in this sample did not increase the solubility of endosulfan I as expected. Normally, high particle concentrations would reduce HLC by increasing the apparent solubility through binding of the pesticide. One possible explanation is that the particulate matter in the water sample contained very little organic matter with which to bind the pesticides. Further conclusions could be made if the organic carbon content of the particles within the different samples had been measured; however, these data were not available. There were not enough data to statistically establish any correlation between HLC for subsurface water and

microlayer at each station versus these measured water parameters.

The changes in HLC versus temperature appeared to follow accepted theory in that all of the experimental determinations consistently showed an increase in HLC with an increase in temperature. This is clearly observed in Table 3 for all of the samples analyzed from the Bering/Chukchi Sea, including the melted Arctic ice sample. Also, these trends were consistent in the tests with distilled water (Figures 2 and 3) and the salt water tests (Figures 4 and 5). The linear least-squares fit values for these trends were variable depending on the water type and compounds (R^2 varied from 0.966 to 0.993) (Table 3 and Figures 2–5). A notable inconsistency of these data versus other data concerning temperature interactions with HLCs was the low slope values ["A" value in the equation $\log H = A(1/T) + B$] observed here, i.e. -768 trifluralin in Chukchi Sea water (Figure 4) and -916 and -873 for chlorpyrifos in the salt solution and Chukchi Sea water, respectively]. Recall that Staudinger et al. (1996) showed the lower range values to be -1700 . It would appear that salt contributes to this effect; however, it also appears that there is something in the natural Chukchi Sea water that also causes this effect. The data in Table 3 list the individual data for each of the temperature settings. Statistical tests for differences were carried out on all of the split samples between subsurface and microlayer. Only at the lowest temperature were the HLC values for surface water significantly different from the microlayer HLCs. Melted Arctic ice was significantly different for each pesticide when compared to the natural water samples. This was not surprising since these differences were likely caused by the large salinity differences in these samples. Also, HLC values for melted Arctic ice were lower than distilled water values at the 20°C test for trifluralin and chlorpyrifos; this again supports the premise that there are other factors present in natural waters that increase the apparent solubility in tests such as these.

Figures 4–7 suggest that assuming exact linearity of log HLCs versus temperature (especially at high salinities) may cause errors in extrapolation to the real world situations. Two plots (Figures 4 and 5) demonstrate this concept. There is an obvious nonlinear change in HLC versus temperature for trifluralin in the 33.3‰ NaCl solution experiment. A similar discrepancy was noted by Kucklick et al. (1991) for artificial sea water, especially for γ -HCH. Also, it appears that the natural water may buffer the drop in HLC that occurs with the salt solution at the lowest temperatures of 11.5 and 8.3°C (Figure 4). Deviation from linearity was also observed for chlorpyrifos in the salt solution (Figure 5); however, this nonlinearity behavior appears more random, cf. the values at 11.5 and 8.3°C . These errant values may be due to chemical reactivity of the pesticides under these test conditions. The natural water samples of subsurface waters from the Chukchi Sea each showed reasonable linearity relative to the log HLC versus temperature for trifluralin ($R^2 = 0.9919$) and chlorpyrifos ($R^2 = 0.9928$). The linearity plots for distilled water for these two compounds were also close to linearity (i.e. $R^2 = 0.9968$ for trifluralin, $R^2 = 0.9836$ for chlorpyrifos). The log HLC versus temperature measurements with microlayer samples had the largest variability of the natural samples tested, especially at the lowest temperature measurements. Student's t test for differences between sample types, i.e. microlayer

versus same-station-collected subsurface water showed that there was a significant difference ($p < 0.05$) for trifluralin at the Chukchi Sea sampling site only at the lowest temperature setting. The other striking difference in this one sample of microlayer was a very high TOC content, 46 ppm, versus that for the subsurface sample from this station, 3.3 ppm. This suggests that for this sample perhaps organic matter may have a role in increasing the apparent solubility of the pesticide and this effect is greater at lower temperatures. This feature could have a significant impact in Arctic regions where cold temperature conditions are common. Figures 6 and 7 show that the relationship between HLC and $1/T$ for chlorpyrifos and trifluralin is parallel except at the low temperatures; this pattern was also observed with the Bering Sea samples. Assuming that the temperatures below 20°C more closely represent the temperatures likely to be present in the Bering and Chukchi Seas, a linear model line was constructed for this range (Figures 6 and 7). These various HLC-versus-temperature fit lines and their corresponding equations can be used to derive site-specific temperature and salinity-corrected HLC values for the tested chemicals. For modeling exercises these can be very important values. It is extremely important to get site-specific data on the air–water gas exchange of these materials to predict their cycling into and out of these systems. It is likely also that the microlayer will be the first layer of the sea surface where these processes will be active; therefore, accurate determination of HLCs in this zone could be quite important.

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