

## Determination of Henry's Law Constants of Halogenated Current-Use Pesticides as a Function of Environmental Conditions.

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### Introduction & Objectives

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. Henry's Law Constants essentially predict air-water partitioning as follows:  $K_H = \frac{C_a}{C_w}$ . 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  $C_w$ . We modified the original wetted wall column (WWC) apparatus design<sup>1)</sup> by providing temperature control during the tests. Therefore we were able to study the effect of temperature on the HLC values. It is generally accepted that both vapor pressure and solubility of pesticides vary in activity inversely as temperature changes, and 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<sup>2)</sup>:  $\ln K_H = - \left[ \frac{\Delta H_{vap} - \Delta H_s^*}{R} \right] \frac{1}{T} + \text{constant}$ .  $H_{vap}$  is the change in enthalpy for vapor pressure and  $H_s^*$  is the enthalpy change for solubility;  $K_H$  is the term for the dimensionless Henry's law constant. Temperature was the major critical variable which was considered; however, natural waters vary in their inorganic salt composition and organic matter makeup. It was our intention to investigate these effects while varying the temperature for current-use pesticides, especially those with wide ranges in HLCs, and which differ significantly in other physical chemical properties.

Several recent publications have dealt with the use of HLCs for environmental predictions. McConnell et al.<sup>3)</sup> and Kucklick et al.<sup>4)</sup> reported on the importance of temperature for explaining flux of HCHs in natural environments. For PCBs, Ten Hulscher et al.<sup>5)</sup> derived a constant factor for temperature correction by determining HLC dependence for congeners from different homologue groups. Iwata et al.<sup>6)</sup> measured the temperature dependence of vapor pressure and solubility for PCBs in seawater and derived their HLCs from these values and Burkhard et al.<sup>7)</sup> have used several different methods to estimate representative HLC-determined temperature

several different methods to estimate representative HLC-determined temperature adjustments. These studies support the importance of the research discussed here.

## Approach & Methods

The HLCs were determined with the WWC by equilibrating the aqueous solutes (chlorpyrifos, trifluralin and endosulfan) in a thin liquid water film on the WWC column wall with a concurrent flow of air. The WWC determination made in this study were done with a 30-cm length column. Water collected from the WWC was passed through a C-18 extraction column. Air from the WWC was passed through columns packed with Chromosorb-102 resin. Dimensionless HLCs were calculated from analyzed concentrations in air and water determined from GC/MS analysis of the C-18 and Chromosorb-102 extracts. Four to six HLC measurements were made for each run.

The adsorbent columns were extracted using acetone/hexane solutions. The extracts were analyzed for Trifluralin and Chlorpyrifos on a HP model 5890 gas chromatograph equipped with an ECD detector and DB-5 fused silica capillary column. Endosulfan was analyzed on a HP model 5989A gas chromatographic mass spectrometer using negative chemical ion detection and a DB-5 fused silica capillary column.

Natural water and surface microlayer samples were sampled and tested from the Bering Sea (Anadyr Bay), Chukchi Sea (Kotzebue Sound) and the Chesapeake Bay (Pt Lookout -Potomac River mouth, Solomons - Patuxent River mouth, and Sandy Point). Melted Arctic ice was sampled and tested from the Chukchi Sea (Ice Edge - Central Chukchi). To investigate the effect of salt concentrations on HLCs, a water solution of NaCl (33.3‰) was used.

## Results and Conclusions

Using the WWC apparatus, the experimental Henry's law constant for technical endosulfan was determined to be close to the calculated value reported by Suntio et al.<sup>9)</sup>. However, when measuring the HLC values of the individual isomers, Endosulfan I and Endosulfan II, it was discovered that HLC for Endosulfan I was approximately 7 times higher than Endosulfan II. It is important to note that it was observed that Endosulfan II had a tendency to convert Endosulfan I during transfer across the air/water interface. This complicated our study of the environmental fate of the Endosulfan II isomer and needs further study to better understand the properties of the technical Endosulfan mixture. The temperature dependence of the HLCs for Endosulfan I is very regular, Fig. 1. The HLC's for technical Endosulfan and its isomers in salt water were all higher than in distilled water. This agrees with the affects of salinity on HLCs which were observed by Kucklick et al. for the hexachlorocyclohexane isomers<sup>4)</sup>.

Results for HLCs versus temperature on laboratory waters (distilled and simulated seawater) established that salinity significantly increased the HLC values for all three pesticides, Table 2. HLC determinations on sub-surface and microlayer samples collected at three shoreline locations on the Chesapeake Bay (CB) indicate that there were only slight differences between these samples and similar samples collected in the Bering/Chukchi seas. Correlations to parameters such as salinity,

particulate matter and total organic carbon (TOC) were attempted. However, none of these except salinity seemed to vary consistently with the HLC values at 20 °C. The salinities of these CB samples were quite a bit lower than the Bering and Chukchi sea samples; and correspondingly, it was noted that the HLCs were indeed closer to those measured in distilled water tests. The WWC determinations of HLCs for chlorpyrifos and trifluralin in natural waters collected from the Bering/Chukchi seas (sub surface, microlayer and melt ice) showed clear variations especially between the melt ice and the other natural samples, Table 3; and also clear differences between artificial seawater (33.3 ‰) and distilled water and the natural water samples, Figures 2 and 3.

The natural waters were studied by varying the temperature and observing changes in HLC, Table 3.. Several plots were performed relating the log of the HLC to the inverse plot of the temperature settings. These plots allowed several trends to be observed; two representative plots are shown, Figs 2 and 3. Following is a summary of some of these observations:

Apparent HLCs were reduced in microlayer samples relative to subsurface samples for some of the tests. For trifluralin, the lowest temperature (4°C) showed significant ( $p < 0.05$ ) change in HLC between the microlayer and subsurface sample. For chlorpyrifos, there was a uniform and often significant differences between the microlayer and the subsurface sample. The large organic carbon differences in these natural water samples had only minimal affects on the HLCs for either of the pesticides. The salt content of the marine water samples increases the apparent HLCs for chlorpyrifos and trifluralin when compared to HLCs for Arctic melt ice.

The variation in HLC with temperature are different for the two pesticides and appears to be correlated with the chemical properties of the pesticides. Apparently other aqueous-phase factors in addition to salinity and total organic carbon content control the HLC values for these pesticides.

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Table 1. Henry's law constants for technical Endosulfan and its enantiomers, Endosulfan I and Endosulfan II.

Henry's Law Constants for Endosulfan (20 °C).			
Chemical Form	HLC (Measured)		HLC (Literature)
	Distilled Water	Salt Water (33.3‰)	Distilled Water
Endosulfan, Technical	$2.65 (0.15) \times 10^{-3}$	$5.43(0.42) \times 10^{-3}$	$1.2 \times 10^{-3(8)}$
Endosulfan I	$2.72 (0.10) \times 10^{-3}$	$5.59(0.23) \times 10^{-3}$	Unknown vapor pressure
Endosulfan II	$0.36 (0.16) \times 10^{-3}$	$0.87(0.23) \times 10^{-3}$	Unknown vapor pressure

Figure 1. Variation in the HLC for endosulfan I versus temperature with distilled water.

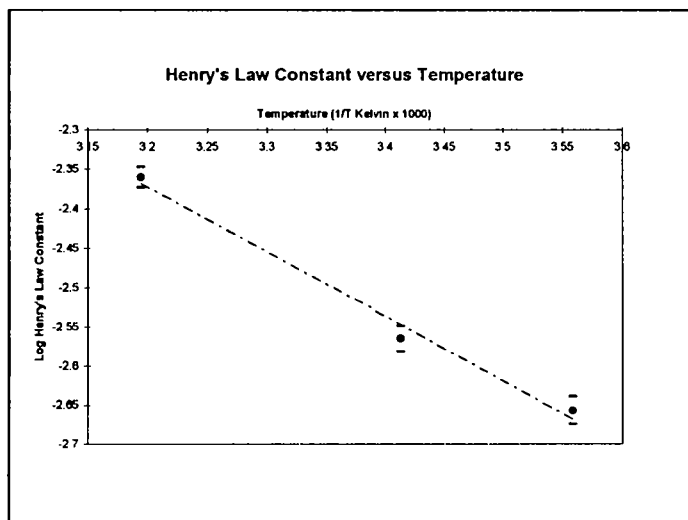


Table 2. Henry's law constants for samples from the Chesapeake Bay (20 °C).

Description	Sample	Date of	Salinity	Particulates	TOC	Trifluraline	Chlorpyrifos	Endosulfan I
	Type	Collection	(‰)	(mg/L)	(ppm)	(Henry's Law Constant x 10-3)		
<b>Laboratory Experiments</b>								
Distilled Water	Lab	-	0	0	0	4.23±0.15	0.12±0.01	2.70±0.10
Salt Water	Lab	-	33.3	0	0	6.18±0.22	0.24±0.06	5.29±0.23
<b>Arctic</b>								
Bering/Chukchi	sub-surface	Aug. 93	32.0	-	2.73	5.28±0.44	0.17±0.02	-
Bering/Chukchi	micro-layer	Aug. 93	-	-	(3.1-46)	5.10±0.30	0.15±0.01	-
<b>Chesapeake Bay</b>								
Pt. Lookout, MD	sub-surface	2-Nov-94	17.0	16	1	4.53±0.26	0.15±0.02	3.35±0.22
Solomons, MD	sub-surface	2-Nov-94	16.0	7	0.6	4.40±0.18	0.16±0.03	3.30±0.24
Sandy Point, MD	sub-surface	2-Nov-94	12.0	320	0.6	4.13±0.99	0.14±0.01	3.78±0.64
<b>Chesapeake Bay (continued)</b>								
Pt. Lookout, MD	micro-layer	2-Nov-94	17.0	30	0.4	4.58±0.22	0.15±0.03	3.55±0.31
Solomons, MD	micro-layer	2-Nov-94	16.0	13	0.5	4.50±0.22	0.14±0.02	3.60±0.18
Sandy Point, MD	micro-layer	2-Nov-94	12.0	6	0.6	4.35±0.10	0.13±0.04	2.98±0.33

Table 3. Changes in Henry's Law Constants with temperature using water collected from the Arctic.

<b>TRIFLURALIN</b>					
Source	Water Type	Henry's Law Constant x 10-3			TOC
		4°C	20°C	50°C	ppm
Bering	sub-surface	3.94±0.15	5.39±0.47	7.47±0.23	2.15±0.15
	surface microlayer	3.53±0.23	5.25±0.31	7.45±0.31	3.14±0.23
Chukchi	sub-surface	3.68±0.19	5.03±0.37	7.48±0.17	3.30±0.22
	surface microlayer	3.30±0.14	4.94±0.21	7.37±0.15	45.5±4.5
Arctic Ice	upper layer	2.90±0.22	4.08±0.28	6.02±0.83	48.8±6.7

<b>CHLORPYRIFOS</b>					
Source	Water Type	Henry's Law Constant x 10-4			TOC
		4°C	20°C	50°C	ppm
Bering	sub-surface	1.41±0.33	1.70±0.33	3.30±0.11	2.15±0.15
	surface microlayer	1.18±0.13	1.46±0.15	3.03±0.20	3.14±0.23
Chukchi	sub-surface	1.40±0.20	1.74±0.23	2.97±0.11	3.30±0.22
	surface microlayer	1.22±0.11	1.51±0.11	2.85±0.07	45.5±4.5
Arctic Ice	upper layer	0.93±0.08	1.10±0.11	2.34±0.20	48.8±6.7

Figure 2. Variation in HLC versus temperature for chlorpyrifos when measured using natural water samples.

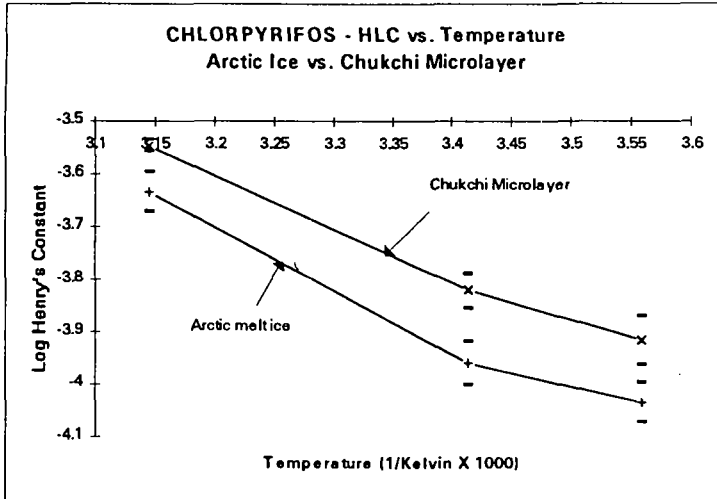


Figure 3. Variation in HLC versus temperature for trifluralin when measured using natural water samples.

