

**MEASUREMENT OF HENRY'S LAW CONSTANT
OF ORGANOCHLORINATED PESTICIDES**

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**by
Serdar Özer**

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İZMİR**

We approve the thesis of **Serdar ÖZER**

Date of Signature

.....

26 June 2005

Assist. Prof. Dr. Aysun SOFUOĞLU

Supervisor

Department of Chemical Engineering

İzmir Institute of Technology

.....

26 June 2005

Assoc. Prof. Dr. Funda TIHMINLIOĞLU

Department of Chemical Engineering

İzmir Institute of Technology

.....

26 June 2005

Assoc. Prof. Dr. Mustafa ODABAŞI

Department of Environmental Engineering

9 September University

.....

26 June 2005

Prof. Dr. Devrim BALKÖSE

Head of Department

İzmir Institute of Technology

.....

Assoc. Prof. Dr. Semahat ÖZDEMİR

Head of the Graduate School

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ABSTRACT

Most of the semi-volatile organic compounds, which are environmentally important, are subject to long range atmospheric transport due to their chemical and physical properties. Their vapor pressure, solubility and indirectly Henry's law constants are the most important parameters defining their fate during transport of these compounds. Especially in the air-water exchange process, Henry's law constant plays an important role. Therefore accurate and direct measurement of the Henry's law constant are required for the most of the compound present in the environment. In this study 17 organochlorine pesticides' Henry's law constants were measured by a dynamic equilibration method at 5, 15, 20, 25 and 35°C in deionized water. The salinity effect on Henry's law constant of these compounds were investigated by using 3% NaCl solution at 15 and 25°C.

For all compounds Henry's law constant showed 90% increases in every 10°C temperature change in deionized water. In the saline water experiments, the H values increased by an average 107% from 15°C to 25°C. The variation in H with temperature was expressed using the van't Hoff type Gibbs-Helmholtz equation. Calculated enthalpy of phase change for each compound, which helps to describe how sensitive is the partitioning between air and water, within the range of the values reported in the literature. The lowest enthalpy of phase change was obtained for heptachlor (26.38 ± 7.72 kJ/mole) and the highest for γ -chlordane (63.32 ± 3.04 kJ/mole). In Gibbs-Helmholtz plots, H values of a compound in saline water were always higher than the H values of that compound in deionized water. Therefore, it was concluded that in the saline water, the air-water partition of these chemicals is shifted to air phase.

ÖZET

Çevresel açıdan önemli birçok yarı uçucu organik bileşik, fiziksel ve kimyasal özelliklerine bağlı olarak uzun mesafeli taşınımına maruz kalmaktadır. Bu bileşiklerin buhar basınçları, çözünürlükleri ve dolaylı olarak Henry sabitleri uzun mesafeli taşınımları sırasındaki kaderlerini belirleyen en önemli parametrelerdir. Özellikle hava-su taşınımı sürecinde Henry sabiti büyük rol oynamaktadır. Bu yüzden Henry sabitinin doğru ve direkt ölçümü gereklidir. Bu çalışmada, 17 değişik organoklorlu pestisitlerin Henry sabitleri deiyonize suda 5, 15, 20, 25 ve 35°C sıcaklarında ve yapay deniz suyunda (3% NaCl) 15 ve 25°C sıcaklıklarında dinamik denge metodu ile ölçülmüştür.

Deiyonize suda tüm bileşikler için Henry sabiti her 10°C yükselişte ortalama %90 artmıştır. Tuzlu suyla yapılan deneylerde, Henry sabitleri 15 ve 25°C dereceleri arasında %107 artmıştır. Organoklorlu pestisitlerin Henry sabitinin sıcaklık bağımlılığı Gibbs-Helmholtz denklemi ile incelenmiştir. Hava ve sudaki dağılımın hassasiyetini anlamaya yardımcı olan faz değişim entalpileri hesaplanmış ve bu değerlerin literatürde bildirilen değerlerle aynı aralıkta olduğu saptanmıştır. Ölçülen en düşük ve en büyük faz değişim entalpisi sırasıyla heptachlor (26.38 ± 7.72 kJ/mol) ve γ -chlordane (63.32 ± 3.04 kJ/mol) için bulunmuştur. Gibbs-Helmholtz grafiklerinde her bileşik için tuzlu sudaki Henry sabitlerinin, deiyonize sudaki Henrysabitlerinden daha yüksek olduğu gözlenmiştir. Sonuç olarak bileşiklerin tuzlu suda, hava-su dağılımının hava fazına kaydığı sonucuna varılmıştır.

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CHAPTER 1

INTRODUCTION

Many organochlorinated pesticides (OCPs) present in the atmosphere and surface waters, detected often far from their original site of application. These chemicals have been found to be widely distributed in the atmosphere because of their moderate vapor pressure, low solubility and low reactivity.

Gas exchange of OCPs is a major pathway of atmospheric deposition among oceans, seas and lakes (Sahsuvar et al. 2003). In these processes Henry's law constants (H) of the compounds, which represents the partitioning between the gas and aqueous phase, are an important physical property to understand and predict the behaviour of a component in the environment.

Therefore accurate knowledge of a chemicals' H and how changes with environmental conditions, including temperature and ionic strength, is essential to predict the environmental behavior, transport, and fate of many classes of organic chemicals. Several methods have been described to obtain H values of different compounds. When direct measurement is not possible or data not available H has been estimated by using vapor pressure and aqueous solubility of a compound. For this estimation H is calculated solid or liquid phase vapor pressure and solubility assuming H to be constant at lower pressure and solubilities. If vapor pressure and solubility data do not refer to the same state, or if the solubility of water in the liquid is large results may not be reliable. Therefore measuring H values directly may result more reliable values of H (ten Hulscher et. al 1992).

In the literature, reported H values of these compounds should be taken into account for the different measurement techniques (Altschuh et al. 1999, Rice et al. 1997, Sahsuvar et al. 2003, Jantunen and Bidleman 2000, Kucklick et al. 1991) and one should note that most of them are quoted only at one temperature or with no indication of the temperature. Since the effective environmental modeling must take into account the effect of the temperature variations. Mackay et al. (1979) estimated that the H of organic compounds will approximately double between 10°C to 65°C. In addition to the effect of temperature on air-water partitioning of these compounds in real

environment (e.g. oceans, salt lakes) the amount of dissolved inorganic salts have an significant effect on H values (Staudinger and Roberts 2001, Schwarzenbach et al. 2003, Kucklick et al. 1991, Xie et al. 1997, Gossett 1987, Peng and Van 1998, Rice et al. 1997). Staudinger and Roberts (2001) reviewed 197 organic compounds and reported an average 88% increase per 10°C rise in temperature. Schwarzenbach et al. (2003) reported that at a moderate salt concentrations typical for seawater (~0.5M), the aqueous solubility (or the aqueous activity coefficient hence H value) was affected for these compounds by a factor of about 3.

In this study dynamic head space method was used. In this method an dynamic equilibrium has been established in a rising bubble between concentrations of the water phase in a stripping column and the air phase in the bubble. Henry's law constant is obtained by the ratio of measured concentrations in the gas phase and the aqueous phase. Advantage of this method is that the measurement of gas phase concentration by accumulating chemicals in a resin column makes easier to obtain H values of relatively less volatile chemicals by increasing purging time. Dynamic head space method has been accepted in the literature, for the friendly experimental set-up, guaranteed achievement of equilibrium of compounds and relatively small loss amount of compounds due to adsorption to the walls (Sahsuar et al. 2003, Bamford et al. 2000, Bamford et al. 1999). In the literature some of the pesticides H values either are not available or the method used for the H values is not directly measured value for a specific compound.

The objective of this study was to measure Henry's law constants of a group of organochlorine pesticides in distilled water and in artificial sea water at temperate temperature ranges by dynamic head space method. Specific objectives of this research were:

- To determine temperature effect on Henry's law constants of OCPs
- To investigate the effect of salinity on Henry's law constant of OCPs.
- To calculate phase change enthalpies of these compounds.

This thesis is divided into five different chapters. The first chapter is an overview and objectives of the study. The second chapter reviews concepts and previous studies in the literature. The third chapter presents materials, methods, and analysis, and quality assurance/quality control applications.

Results and discussions are presented in the fourth chapter. In the fifth chapter the conclusions drawn from this research and recommendations for possible future work are given.

CHAPTER 2

LITERATURE REVIEW

This chapter introduces the structures, properties, sources, environmental fate of OCPs as they are reported in the literature. In addition, the methods of measuring Henry's law constants of related chemicals are going to be examined.

2.1. Chemical Structure and Properties of OCPs

OCPs are a group of synthetic organic chemicals that contain carbon (thus *organo-*), hydrogen, and chlorine. Most of the OCPs are banned products, but they still travel around due to residues present in the environment. Most of these chlorinated compounds were detected in the snow, icecaps of Arctic and Antarctic environment. Therefore, they are the concern of the researchers. The list of industrial and chlorinated compounds which were Arctic environmental concern in 1996 listed by Macdonald et al. (2000) is given in Table 1.

Table 1. Environmentally concerned chlorinated compounds in the Arctic.

Aldrin, dieldrin, endrin
Chlorobornanes, toxaphene
Chlordane
Dichlorodiphenyltrichloroethane (DDT)
Dichlorodiphenyldichloroethene (DDE)
Endosulfans
Methoxychlor
Hexachlorocyclohexanes
Mirex
Trifluralin

These compounds are chemically persistent and semivolatile chemicals. Their vapor pressures are sufficiently high to cause appreciable evaporation over a period of weeks to years, enabling the compounds to cycle between gaseous and condensed

phases in the environment. The presence of chlorine in the organic molecule tends to enhance persistence (Macdonald et al. 2000).

Organochlorinated pesticides can be grouped into several classes. The most investigated and environmentally of interest groups are diphenyl aliphatics, hexachlorocyclohexanes and cyclodienes (WEB_1 2005).

The oldest group of the OCPs is the diphenyl aliphatics, which included DDT and metabolites, dicofol, ethylan, chlorobenzilate, and methoxychlor. DDT (Figure 1) is probably the best known and most notorious chemical of the 20th century. More than 4 billion pounds of DDT were used throughout the world, beginning in 1940, and ending essentially in 1973, till the U.S. Environmental Protection Agency canceled all uses. The remaining first world countries rapidly followed suit (WEB_1 2005).

The mode of action for DDT has never been clearly established, but in some complex manner it destroys the delicate balance of sodium and potassium ions within the axons of the neuron in a way that prevents normal transmission of nerve impulses, both in insects and mammals. It apparently acts on the sodium channel to cause "leakage" of sodium ions. Eventually the neurons fire impulses spontaneously, causing the muscles to twitch-- "DDT jitters"-- followed by convulsions and death. DDT has a negative temperature correlation--the lower the surrounding temperature the more toxic it becomes to insects (WEB_1 2005).

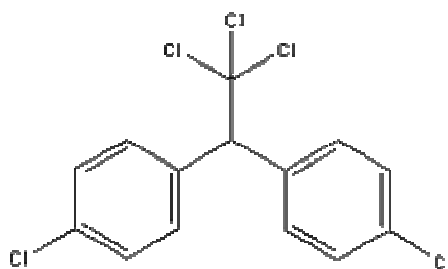


Figure 1. The structure of DDT.

The other commonly used group of pesticide is the hexachlorocyclohexane (HCH), and the insectal properties of HCHs were discovered in 1940 by French and British entomologists. Technical-grade HCH, there are five isomers, α - (60-70%), β - (5-12%), γ - (10-15%), δ - (6-10%) and ϵ - (3-4%). This mixture is marketed as an

inexpensive insecticide, but since γ -HCH is the only isomer that exhibits strong insecticidal properties, it has been common to refine it from technical HCH and market it under the name “lindane”. However all commercially produced lindane contains trace amounts of other isomers (Walker et al. 1999).

All isomers of HCH exhibit relatively high water solubilities and moderately high vapor pressures when compared to other OCPs. Therefore, HCH is usually present in the environment as a gas in the atmosphere or dissolved in water, with only a small percentage adsorbed into particles (Li et al. 2002).

The physical and chemical properties of HCH vary between isomers (Willett et al. 1998). The vapor pressure of α -HCH is somewhat less than that of γ -HCH. α -HCH has also been shown to be slightly more lipophilic than γ -HCH. The Henry’s law constant for α -HCH is about twice as high as that of γ -HCH, so α -HCH is more likely to partition to the air. Another important difference among the isomers is the persistence of the β -HCH isomer which is resistant to environmental degradation. It is also more lipophilic than the other isomers (Walker et al. 1999). Since only γ -HCH have been produced and used through the world, there is a potential for γ -HCH to be transformed into other isomers of HCH. The high relative concentrations of α -HCH in the Arctic suggest that γ -HCH may be transformed into other isomers in the environment (Walker et al. 1999).

β -HCH is the most persistent and bioaccumulative of the isomers and a possible endocrine disruptor. All the HCH isomers are acutely toxic to mammals. In addition, chronic exposure has been linked to a range of health effects in humans, including immunosuppression and neurological problems, and has been shown to cause liver cancer in rats and mice (Willett et al. 1998). Of the different isomers, α -HCH exhibits the most carcinogenic activity and has been classified along with technical-grade HCH as a Group B2 probable human carcinogen by the U.S. EPA (Walker et al. 1999). As the most metabolically stable isomer, β -HCH is the predominant isomer accumulating in human tissues (Willett et al. 1998).

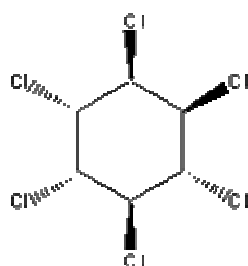


Figure 2. The structure of lindane.

The cyclodienes appeared after World War II: chlordane (CHL), 1945 (Figure 3); aldrin and dieldrin, 1948; heptachlor, 1949; endrin, 1951; mirex, 1954; endosulfan, 1956; and chlordecone, 1958 (WEB_1 2005). Technical chlordane is a complex mixture of chlordanes, nonachlors, heptachlor and other components (Dearth and Hites 1991, Mattina et al. 1999).

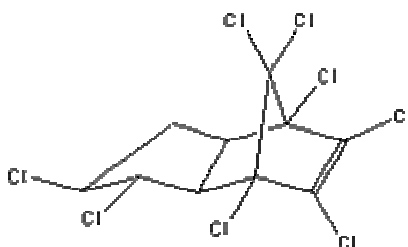


Figure 3. The structure of chlordane.

Endosulfan has a wide range, contact and stomach insecticide, which is effective against numerous insects. Endosulfan exists as two isomers. The technical formulation is approximately 70% endosulfan I (α -endosulfan) and 30 endosulfan II (β -endosulfan) which is still in use in Turkey (Burgoyne and Hites 1993). There were other cyclodienes of minor importance developed in the U.S. and Germany.

Most of the cyclodienes are persistent insecticides and are stable in soil and relatively stable to the ultraviolet of sunlight. Unlike DDT and HCH, the cyclodienes have a positive temperature correlation – their toxicity increases with increases in the surrounding temperature (WEB_1 2005). Structure, important physical and chemical properties OCPs which are going to be discussed here are given in Table 2. The

properties are given to represent each pesticide and values are given at 25°C. Their melting temperatures and boiling temperatures range between 50-230°C and 135-390°C, respectively (WEB_1 2005).

Table 2. Physical properties of Organochlorine Pesticides (WEB_2 2005).

	Molecular Weight g/mole	Water Solubility mg/L	Vapor Pressure mm Hg	H value Pa.m ³ /mole	References for H values
α-HCH	290.8	2.00×10 ⁻²	4.50×10 ⁻⁵	1.24	Altschuh et al. 1999
γ-HCH	290.8	7.30×10 ⁻²	4.20×10 ⁻⁵	0.52	Altschuh et al. 1999
β-HCH	290.8	5.00×10 ⁻²	3.60×10 ⁻⁷	0.04	Altschuh et al. 1999
δ-HCH	290.8	2.13×10 ⁻¹	3.52×10 ⁻⁵	0.04	VP/SOL
p-p'-DDT	354.4	1.70×10 ⁻⁵	1.60×10 ⁻⁷	0.84	Altschuh et al. 1999
p-p'-DDD	320	1.60×10 ⁻³	1.35×10 ⁻⁶	0.67	Altschuh et al. 1999
p-p'-DDE	318	1.30×10 ⁻⁵	6.00×10 ⁻⁶	4.22	Altschuh et al. 1999
Endosulfan I	406.9	5.30×10 ⁻³	3.00×10 ⁻⁶	0.72	Altschuh et al. 1999
Endosulfan II	406.9	2.80×10 ⁻³	ND	ND	ND
Chlorpyrifos	350.6	1.12	2.03×10 ⁻⁵	0.30	VP/SOL
Aldrin	364.9	1.80×10 ⁻³	1.20×10 ⁻⁴	4.46	Altschuh et al. 1999
Dieldrin	380.9	2.00×10 ⁻³	5.89×10 ⁻⁶	1.01	Altschuh et al. 1999
Endrin	380.9	2.60×10 ⁻³	3.00×10 ⁻⁶	0.64	Altschuh et al. 1999
γ-CHL	409.7	5.60×10 ⁻⁴	9.75×10 ⁻⁶	4.92	VP/SOL
α-CHL	409.8	5.60×10 ⁻²	3.60×10 ⁻⁵	35.16	VP/SOL
t-Nonachlor	444.2	8.22×10 ⁻³	1.00×10 ⁻⁶	2.51	VP/SOL
c-Nonachlor	444.2	ND	ND	ND	ND
Heptachlorepoxyde	389.3	2.75×10 ⁻³	1.95×10 ⁻⁵	2.13	Altschuh et al. 1999
Heptachlor	373.3	1.80×10 ⁻³	4.00×10 ⁻⁴	29.79	Altschuh et al. 1999
Endosulfan sulfate	422.9	1.17×10 ⁻³	2.80×10 ⁻⁷	0.03	VP/SOL
Endrinaldehyde	382.9	ND	ND	ND	ND
Endrin ketone	ND	ND	ND	ND	ND
Metoxychlor	345.6	1.00×10 ⁻³	2.58×10 ⁻⁶	0.02	Altschuh et al. 1999

ND: Not Defined, VP/SOL: Estimated H values

2.2. Sources of Organochlorinated Pesticides

OCPs were extensively used in agriculture from the 1950s to the 1970s. Some have been used longer than others, and some, such as lindane, chlorpyrifos, and endosulfan are still in use. Several OCPs, including HCB, DDT, chlordane, heptachlor, dieldrin, and endrin, are among the first persistent organic pollutants (POPs) to be subjected to global restrictions in the Stockholm Protocol. Because of their high stability, OCPs can remain unchanged for a long time in the environment. Early measurements detected OCPs in a wide range of environmental compartments, even in remote regions far from the original site of application (Shen and Wania 2005). In Table 3, estimated global usage of some OCPs are given based on the study of Macdonald et al. (2000).

Table 3. Best estimates of global usage of selected major organochlorine pesticides.

	Period of time	Estimated total global usage (Mt)
DDT	1950 – 1992	2.6
Lindane	1950 – 1992	0.72
Technical HCH	1948 – 1997	10.0
Chlordane	1945 – 1988	0.078
Aldrin	1950 – 1992	0.50
Dieldrin	1950 – 1992	0.034
Endosulfan	1956 – 1992	0.057

In Table 3, the global usage of these compounds are created by using historical, present and predicted usage or sales of these compounds. The inventory of historic use of many of these is still incomplete and further emission estimates on a country wide basis is needed to aid in assessing the role of long-range atmospheric transport and for three-dimensional models of the global movement of pesticides (Macdonald et al. 2000).

Technical chlordane was produced from 1945 until its withdrawal from the world market in 1997, chlordane was used for agriculture, on home lawns and gardens and to treat house foundations for termite protection (Mattina et al. 1999). All cyclodienes were used in greatest quantity as soil insecticides (especially chlordane, heptachlor, aldrin, and dieldrin) for the control of termites and soil-borne insects whose larval stages feed on the roots of plants. The cyclodienes were the most effective, long-

lasting and economical termiticides ever developed. Because of their persistence in the environment, resistance that developed in several soil insects, and in some instances biomagnification in wildlife food chains, most agricultural uses of cyclodienes were canceled by the EPA between 1975 and 1980, and their use as termiticides canceled in 1984-88. (WEB_1 2005).

The usage of technical HCH in China, for instance, was primarily concentrated in the south-eastern part, with no usage in Tibet. The major pesticide use areas in the former Soviet Union include Russia, Ukraine, and the republics of middle Asia. Use of toxaphene in the United States was primarily concentrated in the south-eastern part of the country, and very little or none was used in the state of Alaska. The usage data, based on countries, will only be of limited usefulness unless they are assigned to proper use areas (Breivik et al. 2004).

The main source of these compounds either transport of previously contaminated areas or still being used areas to the atmosphere. Their use in warm climates enhances their global mobility. While some use of these compounds continues, their production and use is in decline and international negotiations are underway to eliminate 12 persistent compounds worldwide, eight of which are pesticides (Rodan et al. 1999). It has long been recognized that OCPs are reaching the Arctic and accumulating in ecosystems (Holden and Marsden 1967, Bowes and Jonkel 1975). Local or regional sources cannot explain the presence of many of these compounds, especially the OCPs that are used outside the Arctic.

2.3. Fate of OCPs in the Environment

As discussed before, persistent organic pollutants (POPs) which is the general name for the most of semivolatile organic compounds like PCB, PAH, and OCPs are resistant to photolytic, biological and chemical degradation so that they are capable of long-range transport. As a result of this phenomenon they have become ubiquitous. They were detected even in the Arctic in 1960s and 1970s where they have never been used or manufactured (Vallack et al. 1998). Atmosphere is the major pathway for the transport and deposition of POPs to ecosystems both far and near source areas. Due to their lipophilic property they are able to accumulate in the ecosystem, and they can also

be released back to the atmosphere by some environmental processes which will be discussed later (Wania and Mackay 1996, Brorström and Löfgren 1998).

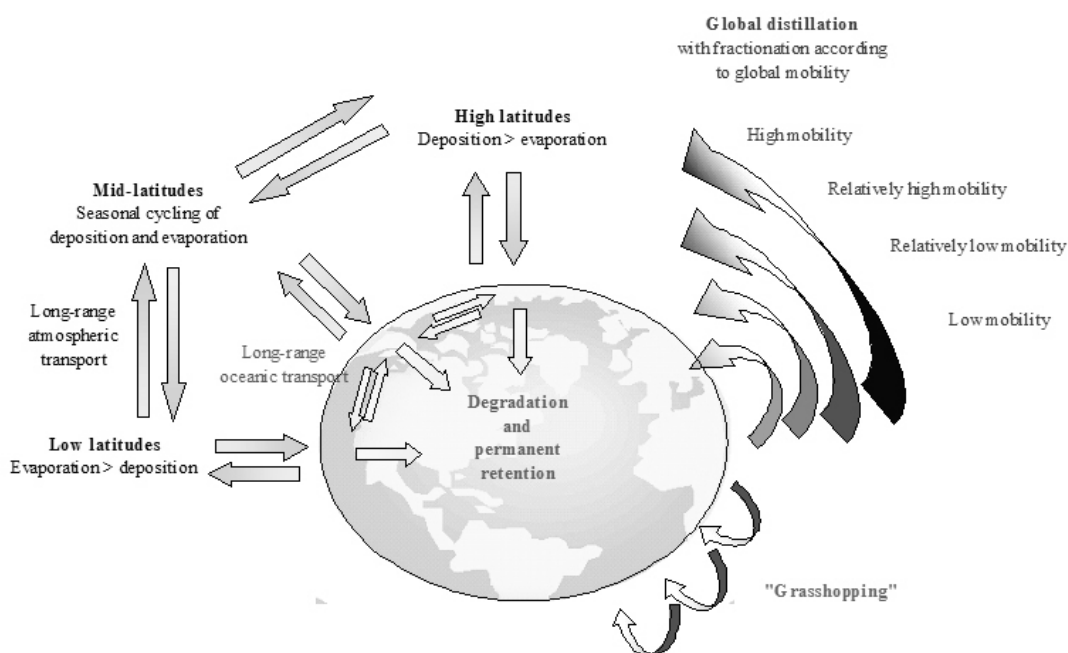


Figure 4. Transportation of POPs (adopted from Vallack et al. (1998)).

POPs have tendency to migrate from warmer regions and deposit in polar regions. This is explained with their moderate volatility and ambient temperature, meaning that POPs tend to volatilize from tropical and temperate regions of the globe, and condense, and then tend to remain in colder regions. The concentration of volatile compounds is thus low in tropical areas, and higher in temperate or Polar Regions (Wania and Mackay 1996). In Figure 4, the schematic view of migration process is summarized.

It has been suggested that POPs migrate to higher latitudes in a series of short jumps, called as “grasshopper effect”, whereby they migrate, remain in the atmosphere and migrate again with seasonal temperature changes at mid-latitudes. Another suggestion is, more highly volatile POPs will tend to remain airborne and migrate faster and further towards the Polar Regions than the less volatile ones. While the cooler conditions favor greater adsorption onto atmospheric particulate matter and promote enhanced adsorption from the vapor phase onto environmental surfaces (e.g. vegetation, water, soil, snow and ice), deposition is the dominating mechanism over evaporation in

polar regions and it is opposite in low latitudes (Vallack et al. 1998, Jones and Voogt 1999).

The properties of OCPs that are key to understanding their movement through the environment include the aqueous solubility, vapor pressure, octanol-water partition coefficient, Henry's law constant, octanol-air partition coefficient, and solubility in octanol (Shen and Wania 2005). Some of these are strongly dependent on temperature. Water temperatures range from approximately 30°C in the equator to -1.7°C in the polar regions. Air temperatures vary seasonally, latitudinally and with altitude from approximately -90°C to 50°C. Thus, the complexities of environmental transport and air-surface exchange cannot be understood without global models that include the temperature dependence of these physicochemical properties.

2.4. The Henry's Law Constant

Henry's law constant represents the air-water equilibrium partition coefficient for a particular chemical compound present in a dilute aqueous solution. It is a key physical property with respect to the compound's behavior and fate in the environment (Staudinger and Roberts 2001).

In dilute solutions of water, the activity coefficient can be assumed different than 1 for the many compound of interest over the concentration range considered, is constant. So that, the equilibrium condition between an aqueous phase and a gas phase can be written as a form known as Henry's law (Schwarzenbach et al. 2003):

$$p_i = \gamma_i \cdot x_i \cdot p_i^* = K_i' \cdot x_i \quad (2.1)$$

$$K_i = \frac{p_i}{x_i} = \gamma_i \cdot p_i^* = \text{constant} \quad (2.2)$$

Where p_i , p_i^* , x_i , γ_i and K_i' denote partial pressure, equilibrium partial pressure, mole fraction, activity coefficient, and Henry's law constant as a partial pressure and mole fraction basis respectively.

Other common ways of expressing air-liquid equilibrium partitioning are to use molar concentrations, either only in the liquid or in both the liquid and the gas phase. In

the first case, we simply have to convert mole fractions to molar concentrations: The Henry's law constant is often expressed either with dimensions of (pressure·volume)/mass (Schwarzenbach et al. 2003):

$$H = p_g / C_w \quad (2.3)$$

where p_g is the gas-phase partial pressure and C_w is the dissolved concentration in units of mass of chemical per volume of water. Furthermore, we should point out that, not only in the engineering literature, but also in many handbooks, H values are often given in units of (Pa·m³/mol).

In this case, the liquid phase concentration is in units of (mol/m³). No matter in what units we express for this parameter, it always reflects the same relative concentrations of the partitioning chemical in the gaseous and liquid phases.

For practical applications, such as for assessing the equilibrium distribution of a given compound in a multiphase system, it is most convenient to use a "dimensionless" air-solvent partition constant. This form uses molar concentrations in both phases. In this case, we denote the air-liquid partition constant as H' . Since $C_g = p_g / RT$, we then obtain the dimensionless Henry's law constant (Schwarzenbach et al. 2003):

$$H' = C_g / C_w \quad (2.4)$$

where the gas-phase concentration (C_g) is expressed in units of mass of chemical per volume of air. Both forms are approximations of the Henry's law constant which assume that C_w is equal to a compound's mole fraction at infinite dilution. H and H' are related by (Schwarzenbach et al. 2003):

$$H' = H / RT \quad (2.5)$$

where R is the ideal gas constant and T is the absolute temperature.

Henry's law is enough to understand air-water equilibrium partitioning of neutral organic compounds and the only required is to know how environmental factors affect the vapor pressure and the aqueous activity coefficient of a given compound

(Schwarzenbach et al. 2003). Staudinger and Roberts (1996) reported the factors effecting H beside temperature, pH, compound hydration, compound concentration and complex mixture effects, dissolved salts, suspended solids, dissolved organic materials, and surfactants. Effect of suspended solids has been investigated through measurement of octanol-water partitioning and only reported main effects are temperature and salinity on air-water partitioning (Schwarzenbach et al. 2003).

2.4.1. Effect of Temperature

It has been known that H values of compounds have a strong relationship with ambient air temperature (Cortes et al. 1998, Hoff et al. 1998, Honrath et al. 1997, Sofuoglu et al. 2001). As the temperature rises, air concentrations increase as a result of volatilization from surfaces such as soil, atmospheric particles, water, and vegetation due to increasing vapor pressure of compounds and consequently resulting in increasing H values.

The processes of volatilization, deposition, transport and transformation for these atmospheric chemicals respond to variations in ambient temperature. This is an important factor for understanding the distribution and movement of POPs far from areas where they are discharged (Gouin et al. 2002). At high temperatures, the air gas phase concentrations increase indicating that volatilization from the Earth's surface (e.g. vegetation, soil, water, etc.). The temperature dependence of H is described by the equation (Schwarzenbach et al. 1993, Bamford et al. 2000):

$$-RT \ln H' = \Delta H_H - T\Delta S_H \quad (2.6)$$

where ΔH_H and ΔS_H are the enthalpy and entropy of the phase change from the dissolved phase to the gas phase. Solving for the term $\ln H'$ yields the Gibbs-Helmholtz equation (Bamford et al. 2000):

$$\ln H' = -\Delta H_H / RT + \Delta S_H / R \quad (2.7)$$

assuming ΔH_H and ΔS_H are independent of temperature (a reasonable assumption over small temperature ranges), this equation describes the dependence of H on temperature.

By directly measuring H at different temperatures and plotting $\ln H'$ versus $1/T$, ΔH_H and ΔS_H are determined from the slope and intercept, respectively.

Historically, the availability of directly measured values for H has been lacking, particularly with respect to establishing its exact dependence on temperature. Staudinger and Roberts (2001) reviewed H values of 197 organic compounds and reported that the average slope of the temperature dependence line ($\Delta H_H/R$ term in Equation 2-7) is 2145 K, while values ranged overall from 128 to 4595 K. These values correspond to an average increase in H by a factor of 1.88 per 10°C rise in temperature, with the overall range of increase seen being from a factor of 1.12 to 3.55 per 10°C rise. Thermodynamically, the slope values found translate to an enthalpy of volatilization of 46.8 kJ/mole on average, with an overall range spanning from 8.2 to 93.3 kJ/mole.

The temperature effect of H in different compounds belong to same structural group may varies. For example, in the polycyclic aromatic hydrocarbons (PAHs), the temperature dependence of H varies 65% between different PAH compounds (Bamford et al. 2000). Therefore it is important to measure Henry's law constant of a specific compound in a wide temperature range.

2.4.2. Effect of Dissolved Inorganic Salts

The effects of dissolved inorganic salt(s) on aqueous solubilities, and activity coefficients of compounds must be considered. Qualitatively, it has been observed that the presence of the predominant inorganic species found in natural waters (i.e., Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , HCO_3^- , SO_4^{2-}) generally decrease the aqueous solubility (or increase the aqueous activity coefficient) of nonpolar or weakly polar organic compounds. This phenomenon is termed the salting-out effect, and depends on the compound and on the type of ions present (Schwarzenbach et al. 2003, Xie et al. 1997).

As a consequence, the change in solubility due to the salting-out effect requires the utilization of Henry's law constants in environmental modeling by adjusting these constants to represent the environmental conditions with dissolved ions, particularly for organic compounds (Rice et al. 1997).

Over a century ago, Setschenow (1889) established an empirical formula to describe salting-out effect:

$$\ln \frac{\gamma}{\gamma_0} = \ln \frac{C_{w0}^{\text{sat}}}{C_w^{\text{sat}}} = k_s C_s \quad (2.8)$$

where γ_0 and γ are the activity coefficients of the organic solute in water and salt solutions respectively, C_{w0}^{sat} and C_w^{sat} are the solubilities of the solute in water and salt solutions respectively, k_s is the ‘‘Setschenow’’ or ‘‘the salting-out constant’’ and C_s is the molar concentration of the salt solution (Xie et al. 1997). The salting constant relates the effectiveness of a particular salt or combination of salts to the change in solubility of a compound. It is valid for a particular salt or salt mixture over a wide range of salt concentrations. Note that the ‘‘salting-out’’ effect increases exponentially with increasing salt concentration and k_s values for a given organic solute and salt composition can be determined experimentally by linear regression of experimental solubilities measured at various salt concentrations (i.e., plots of $\ln C_w^{\text{sat}}$ versus C_s). It should be pointed out that at very high salt concentrations, the effect of the dissolved salts on the molar volume of the solution has to be taken into account. However, as an approximation, in many cases such as seawater this effect may be neglected (Schwarzenbach et al. 2003). In the reality, Henry's law constants or air-water partition coefficients will increase from freshwater to seawater by the factor (γ/γ_0) or $(C_{w0}^{\text{sat}}/C_w^{\text{sat}})$ (Rice et al. 1997). When the saline environment (seawater, salt lakes, subsurface brines) is considered the effect of salinity should be reflected to estimate the transport of chemicals correctly.

Many of the environmentally relevant ions bind water molecules quite tightly in aqueous solution which can be seen even macroscopically in that the volume of the aqueous solution is reduced. As a consequence, amount of free water molecules to solvate an organic compound is reduced. This salting-out results in a decrease in solubility and depending on type of the solute and the salt composition. In addition, because the solution of an organic compound, especially when the compound is large and nonpolar such as OCPs, requires a large number of water molecules, it can be foreseen that larger nonpolar organic compounds will exhibit higher salting-out coefficients as compared to smaller and/or more polar compounds (Schwarzenbach et al. 2003).

The higher the solubility for the compound called nonpolar the higher salting-out coefficient is obtained as compared to smaller or more polar compounds. The salinity will affect aqueous solubility (or the aqueous activity coefficient) by a factor of between less than 1.5 for small, and/or polar compounds, about 3 for large and/or nonpolar compounds at a moderate salt concentration typical for seawater (~0.5M). The differences between k_s values determined in artificial and real seawater are usually only marginal (Schwarzenbach et al. 2003).

Kucklick et al (1991) reported on the importance of temperature and salinity for explaining flux of HCHs in natural environments and showed that Henry's law constants determined at 35 and 45°C in artificial seawater (3% NaCl solution) were significantly higher than in deionized water for both α - and γ -HCH, but not at lower temperatures. Gossett (1987) studied the relationship between ionic strength of KCl and Henry's law constants for three low molecular weight chlorinated solvents and verified the logarithmic relationship between H and salinity that was originally proposed by Setchenow (1889). Gossett (1987) also reported that salinity must reach rather substantial values to exert significant impact. In the case of the tetrachloroethane, the ionic strength of solution must exceed 0.2 M (KCl) to cause a greater than 10% increase in H.

2.5. Measurement of Henry's Law Constants

Henry's law constant constants can be calculated from the ratio of vapor pressure to water solubility. However, for many high molecular weight organic compounds, the reported properties are extremely variable and often the correlation between H and temperature are not well known. Direct determination of H is, therefore, desirable (Sahsuar et al. 2003, Jantunen and Bidleman 2000, Bamford et al. 2000, Fendinger and Glotfelty 1988). Compilations of experimental air-water partition constants can be found in handbooks such as the one published by Mackay et al. (1992-1997), or in review articles including those by Staudinger and Roberts (1996), or Brennan et al. (1998).

Compared to the huge amount of chemicals that are present in the environment, only a few of them have experimentally determined H values. One reason for the lack of experimental data, is that costly investigations needed for a reliable measurement of

H values, especially substances with very low aqueous solubility. Such compounds with low solubility are difficult to deal with due to many reasons: adsorption effects on the walls of the apparatus, measurements close to the analytical detection limits, and losses in the mass balances that may cause considerable faults in the results (Altschuh et al. 1999).

In a defined system, there is only one equilibrium condition and the distribution of the components is a function of equilibrium and flux. The system will always tend to move towards equilibrium due to the driving forces that the equilibrium conditions establish.

Since in a closed system calculations for equilibrium conditions easier, in open systems equilibrium conditions may never be met everywhere in the system just as in natural systems. Natural systems may become very complex. In the presence of natural perturbations (e.g. temperature, solar periods, wind condition), a system will reach a dynamic equilibrium rather than static equilibrium (Logan 1999).

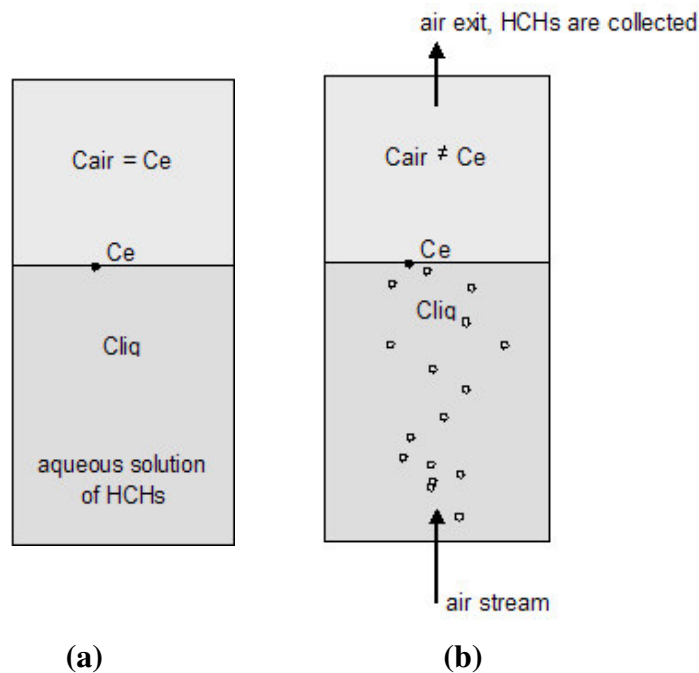


Figure 5. (a) static equilibrium (b) dynamic equilibrium.

As an example, there will be a continuous evaporation from a pool contaminated with pollutant (e.g. an organochlorinated pesticide, DDT, has very low solubility) when it is in outdoor conditions. Velocity of the wind, temperature and air concentration are the parameters that affect the mass transfer rate of chemical from liquid phase to air

phase. In environmental conditions these parameters will change and never be constant, so that an equilibrium concentration could not be obtained in the air phase. Concentration of the pollutant will be around a concentration which represents a dynamic equilibrium (Logan 1999).

Therefore, since Henry's law constants can be measured by either static or dynamic equilibration methods, during modeling of fate of several volatile and semivolatile organic chemicals Henry's law constants which are measured at dynamic equilibrium is preferable.

In Figure 5, the difference in static and equilibration approaches is shown comparing static head space and dynamic head space methods. In static head space, in the closed container after a certain time period the system will reach an equilibrium (Figure 5a). Equilibrium concentration on the interface and equilibrium concentrations in liquid and air phases can be calculated easily. In dynamic head space there is a continuous mass transport through bubbles (Figure 5b). Every time equilibrium conditions change and a new equilibrium condition is set up. In this condition only a dynamic equilibrium can be present just as in environmental conditions.

2.5.1. Static Equilibration

In the static equilibration method the air-water partition constant is directly determined by measuring concentrations of a compound at a given temperature in the air and/or water in closed systems such as in a gas-tight syringe, or in sealed bottles (Schwarzenbach et al. 2003, Gossett 1987, Burkhard et al. 1985). If chemical concentrations are measured only in one phase, the concentration in the other is assessed as difference to the total amount of the related compound in the system. In this approach, the error in determining Henry's law constant can be reduced either by equilibrating a given volume of an aqueous solution of a compound subsequently with several given volumes of solute-free air, or by using multiple containers having different headspace-to-liquid volume ratios.

The main experimental challenges of the static methods are to ensure that equilibrium is reached and also maintained during sampling, and to minimize sampling errors. Since with the static approach, it is possible to use neither very large nor very small air-to-water volume ratios, these methods are primarily suited for compounds

with no extreme preference for one of the phases (Schwarzenbach et al. 2003). Generally, this technique is only sensitive enough for compounds with relatively high H values ($H > 0.1$) because of the limited size of the headspace and water sample (Fendinger and Glotfelty 1988). In more extreme cases, dynamic methods may provide much better results (Fendinger and Glotfelty 1988, Schwarzenbach et al. 2003).

Henry's law constants were determined by Gossett (1987) directly by measuring the vapor concentration and aqueous concentration of the analyte or from gas headspace concentration ratios from pairs of sealed bottles containing different liquid volumes. The author presented measured Henry's constants vs. temperature in the range of 10-35°C for 13 chlorinated hydrocarbons of environmental concern, and data concerning the impact of ionic strength on effective Henry's constant values-with salting-out coefficients-for six of the compounds, with KCl concentrations from 0 to 1.0 M. Burkhard et al. (1985) calculated H values for PCBs between 0 – 40°C and Murphy et al. (1987) calculated H values for PCBs and toxaphene at 20°C. In the literature H values for any OCPs have not been reported by this method due to the reason that will be discussed in dynamic equilibration methods.

2.5.2. Dynamic Equilibration

Widely applied dynamic equilibration methods are bubble (batch air or gas) stripping technique (Mackay et al. 1979, Kucklick et al. 1991, Jantunen and Bidleman 2000, Sahsuvar et al. 2003), wetted wall column (Fendinger and Glotfelty 1988, Brunner et al. 1990, Altschuh et al. 1999), and dynamic head space (Bamford et al. 2000, Sahsuvar et al. 2003).

The dynamic equilibration technique is generally more accurate than bulk equilibration because the measurement is based on a relative concentration change in one phase, and as a result, it is also capable of measuring much lower H. Potential problems associated with the dynamic equilibration technique are incomplete equilibration, preferential association of the analyte with either the surfaces of the rising bubbles or with the purge bottle, and entrainment of solution aerosol into the vapor trap of the apparatus (Fendinger and Glotfelty 1988).

2.5.2.1. Batch Gas Stripping

By using a stripping apparatus (Figure 6b), bubbles of air or another inert gas are produced near the bottom of a vessel and then rise to the surface of the solution, the exit gas achieving equilibrium with the water. Hence, this experimental design requires that the velocity of the rising bubbles is sufficiently small and the height of the well-mixed water column is sufficiently great to establish air-water equilibrium. Furthermore, the bubbles need to be large enough so that adsorption at the air-water interface can be neglected. If all of these are achieved, the air-water partition constant can be determined by measuring the decrease in water concentration as a function of time (Mackay et al. 1979, Schwarzenbach et al. 2003).

This method was used by Mackay et al. (1979) to determine H for hydrophobic organics at environmental concentrations and in natural waters. In principle, the system consists of a known volume of water through a known volume of air sparged under conditions such that the solute concentration in the exit gas is essentially in equilibrium with the aqueous concentration. By using the plot of the solute aqueous concentration of compound versus time, H can be obtained.

A mathematical description of the stripping process can be readily assembled if it is assumed: (i) the system is isothermal, (ii) the liquid phase is well mixed, (iii) the vapor behaves ideally, (iv) Henry's law is obeyed over the relevant concentration range, (v) the volume of liquid remains constant, (vi) the partial pressure of the solute is small compared to the total pressure, and (vii) the solute in the exit vapor is in equilibrium with the liquid. A mass balance for the solute gives the transfer rate as (Mackay et al. 1979):

$$-VdC/dt = PG/RT = HGC/RT \text{ (mole/h)} \quad (2.9)$$

Where G is the gas flow rate (m^3/h), V is the volume of the liquid (m^3), P is the partial pressure, R is the gas constant, T is the system temperature (K), and t is time (h). This equation can be integrated from initial conditions when $t=0$ and $C=C_0$ to give (Mackay et al. 1979):

$$\ln(C/C_0) = -(HG/VRT)t \quad (2.10)$$

A plot of log concentration against time should be linear with a slope of $-(HG/VRT)$ from which H is calculated.

The advantages of this method are the relatively small vessel volumes in gas-water contact and consequently small adsorption areas and equilibration times. A disadvantage of the gas purge method lies in the need of a model for data handling, such as the two film or penetration model. All models are approximations, and the use of mass-transfer coefficients for the evaluation of thermodynamic partition coefficients is a principal disadvantage. A consequence of using such approximations is the possibility of introducing systematic errors of unpredictable amounts (Brunner et al. 1990).

Sahsuvar et al. (2003) applied bubbling stripping technique to HCHs with correction for water losses in the system. The stripping apparatus was same as used previously by Jantunen and Bidleman (2000) and Kucklick et al. (1991). The apparatus consisted of three chambers, an outer insulating air jacket, a middle one for water circulation from a constant temperature bath, and an inner chamber containing 525 ml of the aqueous solution for gas stripping. Bubbling was carried out at a depth of 40 – 50 cm below the water surface through a coarse glass frit. The tube exiting the inner chamber coiled three times to minimize escape of aerosols which might be produced in the bubbling process. Zero grade nitrogen, presaturated with water vapor at the temperature of the experiment, was introduced through the bubbling frit at 0.015 – 0.025 m³/h. Air volumes were calculated from the average flow rate and the duration of the experiment (Sahsuvar et al. 2003). Calculation of H is same as in Mackay et al. (1979).

The H values for toxaphene and two HCH isomers (α - and γ -HCH) were determined using the gas stripping method described by Kucklick et al. (1991) -which was originally taken from Mackay et al. (1979)- for HCHs. The volume and height of the inner chamber are 525 ml and 62 cm. The purge tube, with a coarse frit on the end, is lowered to within a few millimeters of the bottom of the inner chamber, 47 cm below the initial water surface. Kucklick et al. 1991 showed that the air bubbles achieved equilibrium with HCHs in water by sampling at two different depths (45-50 and 26 cm).

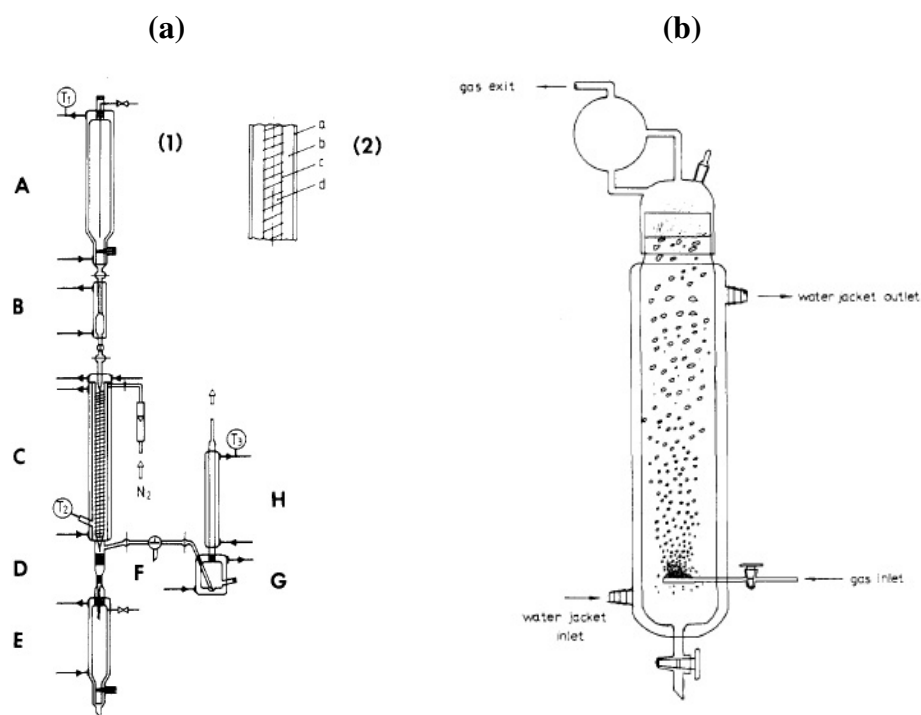


Figure 6. a) Wetted wall column (Source: Brunner et al. 1990),
 b) Bubbling stripping column (Source: Mackay et al. 1979).

2.5.2.2. Wetted Wall Column

An alternative dynamic approach to gas stripping is the concurrent flow technique, which is based on the use of a wetted wall column (WWC) apparatus (Figure 6a). Compound-laden water is introduced continuously at the top of a wetted wall column where it comes into contact with a compound-free gas stream flowing concurrently down the column. As with gas stripping, the major challenge is to allow sufficient contact time to ensure phase equilibrium is reached by the time the two streams reach the bottom of the column. The two streams are separated at the bottom of the column, and either solvent extracted or trapped on solid-phase sorbents for subsequent analysis. To determine the air-water partition coefficient of a given compound, the system is run for a set amount of time. Given knowledge of the flow rates employed along with the compound masses present in the separated phase streams, Henry's law constant can be calculated (Schwarzenbach et al. 2003).

Brunner et al. (1990) identified 58 PCB congeners from a technical mixture of PCBs. From the ratios of the concentrations of the PCB congeners in the gas phase to

the concentrations in the liquid phase the dimensionless H values are calculated. An aqueous solution of PCB congeners is produced by the purging of water through a generator column. This solution is then brought into contact with a gas stream until the partition equilibrium is achieved. An overview of the apparatus is shown in Figure 6b. Water from the feed dosing funnel (A) is purged through the generator column (B) at a constant flow rate. The PCB-loaded water continues to flow into the desorption column (C), where it contacts the gas stream. At the bottom of the column, the water is separated from the gas and flows through the connecting tube (D) into the receiver dosing funnel (E). The gas is conducted into an absorption vessel (G), where the PCBs are dissolved in an organic solvent. The gas then leaves the apparatus through the reflux condenser (H). The mass balances for these runs ranged between 80 and 115%, with most of them between 90 and 107%. The verification of the mass balance and the guaranteed equilibrium as discussed before confirm the high reliability of our values despite of the large standard deviation range.

Altschuh et al. (1999) have measured H for a wide range of compounds including organochlorinated pesticides. For each experimental run the mass balances were determined as a main quality criterion. The mass balances ranged between 70 and 130%, for most of the investigated substances between 90 and 110%.

A WWC was used by Fendinger and Glotfelty (1988) to determine experimentally the air-water Henry's law constants for lindane, alachlor, and diazinon. Lindane, diazinon, and alachlor were introduced into the WWC as aqueous solutes. In a separate experiment lindane was introduced as a vapor. Equilibrium was confirmed for lindane by varying air/water contact time in the WWC.

An important factor in the accuracy of the HLC determination with the WWC system is whether pesticide vapor/solution equilibrium is achieved between the liquid film and concurrent flow of air. H determinations made Mackay et al. (1979) using the gas purge technique have shown that equilibrium is dependent on the contact time between the gas and liquid phase in the purge bottle. In the WWC, contact between the gas and liquid phases is dependent on the water flow and air flow rates and column length. Water flow rates influence the fluid characteristics of the liquid film and residence time within the column. Residence time of the gas phase in the column is inversely proportional to the airflow rate (Fendinger and Glotfelty 1988).

Rice et al. (1997) measured dimensionless Henry's law constants for endosulfans and chlorpyrifos by WWC method at 20°C, both in deionized water and in saline water (3.33% NaCl solution).

2.5.2.3. Dynamic Head Space

The dynamic head space (DHS) method used by Bamford et al. (2000) employs a gas-stripping apparatus where the gas-phase concentration of a chemical in the air passing through a column of water is in equilibrium with the dissolved concentration.

Bamford et al. (2000) measured Henry's law constants for several PCB congeners at 4, 11, 18, 25, and 31°C, and both the enthalpy and entropy of phase change were calculated using the Gibbs-Helmholtz equation.

The gas-stripping apparatus consists of a 122 cm by 15.2 cm diameter glass reactor filled with 10 L of Nanopure deionized water to a depth of 83 cm. Once the reactor was filled, between 130 ml/min and 160 ml/min of compressed air was passed through a hydrocarbon trap to remove possible contaminants and through a 500 ml glass, gas washing bottle to saturate the air with water vapor prior to entering the reactor through two 5 µm pore size air stones mounted at the bottom of the reactor. Gas exiting the reactor first passed through a 5 µm glass impactor to remove possible aerosols created by breaking bubbles, which may potentially interfere with hydrophobic contaminant gas-phase estimates, and then through a cylindrical polyurethane foam plug housed in a glass column to capture vapor phase PCBs. The volumes of air collected ranged from 14 L to 150 L, resulting in less than 2% of gas-phase PCBs breaking through the PUF trap even at the higher sampling volumes.

During each experiment, simultaneous air and water samples were collected every 4 h to 24 h for 3 days to 6 days. The time intervals between samples were dictated by the amount of gas-phase PCB mass collected in the PUF over time. HLC was calculated as the ratio of the time-integrated gas-phase concentration and the average of the two dissolved concentrations (i.e. those measured at the start and end of each air sample) (Bamford et al. 2000):

$$H^i = C_g / ((C_{w(n)} + C_{w(n+1)}) / 2) \quad (2.11)$$

where C_g (ng/L) is the time integrated gas-phase concentration and $C_{w(n)}$ and $C_{w(n+1)}$ are the dissolved concentrations (ng/L) measured at the beginning and end of air sampling period, respectively.

An integrated mass balance equation for the loss of PCBs from solution over time can also be used to calculate H as in Mackay et al. (1979). However, the rate of PCB loss from the dissolved phase over such short time periods of an experiment in our system was small, and changes in the masses of less volatile compounds were close to the analytical detection limits. This suggests evidence of PCB analytes initially absorbing to the glass reactor and over time dissolving off the glass into the water column, buffering the change of PCB concentrations in the water column. Of the initial mass added to the reactor, about 15% of the lighter molecular weight PCB congeners and 60% of the heavier molecular weight PCB congeners absorbed onto the glass reactor. This would result in inaccurate H measurements if an integrated mass balance equation was used; however, at equilibrium, such buffering does not affect the ratio measurements of H from both air and water concentrations.

Tests were performed to ensure that equilibrium was achieved between the gas-phase PCB concentrations in the rising bubbles and those in the dissolved phase by comparing the H values obtained at various purge heights in the reactor (Bamford et al. 1999). These studies showed that equilibrium was reached for these compounds at a water column height of between (53 and 83 cm), and all experiments were conducted in this study at a height of 83 cm.

Sahsuvar et al. (2003) applied the DHS method to HCHs for the first time and compared the results with the results in bubble stripping technique for α - and γ -HCHs.

In the DHS experiments by Sahsuvar et al. (2003), the partial pressure of HCH in the saturated nitrogen stream exiting the experiment vessel was calculated from quantity on the ENV + cartridge, the gas flow and molecular mass using the ideal gas law. Recoveries of the deuterated HCH surrogates from the cartridges averaged $103\% \pm 12\%$ for α -HCH (n=53) and $101\% \pm 7\%$ for γ -HCH (n=57). H was calculated from the partial pressure and the average concentration in the aqueous phase measured at the beginning and end of the nitrogen stream sampling (Sahsuvar et al. 2003).

H values determined by bubble stripping and DHS methods were reported by Sahsuvar et al. (2003). The H of β -HCH is much lower than for the other two isomers and even at long purging times insufficient quantities were removed to produce

measureable changes in water concentration. Consequently, the H of β -HCH was determined only by DHS. Comparison of the two methods run under common temperature conditions for α - and γ -HCH showed good agreement; the ratio of BS/DHS results ranged from 0.63 to 1.16 and averaged 0.99. The agreement between the two methods for α -HCH and γ -HCH gives confidence in the use of DHS alone for β -HCH (Sahsuvar et al. 2003).

CHAPTER 3

MATERIALS AND METHODS

Experimental procedures, quality control and assurance for the measurement of air and water phase concentrations of OCPs, and calculations will be given in this chapter.

3.1. Experimental

A 75 cm-length and 5 cm-diameter water-jacketed glass column filled with 1 L deionized water at a depth of 50 cm for gas stripping experiments (Figure 7). It has been already shown that the equilibrium between gas and air phases can be achieved at depths less than 50 cm-depth for semivolatile organic compounds (Sahsuvar et al. 2003, Jantunen and Bidleman 2000, Bamford et al. 2000, Bamford et al. 1999).

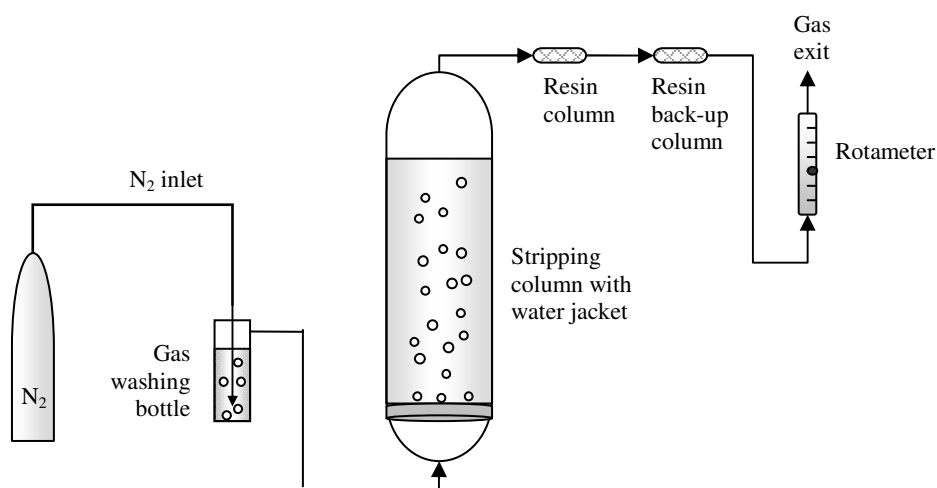


Figure 7. Schematic of the experimental set-up.

Stripping time necessary to reach detectable gas phase concentrations was calculated by using previously reported Henry's law constants. During experiments stripping time was finally adjusted to 9 hours after obtaining measurable amounts of chemicals in aqueous solution. In literature, stripping time for measuring H values of

HCHs by batch gas stripping method were reported 2 to 20 days for ~500 ml solution with an average stripping rate of 200 to 450 ml/min (Sahsuvar et al. 2003, Jantunen and Bidleman 2000, Kucklick et al. 1991) and for measuring H values of PCBs by dynamic head space method were reported 3 to 6 days for 10 L solution with a stripping rate of 130 to 160 ml/min (Bamford et al. 2000).

Initial solubility was set %15 solubility of the least soluble compound p-p'-DDE. The OCPs were prepared in 1 ml methanol and spiked into the column to obtain concentrations about 15% solubility of DDE which is 800 ng/ml. It has been previously reported that methanol at such low amounts has a negligible effect on solubility and H for a diverse set of semivolatile organic compounds (ten Hulscher et al. 1992).

Once the column filled, zero grade nitrogen, presaturated with water vapor, was introduced through a 40 μ m bubbling frit at the bottom of the column at a rate of 175 ml/min. Flow rates of N₂ were measured by a flowmeter (rotameter) and the temperature was controlled by a constant temperature bath. The rotameter calibration checked by a soap-bubble meter at three flow rates in duplicate (n=6). The average percent difference between two flow meters was less than 3.0% (2.4 \pm 1.8%, average \pm SD).

Vapor phase OCPs were captured by a XAD-2 resin filled glass column. Before the resin filled column, pre-baked silanized glass wool was plugged into a 2 cm tubing section to prevent the escape of water droplets that may be produced during the bubbling process. Five ml-water samples were drawn at the surface of the water column at the start and at the end of the each sampling periods. Sampling period was selected as 3 hours after trying longer periods in which water phase concentrations reached near zero values.

Experiments in saline water were conducted using a 3% NaCl solution of in deionized water at temperatures 15°C and 25 °C. Before use, NaCl was baked at 450°C for 2 hours to remove any organic contaminant. Experiments in deionized water were conducted at five temperatures (5, 15, 20, 25, and 35°C).

3.2. Sample Preparation and Analysis

Gas-phase samples were extracted into dichloromethane (DCM) in an ultrasonic bath for 30 min. Water samples were liquid-liquid extracted three times with 5 ml

DCM using a separatory funnel. Then, the solvent for all samples was exchanged into hexane and sample volumes were reduced to 1 ml under a gentle stream of pure nitrogen. Water and gas-phase samples were spiked with 10 ng of BDE-77 (internal standard) prior to analysis.

Samples were analyzed for OCPs with an Agilent 5973 gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD) working at electron capture negative chemical ionization (ECNI) mode. A capillary column (HP5-ms, 30 m, 0.25 mm, 0.25 μ m) was used. The initial oven temperature was held at 50°C for 1 min and raised to 100°C at 25°Cmin⁻¹, 100-300°C at 5°Cmin⁻¹, and held for 7 min. The injector and ion source, and quadropole temperatures were 250, 150, and 150 °C, respectively. High purity methane was used as the reagent gas. The MSD was run in selected ion-monitoring mode. Compounds were identified based on their retention times, target and qualifier ions.

The experimental procedure was applied at five different temperatures including 35, 25, 20, 15, and 5°C and two different temperatures including 15°C and 25°C in 3% NaCl solution, and replicated three times for each temperature. H' was calculated as follows:

$$H' = C_g / ((C_{w(n)} + C_{w(n+1)}) / 2) \quad (3.1)$$

where C_g (ng/L) is the time integrated gas-phase concentration and $C_{w(n)}$ and $C_{w(n+1)}$ are the dissolved concentrations (ng/L) measured at the beginning and end of air sampling period, respectively.

For each individual experiment, three air samples and four water samples were collected to calculate three Henry's law constants. However, since some of the compounds are very volatile so that it was impossible to detect them in water after 3 hours. For some of the compounds during second or third sampling period water concentrations decreased to near zero for such low water concentrations Henry's law constants could not be calculated.

For the compounds of which more than one H value can be obtained, the relative standard deviations (RSD) associated with the mean Henry's law constants were less than 30%, and no systematic differences, within experimental variability, were observed

among different temperatures. On the other hand, for the compounds c-nonachlor, p-p'-DDD, and endosulfan II mean values have an average of 50% (RSD).

The aqueous concentrations were generally decreased over the experimental durations by different amounts among different compounds. For some of the compounds concentrations became close to blank values and for some of them concentrations were approximately same. These results, in the vicinity of changing concentrations from 0% to 100%, were consisted with the previous studies reviewed by Schwarzenbach et al. (1993) reporting that there were no significant effects of solute concentration on measured Henry's law constants.

For δ -HCH, β -HCH, endrin aldehyde, endosulfan sulfate, endrin ketone, and methoxychlor Henry's law constants could not be measured due to air concentrations close to analytical detection limits as a result of very slow volatilization.

3.3. Quality Assurance

Blank amounts, procedural recoveries and of OCPs in water and resin, concentration of OCPs in resin back-up columns were investigated through quality assurance of this study.

3.3.1. Blanks

Blank XAD-2 resin and water samples were prepared to determine if there was any contamination during sample handling and preparation for analysis. As seen in Table 4, the average amounts found in blanks were significantly lower than the sample amounts. Blank correction were done in the results. The average amounts of blanks ranged between 0.06 ± 0.02 ng (c-nonachlor) and 1.22 ± 0.45 ng (chlorpyrifos) for XAD-2 resin samples and between 0.02 ± 0.01 ng (c-nonachlor) and 0.65 ± 0.12 ng (heptachlorepoxide) for water samples. Generally, blank amounts were significantly lower than the sample amounts. Blank amount/sample amount ratios ranged between 0.004 (c-nonachlor) – 0.014 (heptachlorepoxide) and 0.009 (c-nonachlor) – 0.210 (heptachlorepoxide) for gas and aqueous samples, respectively.

The limit of detection method (LOD, ng) was defined as the mean blank mass plus three standard deviations ($LOD = \text{Mean blank value} + 3SD$). LODs ranged from 0.13

ng (c-nonachlor) to 2.57 (chlorpyrifos) for air samples and from 0.05 ng (c-nonachlor) to 1.01 ng (heptachlorepoxyde) for water samples. In general, samples were substantially higher than LODs. Sample amounts exceeding LODs were quantified and blank corrected using the average blank amounts.

Table 4. Average blank values of resin and water samples.

	Resin	Water
	Average \pm SD	Average \pm SD
α -HCH	0.10 \pm 0.04	0.08 \pm 0.01
β -HCH	ND	ND
γ -HCH	0.07 \pm 0.03	0.11 \pm 0.01
δ -HCH	ND	ND
Heptachlor	0.24 \pm 0.04	ND
Aldrin	ND	ND
Chlorpyrifos	1.22 \pm 0.45	0.62 \pm 0.05
Heptachlorepoxyde	0.66 \pm 0.04	0.65 \pm 0.12
γ -CHL	0.27 \pm 0.05	0.05 \pm 0.02
Endosulfan I	0.48 \pm 0.09	0.36 \pm 0.07
α -CHL	0.22 \pm 0.05	0.04 \pm 0.01
t-Nonachlor	0.20 \pm 0.03	0.03 \pm 0.01
Dieldrin	ND	ND
DDE	0.53 \pm 0.11	0.41 \pm 0.05
Endrin	ND	ND
Endosulfan II	0.13 \pm 0.02	0.09 \pm 0.02
DDD	ND	ND
c-Nonachlor	0.06 \pm 0.02	0.02 \pm 0.01
Endrin aldehyde	ND	ND
Endosulfan sulfate	0.03 \pm 0.03	ND
DDT	ND	ND
Endrin ketone	ND	ND
Methoxychlor	ND	ND

3.3.2. Back-up Columns

A backup column was also placed at temperatures 25°C and 35°C in series with first glass column in order to determine possible breakthrough of the chemicals. Amounts ratios back-up column over the first column were found in the range of 3.89% (α -HCH) and 28.94% (Aldrin) at 25°C. The amounts found on this backup columns were close to the blank values. The results clearly indicated that there was not any breakthrough of the chemicals. The temperatures less than 25°C no backup column has been used because breakthrough is less likely at lower temperatures.

3.3.3. Procedural Recovery

Procedural recoveries were tested by adding spike solutions at known concentration to three different blank resin and water samples. These spike recovery samples were treated as real samples. Resin and water recoveries are given in Table 5. While calculating H for each chemical, only recovery corrections has been made for water and no correction has been made for resin concentrations due to high efficiencies achieved (approximately 100%). Similarly, Sahsuvar et al. (2003) was found procedural efficiencies around 100% for H value measurement of HCHs by dynamic head space method. These procedural recoveries are consisted with mass balances which were done to confirm accuracy of the measurement of several OCPs and other semivolatle organic chemicals (Altschuh et al. 1999, Bamford et al. 2000, Brunner et al. 1990).

Table 5. Percent recoveries of resin and water.

	Resin	Water
	Average±SD	Average±SD
α-HCH	103.00±9.89	102.42±9.09
β-HCH	79.60±4.74	85.75±8.35
γ-HCH	94.77±10.06	96.92±12.83
δ-HCH	104.03±9.79	104.42±7.88
Heptachlor	98.87±10.47	65.08±7.34
Aldrin	91.83±13.54	64.67±6.17
Chlorpyrifos	112.33±3.33	93.83±5.05
Heptachlorepoxide	98.80±9.85	72.58±4.04
γ-CHL	89.03±11.77	55.67±6.00
Endosulfan I	98.27±11.53	71.25±7.64
α-CHL	92.70±11.76	58.17±7.42
t-Nonachlor	85.50±12.61	53.25±10.08
Dieldrin	110.57±7.08	76.17±3.83
DDE	96.53±10.54	77.75±10.31
Endrin	111.20±4.71	78.75±0.75
Endosulfan II	101.72±10.04	68.63±4.82
DDD	82.23±5.61	58.67±3.74
c-Nonachlor	90.67±10.96	53.58±7.52
Endrin aldehyde	98.53±4.17	87.75±7.21
Endosulfan sulfat	114.57±6.40	97.92±10.64
DDT	114.63±3.84	73.25±8.79
Endrin ketone	106.77±3.62	92.75±9.38
Methoxychlor	106.07±9.74	86.00±6.16

CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents and discusses the results of experiments for the measurement Henry's law constants at 5, 15, 20, 25, and 35°C in deionized water and at 15 and 25°C in saline water.

The measured results of Henry's law constants for organochlorine pesticides are given in the Tables 6 and 7. For all of the compounds, H increases an average 90% in every 10°C temperature increment. This increase in the salinated water experiments was an average 107% for the range of 15°C to 25°C temperature while in the same temperature range this value was 96% in the deionized water.

This increase in H are close to average increase for many organic compounds of reported by Staudinger and Roberts (2001) as 88%. Furthermore, H values are higher in saline water than in deionized water by different factors ranging from 1.46 to 9.28 (exceptions for c-nonachlor and p-p'-DDD, the H values seem same in deionized water and the saline water) with an average for measured compounds 2.95 at 25°C and 1.11 to 4.69 with an average 2.89 at 15°C. These results are in the range of the factor which are reported by Schwarzenbach et al. (2003) as 3 for large nonpolar organic compounds due to salting-out effect.

Table 8 shows the comparison of H values belong to α -HCH. The H value of α -HCH is the approximately half of the value obtained in the similar studies (Sahsuvar et al. 2003, Jantunen and Bidleman 2000, Kucklick et al. 1991). However, in the study conducted by Altschuh et al. (1999) H value of α -HCH was less than 50% of H value measured in this work. Therefore, it can be concluded that the results are not out of range. Unfortunately, the saline water experiments are not common in the literature. The only study was conducted for the similar compound was used to calculate H value for α -HCH (Kucklick et al. 1991). The temperature and experimental method of this study were different. As explained before measurement methods can bring some difference into the results and these differences can be up 3 factor. The H values measured in this work are about half of the H values reported by Kucklick et al. (1991).

Table 6. Measured Henry's law constants (Pa.m³/mole) in deionized water.

	35°C	25°C	20°C	15°C	5°C
α-HCH	0.639±0.169 ^a	0.286±0.018 ^a	0.231±0.011 ^a	0.137±0.018 ^a	0.070±0.003 ^a
γ-HCH	0.252±0.062 ^a	0.112±0.005 ^a	0.085±0.006 ^a	0.062±0.003 ^a	0.034±0.004 ^a
DDT	2.678±0.403 ^a	1.074 ^b	0.601 ^b	0.523 ^c	0.185 ^b
DDD	2.791±0.540 ^a	1.851±1.037 ^a	1.580±1.163 ^a	0.796±0.242 ^a	0.610 ^b
DDE	29.492 ^c	6.166 ^c	4.345 ^c	4.628 ^c	1.937 ^c
c-Nonachlor	3.606±0.827 ^a	2.939±1.752 ^a	1.747±1.020 ^a	0.939±0.378 ^a	1.037±0.518 ^a
t-Nonachlor	31.940 ^c	10.284 ^c	6.991 ^c	4.819 ^c	1.920 ^c
Endosulfan I	1.109±0.238 ^a	0.895 ^b	0.693±0.189 ^a	0.458±0.095 ^a	0.229±0.032 ^a
Endosulfan II	0.079±0.009 ^a	0.064±0.032 ^a	0.043±0.015 ^a	0.037±0.010 ^a	0.022 ^c
Endrin	0.787±0.117 ^a	0.682±0.261 ^a	0.518±0.135 ^a	0.352±0.067 ^a	0.184±0.016 ^a
Dieldrin	2.276 ^b	1.995±0.805 ^a	1.286±0.452 ^a	0.906±0.313 ^a	0.559±0.181 ^a
Aldrin	79.435 ^b	74.467 ^c	56.077 ^c	56.561 ^c	22.902 ^c
α-CHL	15.284±0.874 ^a	6.733 ^c	3.765 ^c	3.429 ^c	1.741 ^c
γ-CHL	47.854 ^b	16.669 ^c	10.148 ^c	7.162 ^c	2.794 ^c
Chlorpyrifos	15.785 ^b	11.981 ^b	9.783 ^b	6.625±3.376 ^a	2.530 ^b
Heptachlor	68.224 ^c	71.245 ^c	58.998 ^b	36.297 ^c	20.487 ^c
Heptachlorepoxi	2.814 ^b	2.666±0.672 ^a	1.827±0.510 ^a	1.099±0.226 ^a	0.597±0.126 ^a

^a n=3, ^b n=2, ^c n=1

Table 7. Measured Henry's law constants (Pa.m³/mole) in saline water.

	25°C	15°C
α-HCH	0.505±0.048 ^a	0.262±0.015 ^a
γ-HCH	0.247±0.014 ^a	0.137±0.024 ^a
DDT	1.571 ^c	1.104 ^c
DDD	1.837 ^c	1.222 ^c
DDE	15.241 ^c	5.120 ^c
c-Nonachlor	2.001 ^c	1.047 ^c
t-Nonachlor	23.312 ^c	7.585 ^c
Endosulfan I	4.096±0.561 ^a	2.062±0.335 ^a
Endosulfan II	0.597±0.303 ^a	0.414±0.187 ^a
Endrin	3.055±0.734 ^a	1.622±0.503 ^a
Dieldrin	8.828±2.648 ^a	3.749±1.107 ^a
Aldrin	93.232 ^c	66.553 ^c
α-CHL	21.218 ^c	7.306 ^c
γ-CHL	32.148 ^c	11.669 ^c
Chlorpyrifos	38.927 ^c	13.180 ^c
Heptachlor	99.408 ^c	56.636 ^c
Heptachlorepoxyde	12.415±3.133 ^a	5.158±1.051 ^a

^a n=3, ^c n=1

Table 8. Literature comparison of H values for α-HCH.

α-HCH	T (K)	H (Pa.m ³ /mole)	T range (K)	Technique	Reference
<i>Deionized water</i>	298	0.286	278 – 308	DHS	This work
	298	0.62	278 – 308	DHS & BS	Sahsuvar et al. 2003
	298	0.675	283 – 313	BS	Jantunen and Bidleman 2000
	298	0.79	273.5 – 318	BS	Kucklick et al. 1991
	298	0.12	-	WWC	Atschuh et al. 1999
	288	0.137	278 – 308	DHS	This work
	288	0.27	278 – 308	DHS & BS	Sahsuvar et al. 2003
	288	0.3	283 – 313	BS	Jantunen and Bidleman 2000
	288	0.519	273.5 – 318	BS	Kucklick et al. 1991
	<i>Saline water</i>	298	0.505	288 – 298	DHS
288		0.262	288 – 298	DHS	This work
298		0.94	273.5 – 318	BS	Kucklick et al. 1991
288		0.541	273.5 – 318	BS	Kucklick et al. 1991

In Table 9, H values of γ -HCH were compared with the literature. In literature, H value of γ -HCH and α -HCH were measured together. Similar to H value of α -HCH, H value of γ -HCH is the approximately half of the value obtained in the similar studies (Sahsuvar et al. 2003, Jantunen and Bidleman 2000, Kucklick et al. 1991). Yet in the another study conducted by Altschuh et al. (1999), H value of γ -HCH was about four times higher than H value measured in this work. The saline experiments are not common in the literature for this compound, too. Kucklick et al. (1991) measured H values for γ -HCH at different temperature in saline water. The H values measured in this work are about half of the H values reported by Kucklick et al. (1991). As reported in literature It was found that H values of γ -HCH is lower than H values of α -HCH.

Table 9. Literature comparison of H values for γ -HCH.

γ -HCH	T (K)	H (Pa.m ³ /mole)	T range (K)	Technique	Reference
<i>Deionized water</i>	298	0.112±0.005	278 – 308	DHS	This work
	298	0.235	278 – 308	DHS & BS	Sahsuvar et al. 2003
	298	0.285	283 – 313	BS	Jantunen and Bidleman 2000
	298	0.387	273.5 – 318	BS	Kucklick et al. 1991
	298	0.50	-	WWC	Atschuh et al. 1999
	288	0.062±0.003	278 – 308	DHS	This work
	288	0.101	278 – 308	DHS & BS	Sahsuvar et al. 2003
	288	0.127	283 – 313	BS	Jantunen and Bidleman 2000
	288	0.259	273.5 – 318	BS	Kucklick et al. 1991
	<i>Saline water</i>	298	0.247±0.014	288 – 298	DHS
288		0.137±0.024	288 – 298	DHS	This work
298		0.469	273.5 – 318	BS	Kucklick et al. 1991
288		0.285	273.5 – 318	BS	Kucklick et al. 1991

In Table 10, H values of endosulfan I, endosulfan II and chlorpyrifos were compared with the literature. It was found that H values are scarcely different with the values measured by Rice et al. (1997) both in deionized water and saline water. For endosulfans H values measured in this study were lower about an order of magnitude than H values reported by Rice et al. (1997) whereas H value measured for chlorpyrifos was higher than H value reported by same author. Furthermore, measured H values for

endosulfan I and endosulfan II are consisted with H values measured by Altschuh et al. (1999). H values in saline water for these compounds were only reported by Rice et al. (1997). In saline water, measured H values were again scarcely different than reported values by Rice et al. (1997). H values measured in this study are more confident because in this study H values were measured at five different temperatures and these values were correlated with temperature.

Table 10. Literature comparison of H values for endosulfan I, endosulfan II and chlorpyrifos.

Chemical	T (K)	H (Pa.m ³ /mole)	T range (K)	Technique	Reference
<i>Deionized water</i>					
Endosulfan I	293	0.693	278 – 308	DHS	This work
	293	6.626	-	WWC	Rice et al. (1997)
	298	0.69	-	WWC	Altschuh et al. (1999)
Endosulfan II	293	0.043	278 – 308	DHS	This work
	293	0.877	-	WWC	Rice et al. (1997)
	298	0.04	-	WWC	Altschuh et al. (1999)
Chlorpyrifos	293	9.783	278 – 308	DHS	This work
	293	0.317	-	WWC	Rice et al. (1997)
<i>Saline water</i>					
Endosulfan I	293	3.079	278 – 308	DHS	This work
	293	12.886	-	WWC	Rice et al. (1997)
Endosulfan II	293	0.505	278 – 308	DHS	This work
	293	2.119	-	WWC	Rice et al. (1997)
Chlorpyrifos	293	26.053	278 – 308	DHS	This work
	293	0.492	-	WWC	Rice et al. (1997)

In Table 11, the comparison of H values for the rest OCPs available in the literature are shown. H values measured in this work are higher than the values reported by Altschuh et al. (1999). The extreme differences were obtained in this study for aldrin and heptachlor than comparable study. The study was conducted by Altschuh et al. (1999) only at one temperature while the measurements in this work were done at five different temperatures and they are correlated with temperature. Therefore, it can be concluded that the results in this work are more confident. There are no H values in saline water reported for these compounds and these are the first H values reported in saline water.

Table 11. Some of the OCPs' H values from literature

Chemical	T (K)	H (Pa.m ³ /mole)	T range (K)	Technique	Reference
p-p'-DDD	298	1.851	278 - 308	DHS	This work
	298	0.65	-	WWC	Altschuh et al. (1999)
p-p'-DDE	298	6.166	278 - 308	DHS	This work
	298	4.07	-	WWC	Altschuh et al. (1999)
p-p'-DDT	298	1.074	278 - 308	DHS	This work
	298	0.81	-	WWC	Altschuh et al. (1999)
Dieldrin	298	1.995	278 - 308	DHS	This work
	298	0.98	-	WWC	Altschuh et al. (1999)
Endrin	298	0.682	278 - 308	DHS	This work
	298	0.62	-	WWC	Altschuh et al. (1999)
Aldrin	298	74.467	278 - 308	DHS	This work
	298	4.31	-	WWC	Altschuh et al. (1999)
Heptachlor	298	71.245	278 - 308	DHS	This work
	298	28.73	-	WWC	Altschuh et al. (1999)
Heptachlor-epoxide	298	2.666	278 - 308	DHS	This work
	298	2.06	-	WWC	Altschuh et al. (1999)

Due to the use of different experimental techniques for the measurement of Henry's law constant, the measured H Values ranges for the same compound while estimated H values are strongly depends on the correct vapor pressure and solubility data usage. For example for alachlor and dichlorvos Gautier et. al (2003) quoted sum of 15% uncertainties in the estimation of their results. The uncertainties were the result of uncertainties on the calibration curve, on the extraction process. He mentioned that the flow rate variation and the gas aqueous concentration of pesticides also contributes 5% additional error in their study. The total of 20% variation in the measurement could be seen in the data.

Staudinger and Roberts (2001) reported that in a majority of cases (natural waters with moderate contamination or less) temperature dominate as the main parameter affecting H values. However when they investigate H values under the non-temperature effects, they found out H values remained relatively limited, particularly of

the compounds that potentially self-interact and potentially interact with co-solutes, co-solvents, suspended solids, dissolved organic matter and surfactants-interactions which are inherently more difficult to analyze in the laboratory. When non-temperature effects may be significant, the other conditions such as pH, compound hydration, compound concentration and complex mixture effect, and the natural environmental parameters may be also important. In this study only the dissolved salt concentration was investigated and most of the compound got affected. Complex mixture effect would be important for this research. Generally measured H' values were in the range of literature. Unfortunately there was not much literature measurement for these complex mixture with this method available.

Henry's law constant shows an indirect way for the estimation of air-water exchange of pesticides in the natural environment. Temperature effect in the environmental modeling would be important especially for colder bodies of water where gas transfer can be a significant input process. It is generally accepted that both vapor pressure and solubility of pesticides vary in activity inversely as temperature changes. Their logarithmic values vary linearly with temperature as shown in Equation 2-7 under the ideal conditions e.g. distilled water and in dilute solution. Temperature dependency of Henry's law constant in deionized water are investigated by Gibb-Helmholtz equation (Equation 2-7). There is a strong correlation between the experimental H' values and temperature as seen in Figure 8 – 14. In Figures 8 – 14, gray legends represent H' values in deionized water and white legends represent H' values in saline water. Trend lines were drawn for H' values of each compound in deionized water. Plots were drawn by grouping compounds according to their main structural groups.

The variation in H' with temperature was expressed using the van't Hoff type Gibbs-Helmholtz equation. Assuming enthalpy change and entropy of phase change are independent of temperature over the experimental temperature range, the slope and intercept of the line were obtained from the plot of $(\ln H')$ vs. $(1/T)$ yields the enthalpy (ΔH_H , kJ/mol) and entropy (ΔS_H , kJ/mol.K) of phase change, respectively. The r^2 values for the plots of $(\ln H')$ vs. $(1/T)$ ranged between 0.80 and 0.99 (Table 10) indicating the assumption that ΔH_H and ΔS_H are constant over the experimental temperature range and that the temperature dependence of H' can be accurately modeled by van't Hoff equation is valid. The slopes (A) and the intercepts (B) for the Equation 2-7 [as $\ln H' = A/T + B$] were tabulated in Table 12.

Table 12. Slopes and intercepts of the $\ln H'$ vs. $1/T$ plots.

	A ($=\Delta H/R$)	B ($=\Delta S/R$)	r^2
α -HCH	-5927.0 \pm 301	10.88 \pm 1.03	0.9923
γ -HCH	-5289.6 \pm 316	7.82 \pm 1.08	0.9894
p-p'-DDT	-7163.4 \pm 666	16.29 \pm 2.28	0.9747
p-p'-DDD	-4467.8 \pm 449	7.60 \pm 1.54	0.9705
p-p'-DDE	-6879.4 \pm 1519	17.48 \pm 5.2	0.8723
c-Nonachlor	-4154.7 \pm 980	6.80 \pm 3.35	0.8571
t-Nonachlor	-7554.9 \pm 495	20.01 \pm 1.69	0.9873
Endosulfan I	-4317.2 \pm 563	6.40 \pm 1.92	0.9515
Endosulfan II	-3396.6 \pm 214	0.65 \pm 0.73	0.9883
Endrin	-3973.5 \pm 529	4.94 \pm 1.81	0.9456
Dieldrin	-4145.9 \pm 456	6.52 \pm 1.56	0.9649
Aldrin	-3186.6 \pm 899	7.06 \pm 3.07	0.8074
α -CHL	-5831.2 \pm 667	13.67 \pm 2.28	0.9622
γ -CHL	-7616.3 \pm 366	20.62 \pm 1.25	0.9931
Chlorpyrifos	-5720.4 \pm 603	13.61 \pm 2.06	0.9677
Heptachlor	-3173.5 \pm 929	6.82 \pm 3.19	0.8537
Heptachlorepoxyde	-4528.8 \pm 784	8.09 \pm 2.68	0.9175

Sahsuvar et al. (2003) reported ΔH_H , were 59.3 \pm 1.6, 65.1 \pm 1.3 and 61.4 \pm 3.1 kJ/mole for α -, β - and γ -HCH, respectively. In this work ΔH_H for α -HCH and γ -HCH were found 49.28 \pm 2.50 and 43.98 \pm 2.63 kJ/mole. These may be compared to enthalpies of vaporization (ΔH_{vap} , kJ/mol) of 68.5 and 70.5 kJ/mol for α - and γ -HCH (Hinckley et al. 1990). Since $\Delta H_H = \Delta H_{\text{vap}} + \Delta H_{\text{sol}}$, gives ΔH_H this value should be lower than ΔH_{vap} if the enthalpy of water solubility, ΔH_{sol} , is a positive number (Paasirvirta et al. 1999). This is often the case for high molecular organic chemicals (Schwarzenbach et al. 2003). For example, ΔH_{sol} ranged from 18.2 to 41.3 kJ/mol for PCB congeners, chlorobenzenes and dibenzofuran (Shiu et al. 1997). Bamford et al. (1999) measured H for polycyclic aromatic hydrocarbons (PAHs) and reported ΔH_H values ranging from 35.4 to 66.4 kJ/mol for 2-4 ring compounds. A similar study for 26 polychlorinated biphenyl (PCB) congeners yielded an average ΔH_H of 66.6 kJ/mol in a range of 14.5 to 164.0 kJ/mol (Bamford et al. 2000). On the average, ΔH_H was 24% lower than ΔH_{vap} , but explainably higher than ΔH_{vap} for some of the heavier PCB congeners. Staudinger and Roberts (2001) reviewed the temperature dependence of H for a wide variety of chemicals and found ΔH_H values ranging from 8.2 to 93.3 kJ/mol with an average of 46.8 kJ/mol. The range and mean for 8 pesticides were 16.8 to 87.8 and 43.3 kJ/mol

while in the study this range was found 26 to 63 kJ/mol (Table 13). Consequently, it was concluded that ΔH_H values calculated for all compounds are consisted with the reported values of similar semivolatile compounds. Reported ΔH_{vap} values for HCHs in the literature are higher than calculated ΔH_H values in this study as expected.

As seen in the plots (Figures 8 – 14) saline water H values are always above the regression line belonging to deionized water. Slopes for the two points of saline water seem to be not different than the slopes in deionized water, however, more data at other temperatures is required for a healthy comparison. Furthermore, it can be concluded that for all compounds in saline water partition of compounds is shifted to air phase.

Table 13. List of enthalpy and entropy of phase change calculated in this work.

	ΔH (kJ/mol)	ΔS (kJ/mol.K)
α -HCH	49.28±2.50	0.09±0.01
γ -HCH	43.98±2.63	0.07±0.01
p-p'-DDT	59.56±5.54	0.14±0.02
p-p'-DDD	37.15±3.73	0.06±0.01
p-p'-DDE	57.20±12.63	0.15±0.04
c-Nonachlor	34.54±8.15	0.06±0.03
t-Nonachlor	62.81±4.12	0.17±0.01
Endosulfan I	35.89±4.68	0.05±0.02
Endosulfan II	28.24±1.78	0.01±0.01
Endrin	33.04±4.40	0.04±0.02
Dieldrin	34.47±3.79	0.05±0.01
Aldrin	26.49±7.47	0.06±0.03
α -CHL	48.48±5.55	0.11±0.02
γ -CHL	63.32±3.04	0.17±0.01
Chlorpyrifos	47.56±5.01	0.11±0.02
Heptachlor	26.38±7.72	0.06±0.03
Heptachlorepoide	37.65±6.52	0.07±0.02

The only difference observed for the compounds of p-p'-DDD and c-nonachlor. No significant salting out effect on Henry was observed for these two compounds. In the literature salting-in effect is also mentioned by Chung et al. (2005) which refers the increase in salt concentration increases the gas solubility in the solution. This effect will be obtained by using $\ln(H_A/H_A^*)=k_s \cdot I$ where H_A^* is the Henry's law constant in the salt solution, k_s is the Setchenow coefficient, and I is the ionic strength of the solution. A negative value for k_s corresponds salting in effect.

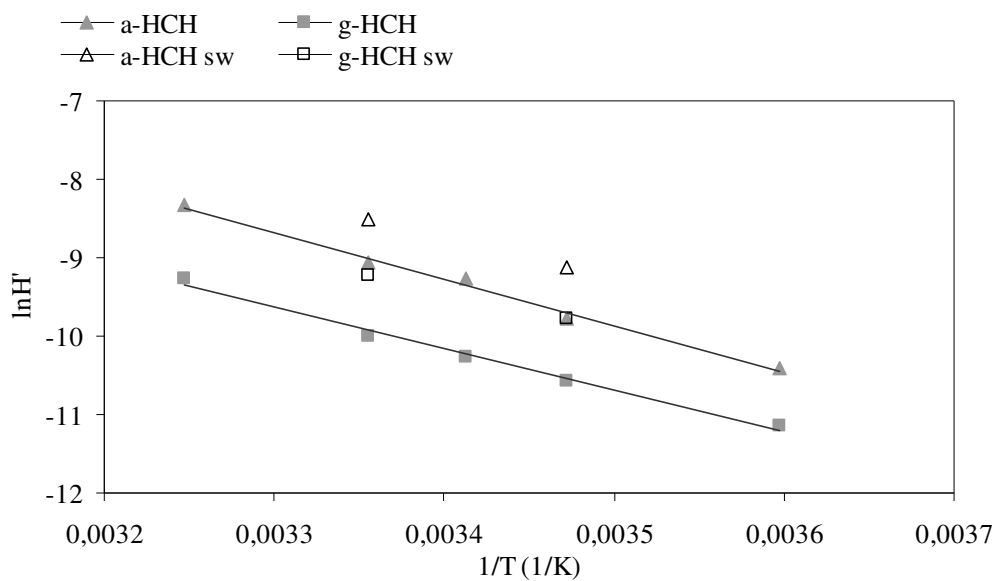


Figure 8. Measured H' values for α -HCH and γ -HCH over the temperature range 5 to 35°C in deionized water and saline water (sw).

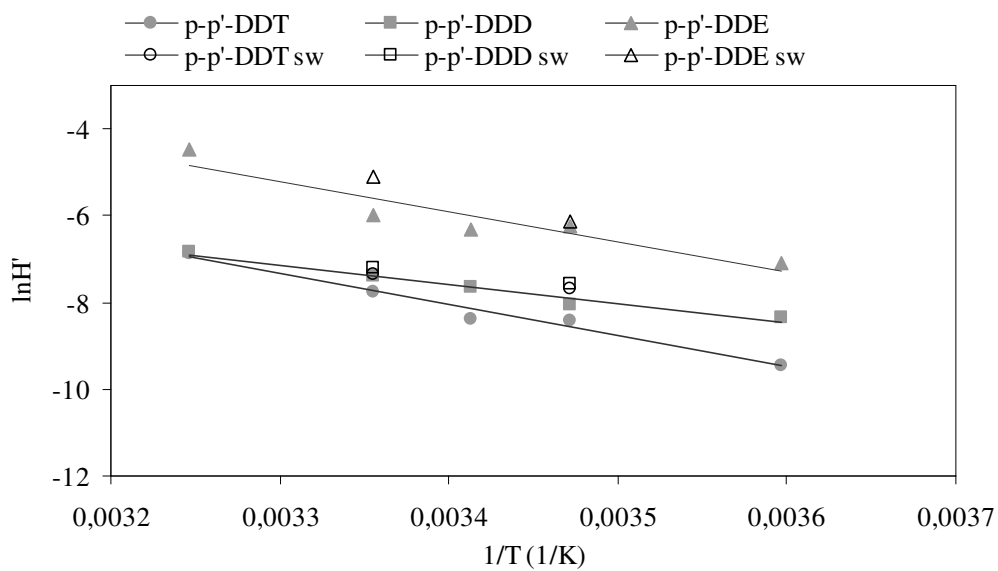


Figure 9. Measured H' values for p-p'-DDT, p-p'-DDD, and p-p'-DDE over the temperature range 5 to 35°C in deionized water and saline water (sw).

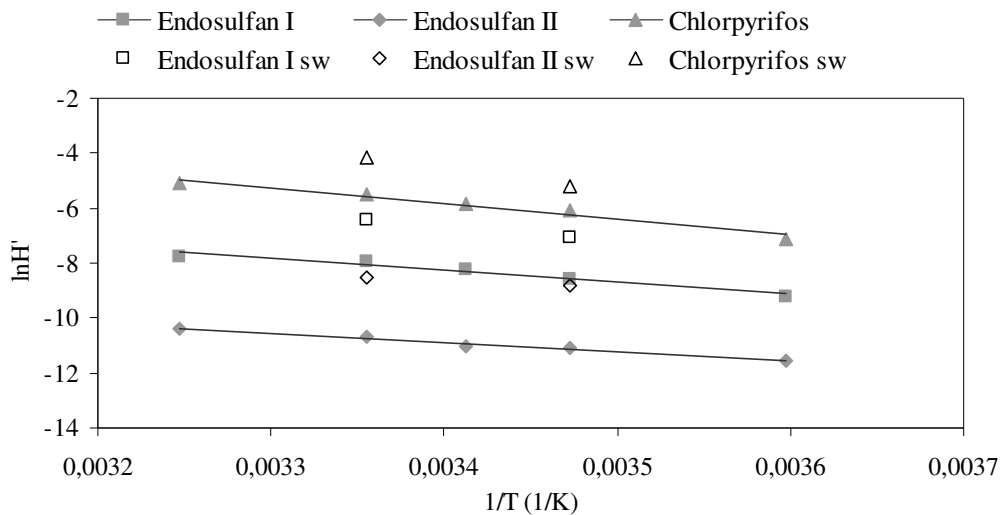


Figure 10. Measured H' values for endosulfan I, endosulfan II, and chlorpyrifos over the temperature range 5 to 35°C in deionized water and saline water (sw).

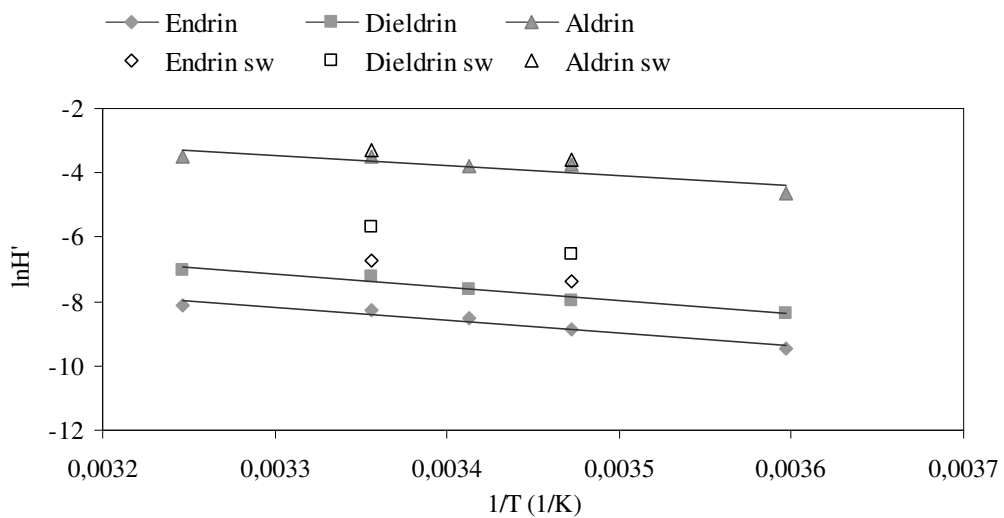


Figure 11. Measured H' values for endrin, dieldrin, and aldrin over the temperature range 5 to 35°C in deionized water and saline water (sw).

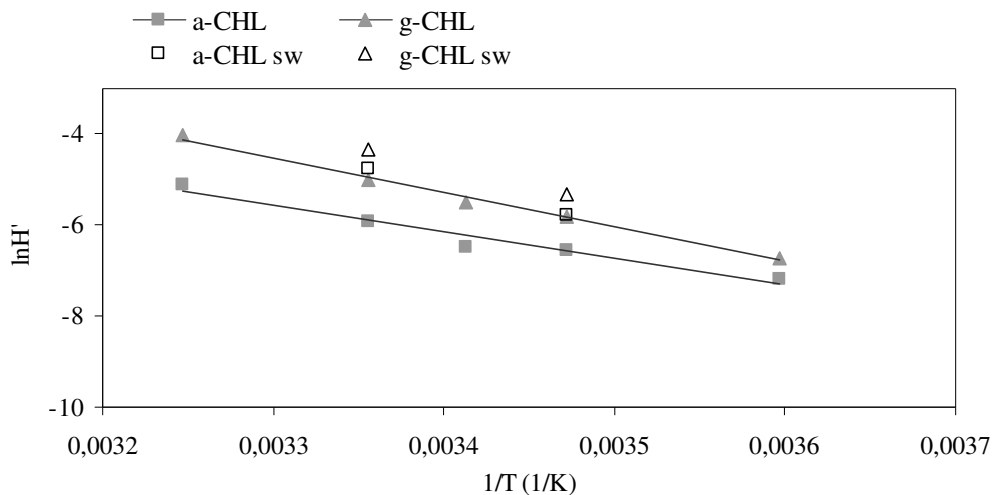


Figure 12. Measured H' values for α -CHL and γ -CHL over the temperature range 5 to 35°C in deionized water and saline water (sw).

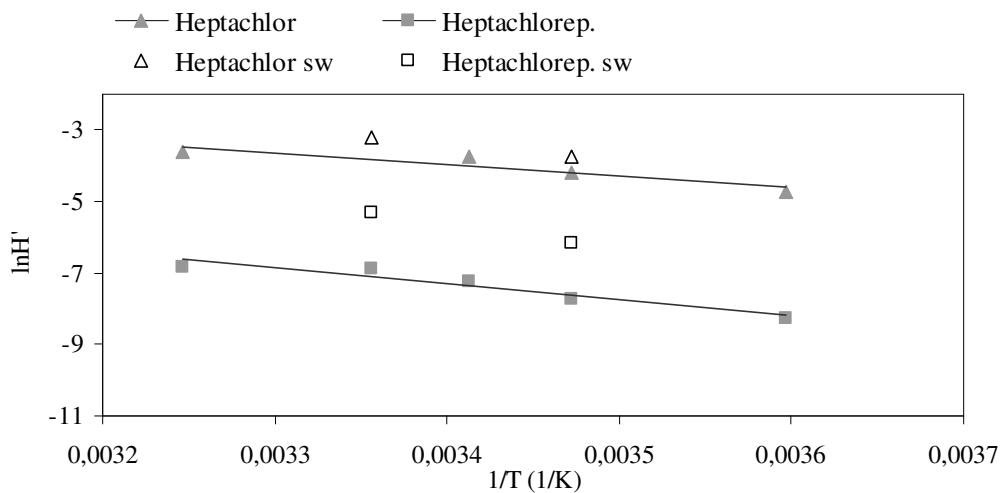


Figure 13. Measured H' values for heptachlor and heptachlorepoxide over the temperature range 5 to 35°C in deionized water and saline water (sw).

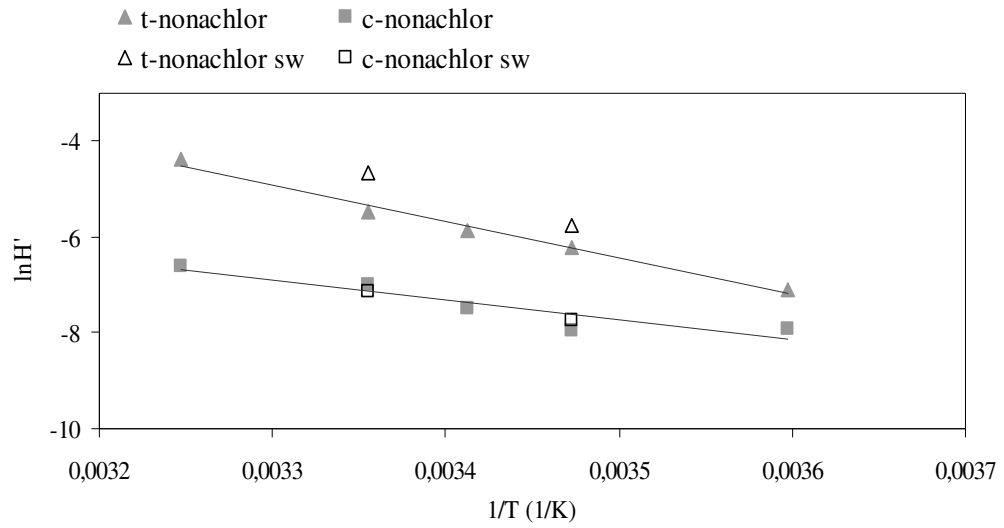


Figure 14. Measured H' values for t-nonachlor and c-nonachlor over the temperature range 5 to 35°C in deionized water and saline water (sw).

CHAPTER 5

CONCLUSION

In this work, Henry's law constants of 17 organochlorine pesticides were measured by a dynamic equilibration method at 5, 15, 20, 25 and 35°C in deionized water and at 15 and 25°C in artificial seawater (3% NaCl solution).

For all compounds Henry's law constant showed 90% increases in every 10°C temperature change in deionized water.

In the saline water experiments, the H values increased by an average 107% from 15°C to 25°C. Measured H values in this work are generally in the range of values reported in the literature. The differences in the values upto three times are common in the literature and the results of this study are in the range of the literature values.

Temperature dependency of OCPs were investigated by using Gibbs-Helmholtz equation. It was seen that H values of the pesticides are strongly dependent on temperature. This result implies that air-water exchange of these compounds in colder area is more significant.

The r^2 values for the plots of $(\ln H')$ vs. $(1/T)$ ranged between 0.80 and 0.99 indicating the assumption that ΔH_H and ΔS_H are constant over the experimental temperature range, and that the temperature dependence of H can be accurately modeled by van't Hoff equation is valid. Calculated enthalpy of phase change, which helps to describe how sensitive is the partitioning between air and water, within the range values reported in the literature mostly available compound is HCHs in the literature.

It was concluded that in saline water air-water partition of these chemicals is shifted to air phase. Since enthalpy of phase change seems to be not changing in saline water, this is explained by decrease in entropy of phase change due to decrease in the volume of the free water molecules in which chemicals are dissolved due to the salting-out effect.

CHAPTER 6

FUTURE RECOMMENDATIONS

In the study, replication in the measurement of H is between one and three due to the fast evaporation of chemicals resulting in aqueous concentration close to blank values during three hour experimental period. Number of replication of H measurements can be increased during shorter experimental periods and accuracy of the H values are therefore increased.

Furthermore, measurement of H values in saline water at different temperature to regress Gibbs-Helmhotz equation could be a promising future work. Because air-water partition of these chemical are generally present in saline environments, measurement of H values with respect to salinity and temperature results in improvement in the accuracy of the modeling of the environmental fate of these chemicals.

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